A Final Report On

"Understanding the Nature and Reactivity of Residual Lignin for Improved Pulping and Bleaching Efficiency"

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UNDERSTANDING THE NATURE AND REACTIVITY OF RESIDUAL LIGNIN FOR IMPROVED PULPING AND BLEACHING EFFICIENCY

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Project Summary

The overall project has proceeded well. We have obtained very significant findings and achieved most of the proposed tasks for an original three-year project:

1. Development of a direct procedure for the determination of diphenylmethane units
2. Determine the reactivity of diphenylmethane dimers
3. Determine the role of lignin condensation in kraft delignification
4. Determine the reactivity of kraft pulp lignin *in situ*
5. Determine the impact of pulping conditions on the nature of residual lignin
6. Determine the impact of pulping conditions on the reactivity of residual lignin

However, we have encountered some unanticipated difficulties in analyses of the complicated lignin condensed structures especially on Task 3 to "Determine the Role of Lignin Condensation in Kraft Delignification". This setback was mainly attributed to the finding that the proposed nitrobenzene oxidation (NO) and permanganate oxidation (PMO) techniques were capable of detecting only certain types of lignin condensed units, and are not suitable for a quantitative determination of the diphenylmethane (DPM) type units. In an attempt to overcome these drawbacks, we were approved for a two-year no-cost extension to complete the project.

We have pursued several additional tasks, which are marked in the report. On Task 1, the evaluation of ozonation reactions as a method for analyzing the α-condensed units was added. This ozonation technique has been shown to be a great complement to the other two procedures (NO and PMO) in detecting the DPM structures. On Tasks 2, 3, and 4, we have expanded to include the reactions toward the laccase-mediator-system (LMS). This part of the study provides further insights into a novel type of the delignification mechanism, which is distinctly different from most common bleaching agents.

The major milestones achieved are:

1. Three analytical methods (NO, PMO, and ozonation) have been developed for detecting the DPM condensed units of residual lignin *in situ*.
2. The phenolic lignin DPM model dimers have been shown being quite sensitive to molecular O_2 in alkalis, and also reactive toward other non-chlorine delignification agents including chlorine dioxide, alkali peroxide, and ozone.
3. Our results confirm that the alkaline condensation reactions are largely limited to the α-5 DPM type, whereas the 5,5'-DPM type appears to be insignificant.
4. The delignification behavior of softwood kraft pulps toward non-chlorine bleaching agents has been shown to vary widely in terms of the relative degradation of the phenolic and etherified structures.
5. Alkaline pulping conditions have a significant influence on the nature of residual lignin notably in terms of the phenolic hydroxyl group (PHOH) content.
6. Alkaline pulping conditions have an appreciable effect on the reactivity of residual lignin as clearly demonstrated in response to O_2 delignification.
7. The benzylic oxidation of etherified lignin units has been shown to be significant in O_2 delignification, and its enhancement provides a facile means for improving the O_2 bleaching efficiency.
8. The LMS delignification mechanism is very unique, and unlike most chemical agents does not depend on the degradation of the phenolic lignin structures.

INTRODUCTION

One of the most formidable challenges in kraft pulping to produce bleached chemical pulps is how to effectively remove the last 5-10% of lignin while maintaining the fiber quality. To avoid a severe fiber degradation, kraft pulping is usually terminated in the 25-30 kappa number range and then followed by an elementally chlorine free (ECF) or a totally chlorine free (TCF) bleaching sequence to reduce the environmental impacts (1).

The chemical nature that results in a slow removal of the residual lignin is not entirely clear, and is generally thought to be due to the presence of low-reactivity lignin structures (2-8). Of particular interest is the possible role of diphenylmethane (DPM) chemical structures *5* and *9* (Figure 1.1). The formation of these units has been well established in the lignin model compound reactions (2-4), but it has not been clearly defined in the residual lignin.

One of the major difficulties encountered in analysis of the pulp residual lignin *in situ* is the lack of a selective technique capable to reveal different types of condensed units. As illustrated in Figure 1.2, the condensed units include the C_5 – substituted structures *2-4* already present in the wood lignin, and those suspected DPM units *5-7* that may be formed during the pulping or other chemical treatment processes.

Many prior studies on the residual lignin analysis were conducted on isolated lignin samples (9-18) based on acid or enzymatic hydrolysis of the fiber matrix. A major advantage of this approach is that the lignin preparations can be analyzed by both physical and chemical techniques, notably the ^{13}C- and ^{31}P-NMR spectrometry (19, 20). However, it is difficult to isolate the residual lignin quantitatively. Also there are concern on the possible occurrence of chemical modification during the preparation process (18, 21).

Our interest has been on a direct analysis of the residual lignin *in situ*. However, a major challenge of this approach is the limitation of chemical methods capable of revealing different types of the condensed and the lignin-carbohydrate units. Recently, we have shown that the periodate oxidation reaction (22,23) is a very useful procedure to determine the phenolic hydroxyl group (PHOH) content of residual lignin *in situ*. This project is aimed at developing other chemical methods to better understand the nature of DPM units in the residual lignin. The initial working hypothesis was based on that nitrobenzene oxidation (NO) of the α-5 lignin DPM dimer I yielded a characteristic product *14* (Figure 1.3), which may be used to detect this type of structures in the residual lignin.

