

Lignin from Agro Residues during Pulping and Bleaching : A Review

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ABSTRACT

This paper reviews the published literature on structure of lignin from non-wood residues and it is noticed that the non-wood lignin contains more of p-hydroxy phenyl propane units. The paper looks at the implications of this on the chemistry of pulping and bleaching. From the analysis of the chemistry involved, it follows that the pulping and bleaching of these raw materials produce much less quantity of toxic organo-chlorine compounds even with conventional bleaching as compared to wood as the formation of the precursors during pulping will be minimal due to unique structural character of lignin present in the non-wood raw material.

INTRODUCTION

The use of Agro residues, which is the major source of non-wood fibres in pulp and paper production has shown an increasing trend in recent times due to ecological consideration as they prevent the denudation of forests. It is also well known that non-wood materials can be delignified more easily than wood chips under alkaline conditions.

Recent investigations in the structure of lignin from wheat straw, bagasse and kenaf have shown that non-wood lignin contains, in addition to the Guaiacyl (G) and Syringyl (S) propane units, a significant amount of p-hydroxy phenyl propane (H) units (1, 2 and 3). The present paper reviews the findings of these studies and looks at the implications of these findings on chemistry of pulping and bleaching of these raw materials vis-à-vis generation of toxic organo chlorine compounds like dibenzodioxin and dibenzo furans during processing.

The pathways of dioxins formation during pulping

Many of the negative environmental effects of pulp production arise from the formation of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzo furans (PCDF). Despite a large number of organochlorine compounds during pulping and bleaching process, only seventeen are generally considered as toxic and these are co-geners chlorinated at 2- 3- 7- and 8- positions of the dibenzodioxin and dibenzofuran structure.

Evaluation of the comparative toxicity of these seventeen compounds have shown that 2,3,7,8 TCDD (III) is the most toxic having a value of 1.0 in the

international toxicity factor. The 2, 3, 7, 8, 9 penta chloro dioxin PCDD has a toxicity value of 0.5 and 2,3,7,8 tetra chloro dibenzo furan (TCDF) (II) has toxicity of 0.1 in the international toxicity factor scale. The relative toxicity levels of other important toxic organo chlorine compounds are given in Table 1 and 2.

The United States Environment Protection Agency have revised their existing discharge norms under

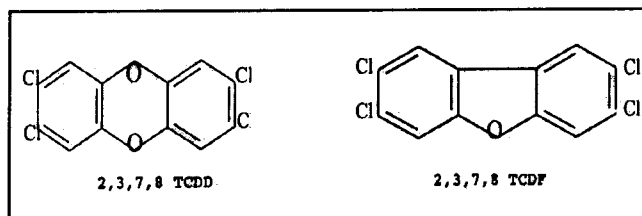


Table 1 Toxicity equivalent factors

Dioxin congeners		Toxicity equivalent factors
2, 3, 7, 8	TCDD	1.0
Other	TCDD	0.0
1, 2, 3, 7, 8	PeCDD	0.5
Other	PeCDD	0.0
1, 2, 3, 4, 7, 8	HxCDD	0.1
1, 2, 3, 6, 7, 8	HxCDD	0.1
1, 2, 3, 7, 8, 9	HxCDD	0.0
Other	HxCDD	0.01
1, 2, 3, 4, 6, 7, 8	HpCDD	0.01
1, 2, 3, 4, 7, 8, 9	HpCDD	0.01
Other	HpCDD	0.0
	OCDD	0.0

Table 2 Toxicity equivalent factors

Dioxin congeners		Toxicity equivalent factors
2, 3, 7, 8	TCDF	1.0
Other	TCDF	0.0
1, 2, 3, 7, 8	PeCDF	0.5
Other	PeCDF	0.0
1, 2, 3, 4, 7, 8	HxCDF	0.1
1, 2, 3, 6, 7, 8	HxCDF	0.1
1, 2, 3, 7, 8, 9	HxCDF	0.1
Other	HxCDF	0.0
1, 2, 3, 4, 6, 7, 8	HpCDF	0.01
1, 2, 3, 4, 7, 8, 9	HpCDF	0.01
Other	HpCDF	0.0
	OCDF	0.0