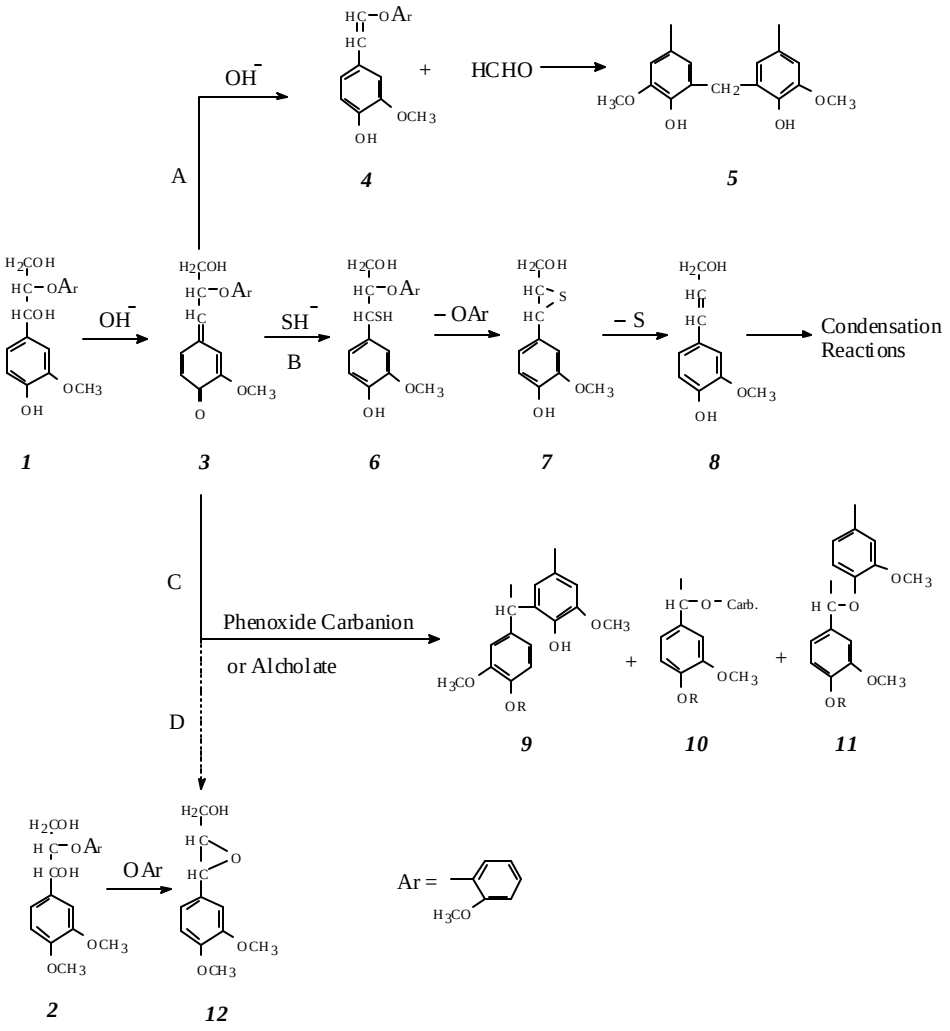
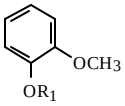


Figure 1.1. Major types of alkaline lignin condensation reactions.

Uncondensed



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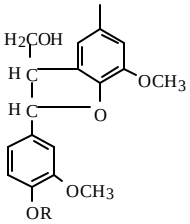
C_5-Substituted Units in the Wood Lignin



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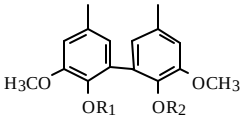

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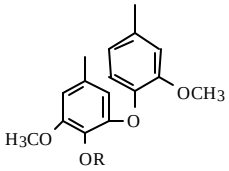

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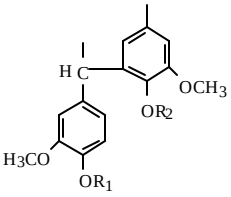
Diphenylmethane Types Condensed Units



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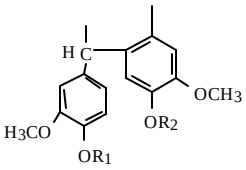

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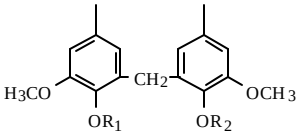

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Figure 1.2. Major types of guaiacyl nuclei.

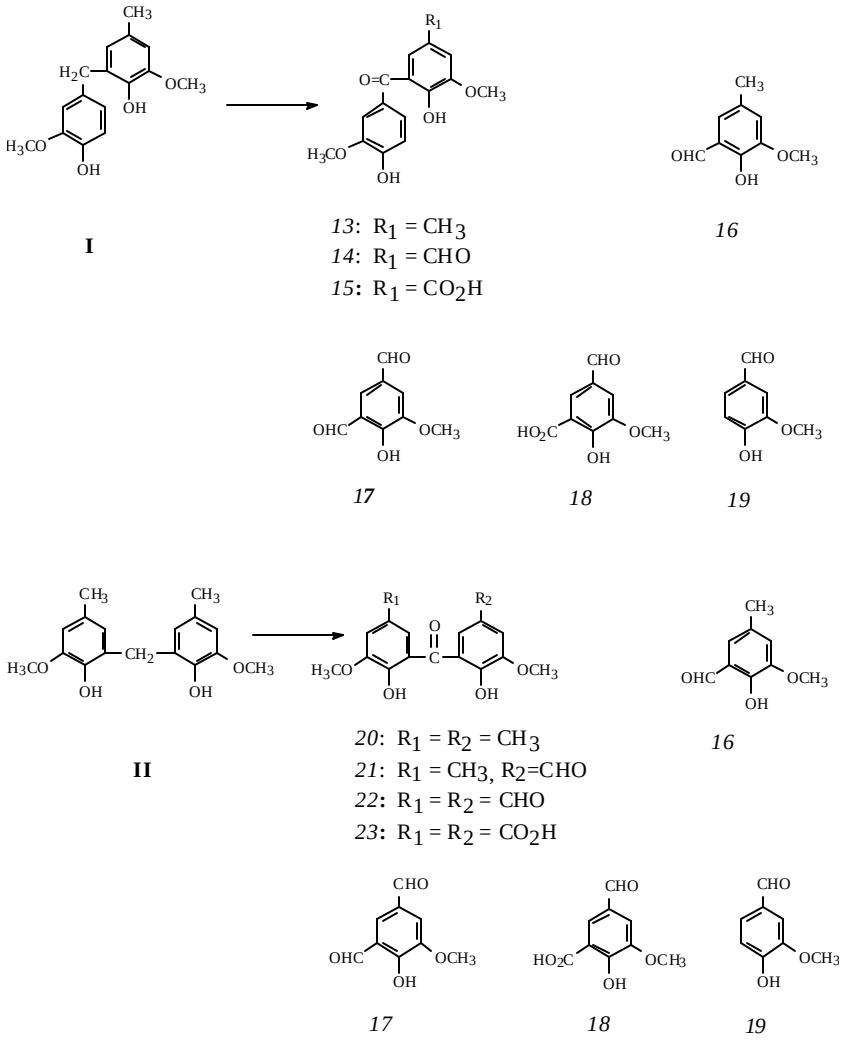

Figure 1.3. Possible products from nitrobenzene oxidation of the α-5 and 5,5'-DPM lignin model dimers.