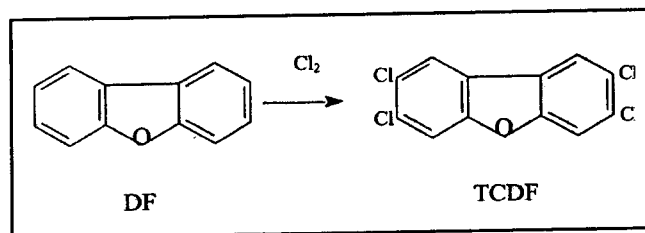
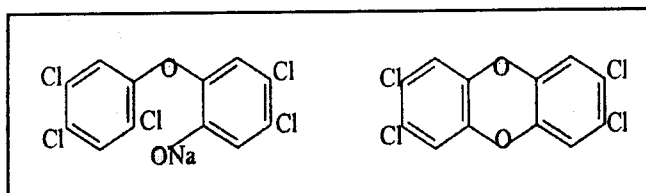
'Cluster Rule' for protecting health and environment in 1998. As per these concentration of dioxin should be less than 10 pico grams/lit and furan should be less than 32 pico grams/lit. Similarly Canada has specified that the concentration of 2,3,7,8 TCDD and 2,3,7,8 TCDF in the paper mills waste water should not exceed 15 and 50 pico grams/lit respectively.

Reaction pathways of TCDD and TCDF formation

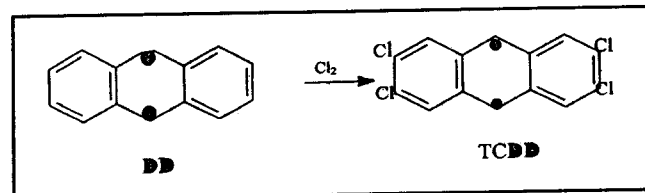
The formation of these toxic chlorinated dibenzodioxin and dibenzofurans can be considered as arising by three main path ways.

1. Combination of chlorine radicals with hydrocarbon structures at high temperatures (3).
2. Condensation of chlorinated sodium phenolate structure (4).
3. Electrophilic substitution of chlorine of the corresponding unchlorinated precursor compound (5,6).

Of all these, the last mentioned pathway viz, the electrophilic substitution of the precursors is the most important on leading to the formation of these toxic chlorinated dioxins. The present paper examines, based on established theories of mechanistic organic chemistry the possibilities of the formation of these precursors viz dibenzodioxin and dibenzofuran. The lignin present in bagasse has a different structure from wood lignin, during pulping and bleaching.

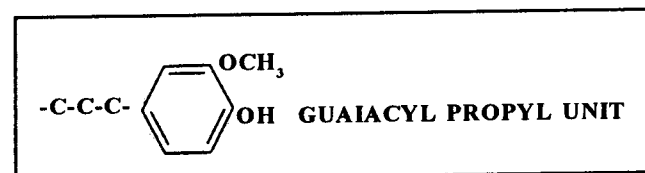


Review of the studies done on structure of the bagasse lignin



As pointed out bagasse lignin contains in addition to guaiacyl (G) and syringyl (S) units, a significant amount of p-hydroxy phenyl propane (H) units.