SCOPE OF WORK

The objective of this project, as stated in the proposal was to develop a feasible strategy to improve the overall kraft pulping and bleaching process efficiency by gaining a further understanding the nature and reactivity of the residual pulps lignin *in situ*. The specific tasks were:

1. Development of a direct procedure for the determination of diphenylmethane units
2. Determine the reactivity of diphenylmethane dimers
3. Determine the role of lignin condensation in kraft delignification
4. Determine the reactivity of kraft pulp lignin *in situ*
5. Determine the impact of pulping conditions on the nature of residual lignin
6. Determine the impact of pulping conditions on the reactivity of residual lignin

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TASK 1

Developments of a Direct Procedure for the Determination of DPM Units

Our proposed approach to develop a direct procedure for determining the DPM units was based on the formation of characteristic products in nitrobenzene oxidation (NO) (24) or in permanganate oxidation (PMO) (25). For example, the dimeric product diguaiacylketone aldehyde *14* and divanillin methane *22* from NO shown in Figure 1.3 may be used to detect the α-5 and 5'5- DPM units, respectively. In addition to the proposed tasks, we have pursued a new task on ozonation (26), which was added to this project in view of its potential application.

A portion of the dimer reactions under NO, PMO, and ozonation conditions have been published or presented at professional conferences (27-30). Detailed experimentation of these procedures was discussed in these publications, and will only be briefly outlined in this report.

Subtask 1.1 Preparation of DPM lignin model dimers

Three lignin DPM model dimers (I, II, and III) were prepared as proposed using reported procedure (31). Figure 1.4 illustrates the general reaction scheme. Additionally, we have prepared a methyl-substituted α-5 dimer IV and a propyl 5,5'-DPM dimer V to evaluate the influence of side chain units on the dimer reactivity.

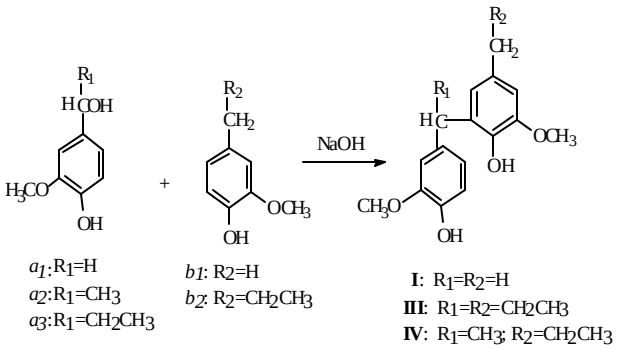


Figure 1.4. Reaction schemes in the preparation of lignin DPM model dimers.

Subtask 1.2 Preparation of diguaiacylketone

Diguaiacylketone *14* was successfully isolated from the NO products of α-5 dimers I and III, and identified based on the GC-MS characteristics of its trimethylsilyl ether, [M+] *m/z* 446. Figure 1.5 provides new insights into the degradation mechanism of dimer I. In contrast to our earlier contention and the report of Chan *et al*. (32), the initial oxidation occurs at the methyl group (Reaction B) instead of the methylene group (Reaction A). We have identified the initial degradation product as *13X* and not the compound *13*. It should be noted that both compounds *13* and *13X* have an identical mass, and could not be differentiated based on the mass spectra analysis alone.

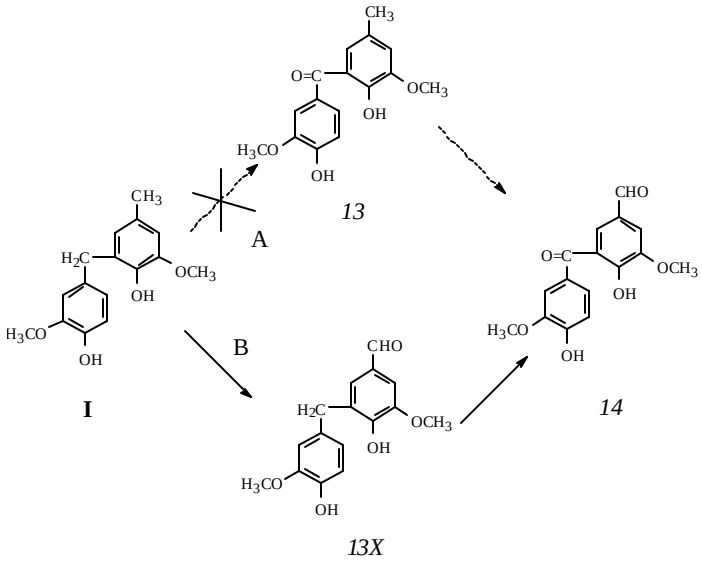


Figure 1.5. A proposed scheme on the formation of dimeric products in NO of α-5 dimer.

Figure 1.6 illustrates a proposed reaction scheme to account for the NO products from the α-5 dimer. A major reaction was initiated from oxidation of the α-methy groups leading to the formation of the diguaiacylaldehyde *9* (29%), and a small amount of the diguaiacylketone aldehyde derivative *14* (5%). The oxidation may proceed through the benzylic carbinol intermediates 9_a and 9_b, which are expected to be rather reactive under the alkaline NO oxidation conditions. The formation of monomeric products was probably resulted largely from decomposition of these diguaiacylcarbinol intermediates 9_a and 9_b, because the diguaiacylketones *14* is expected to be rather stable under the NO conditions.

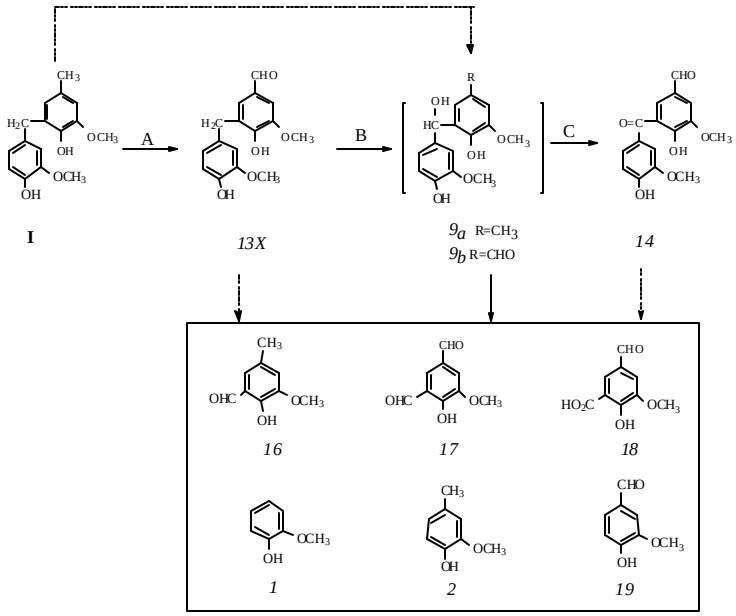


Figure 1.6. A proposed scheme for the NO of α-5 dimer.

Similarly, we have observed the initial oxidation of 5,5'DPM dimer II occurs at methyl group (Reaction B) instead of the methylene group (Reaction A) as indicated in original proposal. The major product identified was a dialdehyde product *21X* and not a ketol aldehyde *21* as previously suggested (32). These two compounds also have an identical mass, and their structures can not be determined based on the mass data alone. Thus, compound *21X* instead of the proposed dialdehyde ketone *22* was isolated, and used to detect the 5,5'-DPM units in the pulp lignin. Thus, the methylene group of the 5,5-DPM dimer II was fairly resistant to oxidation. This dimer gave two 5,5-DPM aldehydes *20X* (5%) and *21X* (53%) corresponding to the oxidation of one and two methyl groups, respectively (Figure 1.7). These new findings incorporated with our earlier results have been published (27).

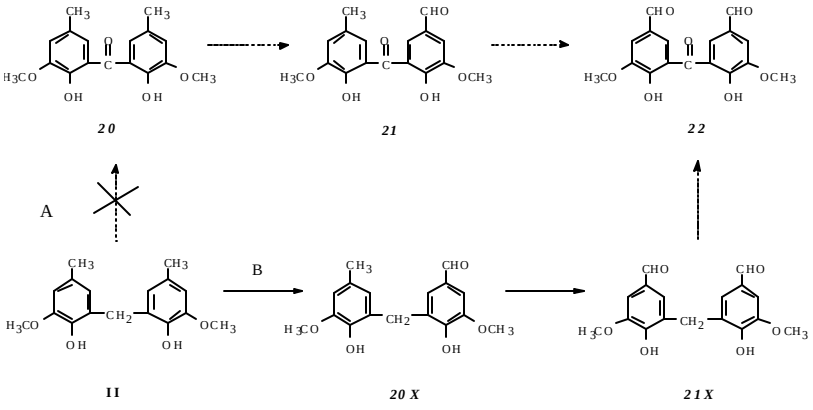


Figure 1.7. A proposed scheme on the NO of 5,5'-DPM dimer II.

Subtask 1.3 Influence of NO conditions

We have examined the influence of NO conditions on the product yield of α-5 dimer with respect to temperature (160-180 °C), alkalinity (1-4 M NaOH), and nitrobenzene concentration (2-12% of alkali).

As indicated in Figure 1.8, the yields of diguaiacyl ketone aldehyde *14* and vanillin *19* were significantly increased with raising reaction temperature (3A), and were slightly affected by alkalinity within the 1-3M range (3B). In a higher alkali (4 M), the vanillin yield was drastically reduced, whereas the ketone aldehyde yield remained relatively unchanged. On the other hand, an increase of nitrobenzene concentration slightly increased the ketone yield and has little effect on the vanillin formation (3C). It follows that the optimal conditions for the formation of diguaiacylketone aldehyde are to conduct oxidation in a 2 M NaOH solution containing 12 % nitrobenzene at 180 °C for 3 h. However, under these optimal conditions, the yield of diguaiacylketone aldehyde from a methyl α-5 dimer was still less than 5%.

Similarly, the results on NO of the 5,5'-DPM dimer II are illustrated in Figure 1.9 for two major products, 5,5'-divanillin methane *21X* and 5-formyl cresol. As indicated, the optimal conditions for a maximum yield of 5,5'-divanillin methane *21X* from the 5,5'-DPM units are to conduct oxidation in about 3 M NaOH solution containing 10% nitrobenzene at 170°C for 3 h.

A portion of the results was presented at the Spotlight on Research '97 Graduate and Undergraduate Research Symposium of the SUNY College of Environmental Science and Forestry on April 18, 1997.

Conceptually, the DPM units can be determined by the formation of the characteristic dimeric products, α-5 diguaiacylketone aldehyde *10* and 5,5'-divanillin methane *21X* from the α-5 and 5,5'-type units, respectively. However, the observed low yield of diguaiacylketone aldehyde *14* (5%) even from the unsubstituted α-5-dimer would make it very difficult for a quantitative determination of these condensed units in the residual lignin.

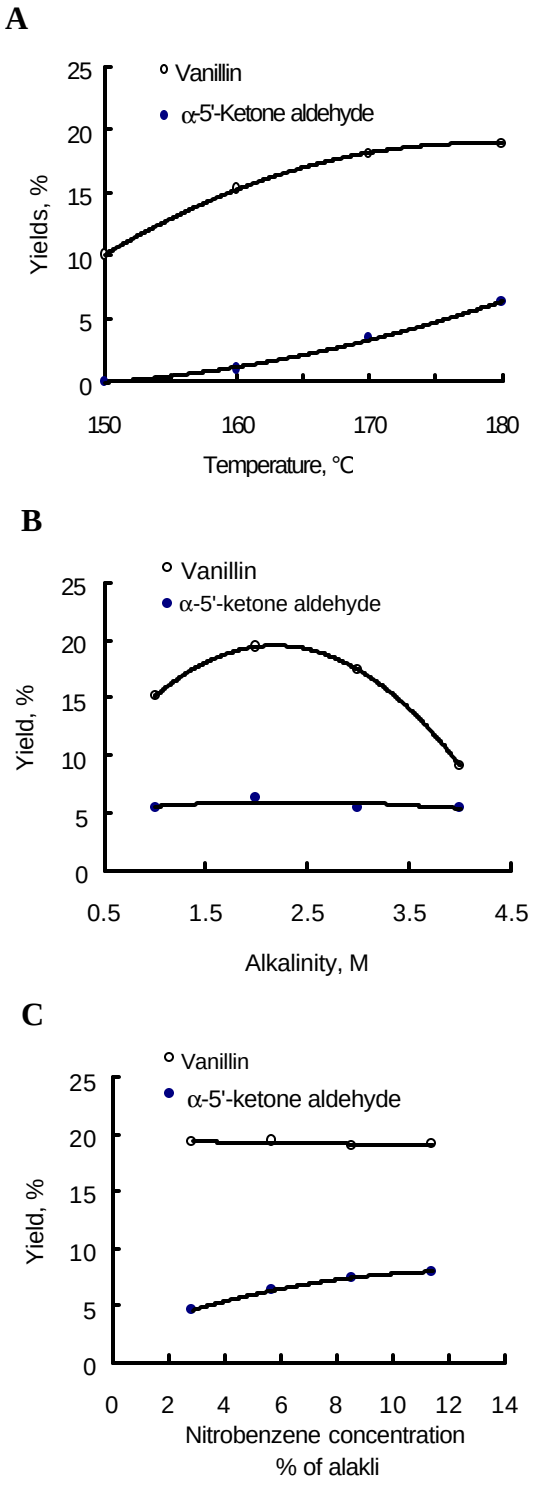


Figure 1.8.. The influence of temperature (A), alkalinity (B) and nitrobenzne concentration (C) on the α-5 diguaiacylketone aldehyde *14* and vanillin yields from NO of the α-5 dimer I.