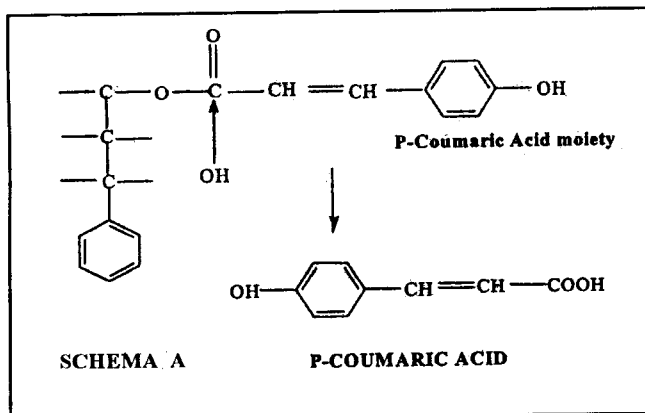
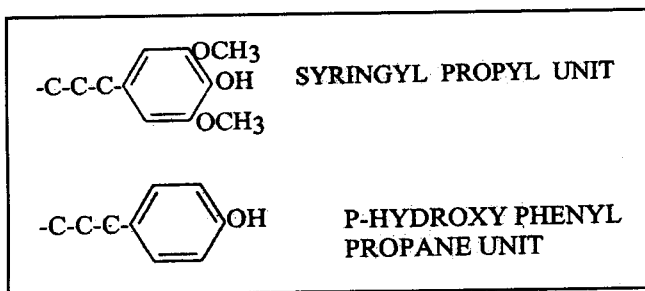
It has been found that the bagasse lignin contains 1.10 unit of syringyl units for every guaiacyl units and 1.21 units of p-hydroxy phenylpropane units. The p-hydroxy phenylpropane units are generally attributed to the presence of p-cumaric acid moiety and they are present in both as ester of gamma hydroxyl groups of lignin (7-9) and partly as alpha-aryl ether structure (8, 10 & 11).



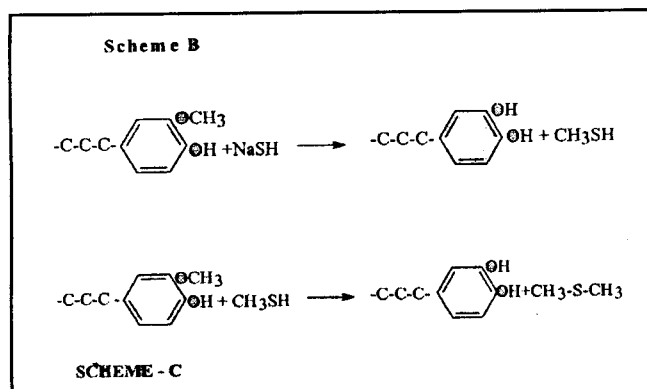
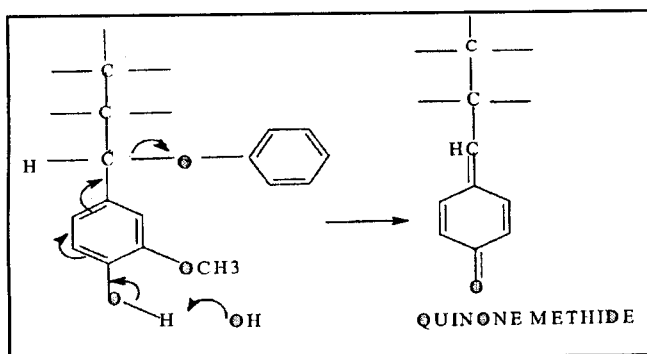
The presence of ester groups makes this easily liable for alkaline cleavage which generates hydrophilic carboxylic acid by B_{AC}2 mechanism (Schema A). The presence of alpha aryl ether linkage with a p-hydroxyl group in aromatic ring leads to formation of quinone methides intermediate resulting in easy cleavage of all alpha aryl ether bonds (Schema B).

Cleavage of α-aryl ether bond to produce Quinone-methide intermediate.

Both the reactions are faster reactions having low activation energy in contrast to cleavage of β-aryl ether linkage, which is a slow reaction and high activation energy. For this reaction only sodium hydroxide is needed. Hence the sodium sulphide present can be more effectively used for demethylation reactions of methoxyl groups (scheme C) whose concentrations are much less when compared to wood, therefore, leading to a greater removal of lignin in pulping and also resulting in residual lignin having less methoxyl groups and more



hydroxyl groups. Also sodium sulphide in water gives rise to the formation of SH^- ions, which act as nucleophile and cleave the conventional β -0-4 ether linkage which has high activation energy.