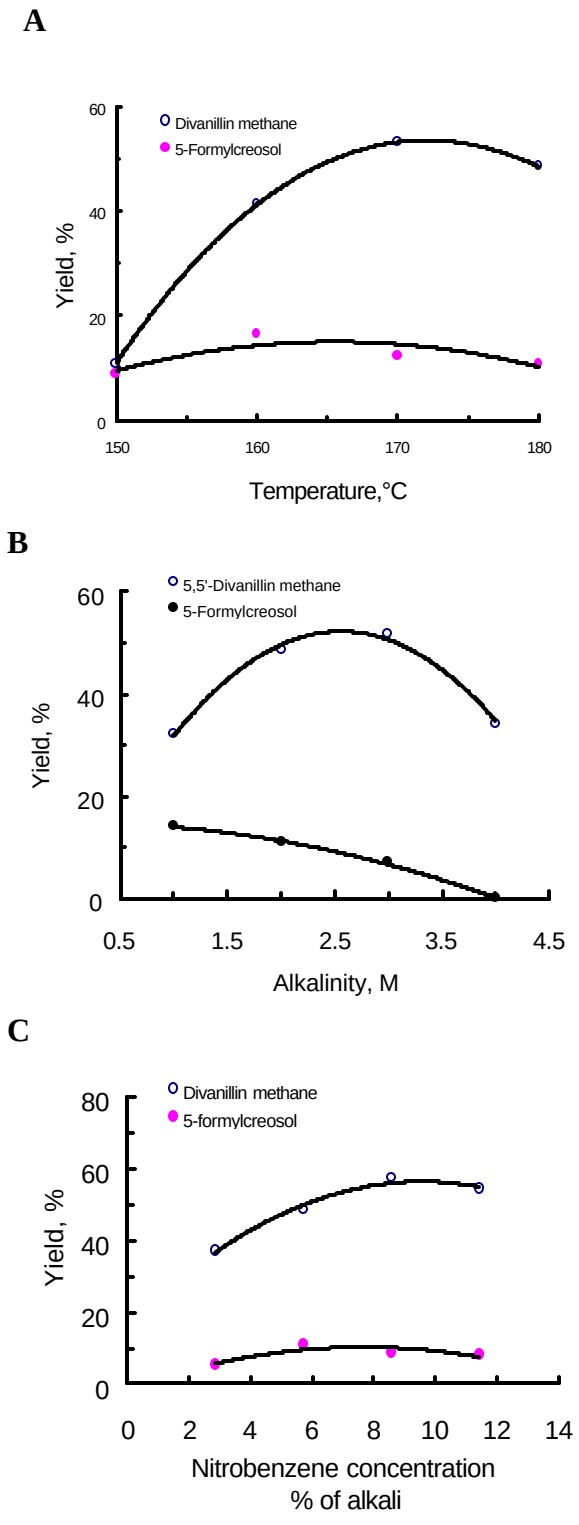


Figure 1.9. The influence of temperature (A), alkalinity (B) and nitrobenzne concentration (C) on the yield of 5,5'divanillin methane *21X* and 5-formylcreosol from NO of 5,5'-DPM dimer II.

Subtask 1.4 Combined NO and permanganate oxidation

We have examined the reactivity of methylated DPM dimers (I and II) (Figure 1.4) under typical permanganate oxidation (PMO) conditions (25). Figure 1.10 lists the PMO products identified, and the product yields are shown in Table 1.1. Major interests are in the formation of dimeric products characteristic of the parent dimers including diguaiacylketone product 3_b from the α-5 unit, and products 4_b plus 5_b from the 5,5'-DPM structure. These products will be used to detect the DPM condensed units present in residual lignin. It should be noted, however, that the permanganate oxidation technique can detect only those DPM units that are phenolic.

It appears that the side-chain structure has a profound influence on the yield of oxidation products as indicated in Figure 1.11 for the substituted α-5 dimers. In comparison, the unsubstituted α-DPM dimers favor the diguaiacylketone formation, whereas the substituted dimers facilitate the side-chain cleavage reactions as reflected in a higher yield of monomeric products. Interestingly, the major dimer product from a methyl α-5 dimer (IIIa) was resulted from the methyl group oxidation. Thus, the efficiency of side chain oxidation could be a factor affecting the formation of the diguaiacylketone acid derivatives.

Also, we have observed that a NO pretreatment of the DPM dimer significantly reduced its yield of diguaiacylketone acid product by approximately 30% in a subsequent PMO. This yield reduction is likely due to the dimer degradation to monomeric products. Thus, the combined NO and PMO method is a not viable procedure for determination of the DPM condensed units, and will not be used further in this project.

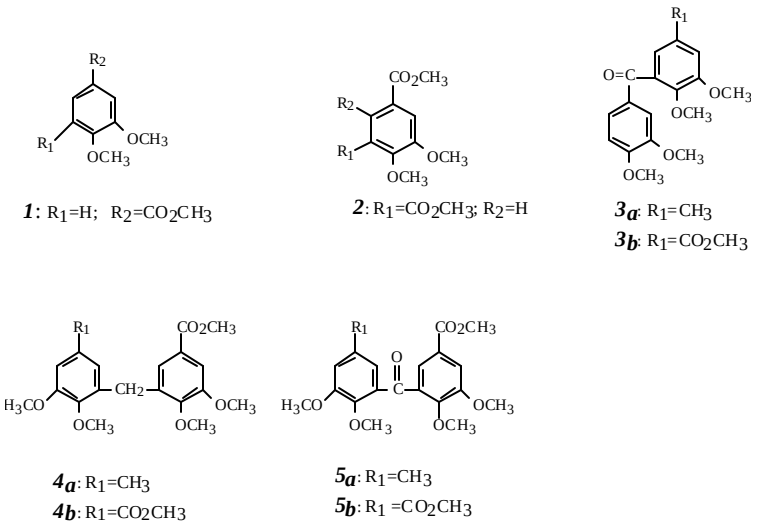


Figure 1.10. Products identified from permanganate oxidation of the α-5 I_b and 5,5'-DPM II_b dimers.