With the conditions of pulping not being maintained drastic, the condensation reactions to give the dioxin precursors like dibenzo dioxin and dibenzo di furan do not occur effectively. Further in the bagasse the p-

hydroxyl phenyl propane units have less number of hydroxyl groups in the aromatic ring, compared to both soft wood and hard wood lignin.

The studies on the soda pulping of bagasse carried out by Huamin Zhai and Yuan Zong Hai has shown the first rapid phase extending to 75% delignification can be directly achieved, and it is contributed by the cleavage of p-coumaric acid moiety.

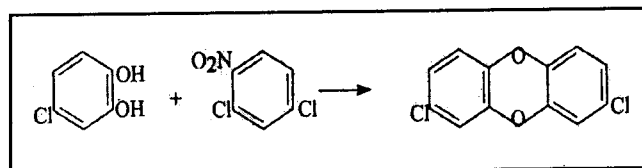
When the delignification proceeds in the fast rate the possibility of the formation of these dibenzodioxins and furans precursors are practically very little. We have come to this conclusion after examining the chemistry of formation of dibenzodioxin and furans.

Normal methods of preparation of dibenzo dioxins and dibenzofurans

Literature has shown that for the preparation of Dibenzo Dioxins in reasonable yield is condensation of chloro substituted Catechols with Chloro substituted O-Chloro-Nitrobenzene (12, 13 & 14).

There is no report in literature about the formation of dibenzodioxin by self condensation of phenols. For formation of dibenzodioxin the aromatic ring should have two hydroxyl groups ortho to each other i.e. Catechol derivatives. Hence logically we can infer that the formation of dioxin precursors will not be significant during pulping of non wood lignin's, which contains mostly p-hydroxyl phenyl propane units.

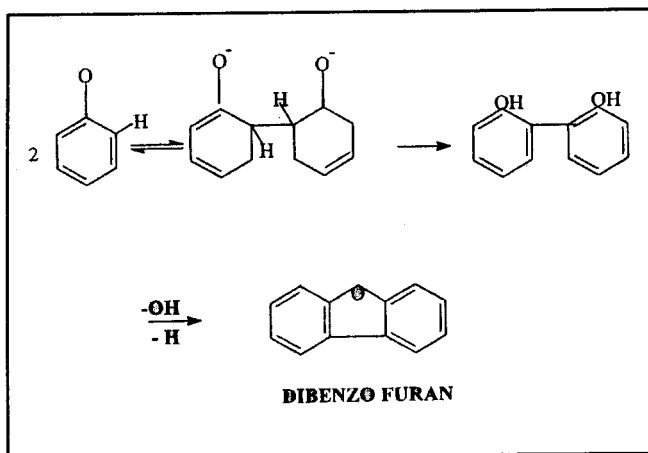
There is no report in the literature about the formation of dibenzodioxin by self condensation of phenols. Hence it is obvious that the formation of dioxin precursors will not be significant during the pulping of non woods.



Similarly the conditions in pulping are not favourable to the dibenzofurans from these raw materials. The literature survey shows that when these dibenzofurans are formed from phenols as precursors, it proceeds through a free radical mechanism, which undergo condensation in the temperature ranges of 500-840°K (15). But during pulping, the conditions are highly ionic because of high pressure and the temperatures are also much less.

Dibenzofurans are formed from phenols and condensation takes place in the temperature ranges of 500 to 800 deg. kelvin as per the reactions shown below.

In case of pulping of non-wood fibres the conditions are highly ionic because of alkaline cooking liquor and



maintaining the end pH 11.5 to 12.0 and the temperature also of the order of 420-440 deg. kelvin. Hence the free radical condensation is not favoured under these conditions. Thus the formation of the dibenzofurans during the pulping of bagasse will be very minimum. Thus the formation of dibenzofurans during the pulping of bagasse will be very minimum.

CONCLUSION

It follows from the review of recent publications on the structure of lignin from Agro residues like bagasse and examination of the chemistry of formation of these toxic organo chlorine compounds like TCDD and TCDF. The formation of these toxic compounds will be minimum and below the threshold toxic levels during pulping and bleaching of these raw materials.

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