Table 1.1. Product yields from PMO of dimer I and II[a]

Products[b]	Product Yield, mole % of Dimer	
	Ib	II_b
Unreacted Dimer	2.0	6.5
1	3.4	-
2	4.1	6.7
3a	3.2	-
3b	32.7	-
4a	-	4.3
4b	-	6.0
5a	-	8.5
5b	-	7.3

[a]Refer to structures in Fig. 1.4.
[b]Refer to compounds in Fig. 1.10.

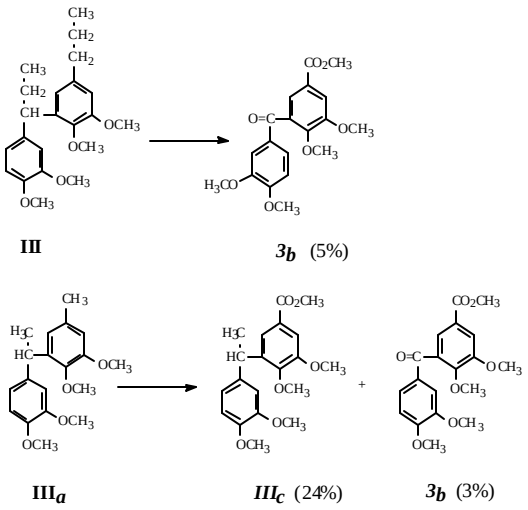


Figure 1.11. Dimeric products from PMO of the substituted α-5 DPM dimers.

Subtask 1.5 (New) Ozonation

The use of ozonation in structural analysis of lignin (26) was investigated mainly by Nakano *et al.* (33) and by Sarkanen *et al.* (34). Unlike most other chemical degradation methods, the ozonation procedure is based on products derived from the side chain units, and thus is applicable to both the phenolic and etherified lignin components. Figure 1.12 indicates the formation of structurally significant oxidation products from ozonation of lignin model dimers (33, 34). The β-O-4 dimer VI gave the characteristic tetronic acid *24*, a mixture of erythronic and threonic acid, whereas the β-5 dimer VII gave two isomeric 2-hydroxy-3-hydroxymethylbu-tanedioic acids *25*. In order to pursue the idea that ozonation may be useful for detecting the DPM units, we have synthesized an α-type condensed dimer VIII and examined its behavior toward ozonation.

The ozonation of the α-aryl dimer VIII was conducted in a mixed solvent consisting of acetic acid, water and methanol (16:3:1) at 0°C for a prescribed period. This dimer was quite reactive toward ozonation. Among the ozonolysis products identified, the formation of a malonic acid derivative *26* (10.2%), and 3,4 - dihydroxybutanoic acid *27* (5.6%) were most informative, as they will also be used to detect the α-DPM units in the residual lignin. However, a relatively low yield of these two products (~15%) suggests the involvement of other degradation pathways. The extent to which the yield of these products may be increased by modification of ozonolysis reactions merits a further investigation.

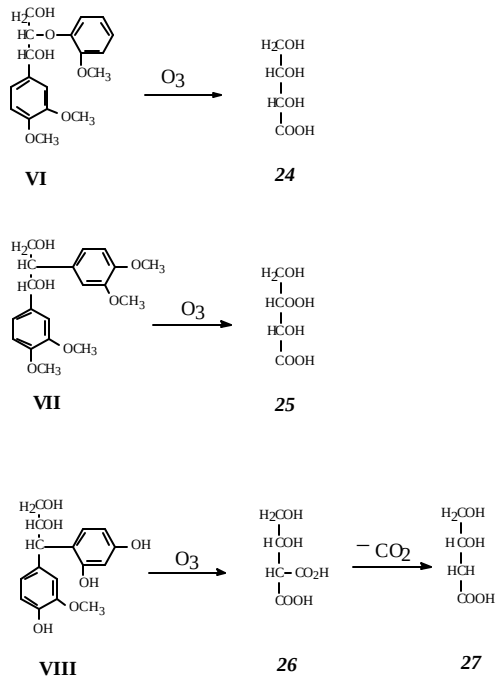
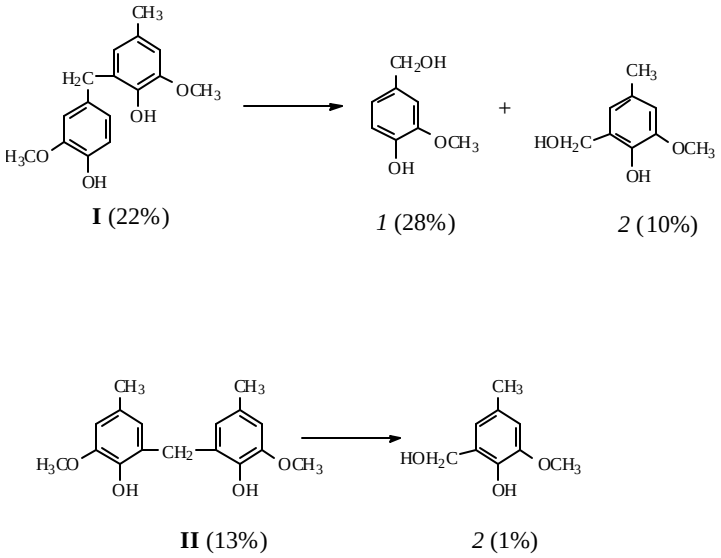


Figure 1.12. Structurally significant products from ozonation of lignin model dimers.

TASK 2

Determine the Reactivity of DPM Dimers

We have previously shown (36, 37) that the DPM dimers are not stable under mild alkali-O_2 conditions resulting in a significant formation of monomeric products. As indicated in Figure 2.1, on mild alkali-O_2 treatments (0.5 M NaOH at 55°C), the cleavages of the α-5 (I) and 5,5'-type (II) DPM dimers all gave the alcohol-type products (vanillyl alcohol *1* or 5-hydroxymethylcreosol *2*). Similar studies are extended to determine their reactivity under alkaline pulping conditions (35,38) and toward other non-chlorine bleaching agents including chlorine dioxide and alkali – peroxide, and a Lacaase-Mediator-System (LMS). The latter LMS was a new subtask.



I (22%) *1* (28%) *2* (10%)

II (13%) *2* (1%)

Figure 2.1. The formation of monomeric products from a mild alkali-O_2 treatment of DPM model dimers in 0.5 M NaOH at 55 °C for 1 h (37).

Subtask 2.1 Under Alkaline Pulping Conditions

The reactivity of phenolic lignin DPM model dimers I and II (Fig. 1.4) under alkaline pulping conditions were pursued in this study in order to understand the fate of these condensed units in the alkaline delignification process. The alkaline stability of these dimers were examined in soda (1 M NaOH) and kraft (1 M NaOH + 0.3 M Na_2S) liquors at 170° for 3 h. In one series, the reactions were conducted in the presence of air, whereas in another series, the reaction vessels were purged with and sealed under N_2 atmosphere. As indicated in Table 2.1, these DPM dimers were not entirely stable under alkaline pulping conditions, and were very sensitive to traces of molecular O_2 present in air.

Table 2.1. Alkali stability of lignin DPM model dimers[a] in soda (1 M NaOH) and in kraft (1 M NaOH + 0.3 M Na_2S) liquors at 170°C for 3 h

Dimer	Dimer Remained, %			
	Soda		Kraft	
	Air	N_2	Air	N_2
I	53.7	82.9	88.8	95.8
II	56.3	88.8	89.4	96.9

[a] Structures are shown in Fig. 1.4.

Under normal soda cooking conditions in the presence of air, the dimer degradation was 44 and 46% for the 5.5'-DPM and α-5 type, respectively. Also, the degradation was drastically reduced to 11 and 17%, respectively with a N_2 purge of the mixture prior to heating. Interestingly, these dimer degradation in soda cooks, unlike under mild alkali-O_2 reactions (Fig. 2.1), resulted in little formation of the monomeric products detectable by the GC analysis. Thus, the reaction is likely to involve some unknown condensation processes as indicated by the appearance of immobile components on TLC analysis of the product mixture.

Also, it is evident that the DPM dimers were considerably more stable in kraft liquor containing sodium sulfide than in soda liquor under otherwise similar cooking conditions. For example, the sodium sulfide addition reduced the degradation of α-5 dimer I from 46 to 11%. Since these dimers were shown previously being sensitive to oxygen in dilute alkali solution, the stabilizing effect of sodium sulfide may be partly attributable to its ability to react with molecular O_2 at elevated temperatures. This contention is also consistent with the finding that the dimer stability in kraft cooks, like in soda cooks, can be further improved by a N_2 purge of the reaction vessels prior to heating.

Judging from the behavior of DPM dimers, it is anticipated that the phenolic DPM units if were generated in kraft pulping would survive the harsh cooking conditions, and would largely remain in the pulp residual lignin. However, in the presence of molecular O_2, they could be transformed into a variety of products including stable condensed structures. Thus, the extent of such transformations would vary with the availability of molecular O_2 present in a pulping system, and it may play a role in affecting the reactivity of residual pulp lignin.

Additionally, the reactivity of three α-5 dimers I, III, and IV was determined under mild alkali-O_2 conditions (in 0.5 M NaOH at 70°C) to reflect the effects of α substituted groups. As indicated in Table 2.2, the nature of α-alkyl groups has a profound influence on the reactivity of α-5 dimers, which increased in the order of group, hydrogen (I) < methyl (IV) < ethyl (III). However, the types of degradation products were practically the same indicating the involvement of a similar mechanism. This part of the study combined with our related works were presented at the 9th International Symposium on Wood and Pulping Chemistry in Montreal, June 9-12, 1997.

Table 2.2. The influence of side chain units on the reaction rate of α-5 DPM dimers conducted in 0.5 M NaOH – O_2 solution at 70°C

Dimers[a]	Rate constant ($10^3 \times k_{obs}$ min^{-1})
I	44.6
IV	51.2
III	85.9

[a] Refer to Fig. 1.4.

Subtask 2.2 Chlroine Dioxide

The lignin DPM dimers I and II were treated with chlorine dioxide using a 1:1 molar ratio at ambient temperature for 1 h. As indicated in Table 2.3 both the α-5 I and the 5,5'-DPM II dimers were very reactive resulting in approximately 80% degradation. Also, the phenolic dimer I after a pre-methylation with dimethyl sulfate significantly reduced its degradation to only 13% degradation. Thus, the etherified unit is fairly stable toward chlorine dioxide. Interestingly, we have detected the formation of a diguaiacylketone product from the reaction of the methylated dimer I with chlorine dioxide. This suggests that the α-methylene group is labile to oxidation. This type of oxidation as observed under NO and PMO condition is likely to involve in the chlorine dioxide bleaching as well.

Table 2.3. Reactivity of lignin DPM dimers in chlorine dioxide solution[a] at pH 4 and ambient temperature for 1h

Dimer[b]	Dimer remained, %
I	18
I (premethylated)[c]	87
II	22

[a] A 1:1 molar ratio of dimer : chlorine dioxide was used.
[b]Refer to Fig. 1.4.
[c]With dimethyl sulfate

Subtask 2.3 Ozone

The reaction of lignin DPM model dimers I and II with ozone was conducted in a solvent mixture of acetic acid : water : methanol (16:3:1) at 0°C. As indicated in Table 2.4, these dimers were very reactive giving significant amounts of malonic acid. This acid is likely resulted from the ring degradation, and also may have a diagnostic value in detecting the 5,5'-DPM unit in the residual lignin. These results suggest that the ring degradation is an important reaction in ozonolysis of the lignin DPM units.

Table 2.4. Yields of malonic acid from ozonation of lignin DPM model dimers[a] at 0°C for 1 h.

Reaction time, min	Yield of malonic acid, mole %	
	I	II
10	20	12
30	20	23
60	28	24
120	21	16

[b]Refer to Fig. 1.4.

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Additionally, we have examined the ozonation of diphenylmethane at 0°C for 30 min and practically all the startling materials were degraded. As indicated in Table 2.5, the major products were maleic acid, benzophenone and benzoic acid. Small amounts of diphenylcarbinol and malonic acid were also detected. The formation of these products may be explained in terms of two pathways (Figure 2.2).

Table 2.5. Products identified from ozonation of diphenylmethane I at 0°C for 30 min

Products	Yield, mole%
Diphenylcarbinol	0.2
Benzophenone	12.4
Benzoic acid	3.0
Maleic acid	33.2
Malonic acid	0.2

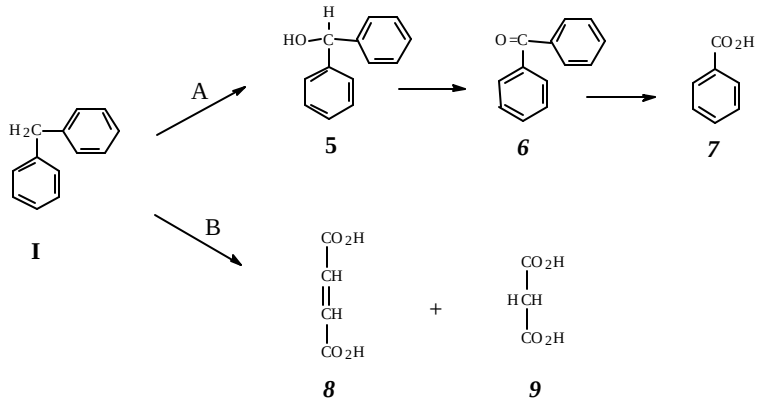

Figure 2.2. Ozonlysis of diphenylmethane.

Reaction A involves oxidation of the methylene group, which leads to the formation of diphenylcarbinol *5*, benzophenone *6*, and benzoic acid *7*. Reaction B involves the degradation of aromatic rings, and would account for the formation of maleic *8* and malonic *9* acids.

Based on the product distribution, the ring degradation pathway was shown to be slightly more favored than the methylene group oxidation. As indicated earlier, the oxidation of methylene groups was a significant reaction under NO and PMO conditions and also involved in the chlorine dioxide reaction. Thus, there is a certain similarity among these oxidative processes.

Subtask 2.4 Alkali peroxide

The reactivity of DPM dimers in alkali-peroxide solution was determined for the α-5 (I) and 5,5'-(II) types, and the results are summarized in Table 2.6. Since these dimers in alkali were very sensitive to molecular O_2, the peroxide reaction was conducted under N_2 atmosphere in order to reflect the intrinsic effect of peroxide.

Compared with the alkali-O_2 system (37), the DPM dimers were considerably less reactive, but formed similar types of monomeric products under the experimental alkali-peroxide conditions used. Thus, the reaction mechanism involved appears to be quite similar between these two oxidative systems.

Table 2.6. Reactivity of DPM dimers in alkali-peroxide solution [a] at 80°C for 4 h

Dimer	NaOH, M	Dimer remained, %
I	0.1	54
I	0.5	43
II	0.1	75
II	0.5	50

*Dimer (0.045mmol) dissolved in 30% aqueous dioxane (4 mL) containing 0.1 or 0.5 M NaOH was reacted with a mixture of H_2O_2 (0.23 mmol), Na_5DTPA (0.11 mmol) and $MgSO_4$ (0.01 mmol) under N_2 conditions.

Subtask 2.5 (New) Laccase-Mediator-System

The reactions of DPM dimers in a laccase-mediator-system (LMS) were examined using laccase from *Botrytis cinerea* and 1-hydroxybenzotriazole (HOBT) as a mediator (39). As indicated in Figure 2.3, the dimer structure has a profound influence on the reactivity of DPM dimers. The phenolic α-5 dimer I gave no dimeric products, while the methylated α-5 dimer Ib gave a high yield of the diguaiacyl ketone resulting from oxidation of the methylene group. On the other hand, the methylene group of the phenolic 5,5'-DPM dimer II was fairly resistant to the enzyme action. A 40% transformation of this dimer was accompanied by a small formation of the mono- and di-benzaldehyde derivatives resulting from oxidation at the methyl function. Also, the methylated 5,5'-DPM dimer II_b was practically stable.

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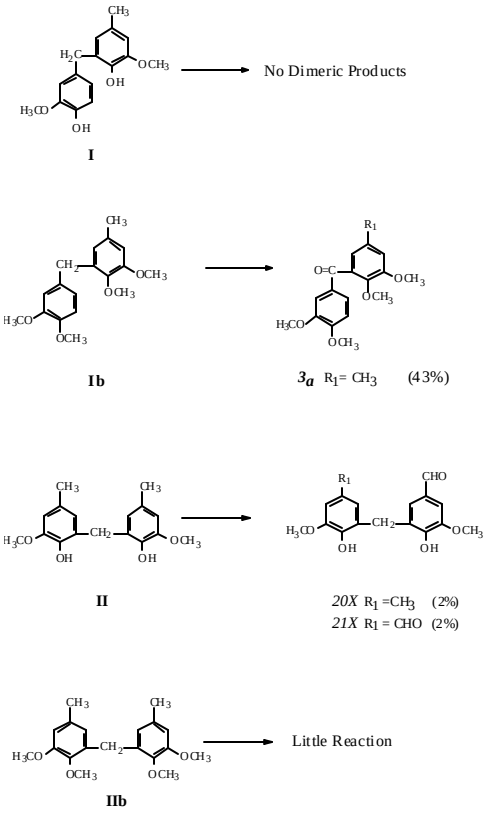

Figure 2.3. Major products from the LMS oxidation of lignin DPM model dimers.

TASK 3

Determine the Role of Lignin Condensations in Kraft Delignification

The purpose of this Task was to determine the significance of lignin condensation reactions in a typical kraft cooking of softwood using the novel analytical techniques developed in Task 1. As discussed, the α-5 and 5,5' DPM-condensed units may be determined by the formation of characteristic products in NO (Figs. 1.5 and 1.7), PMO (Fig. 1.10), and ozonation (Fig. 1.12). Each of these techniques, however, has its limitation, and can only detect certain type of the condensed units. All the techniques we have developed so far are still not suitable for a quantitative determination. Thus, the original objectives of this task were only partially achieved.

Subtask 3.1 Preparation of kraft pulps

A series of kraft pulp from batch cooking of loblolly pine were prepared using a typical kraft liquor (1 M NaOH plus 0.2 M Na_2S) at a liquor to wood ratio of 5 for different duration. A total of 7 pulp samples extending to 15 kappa number were prepared. These samples, as indicated in Fig. 3.1A, represent three different phases of the kraft delignification.

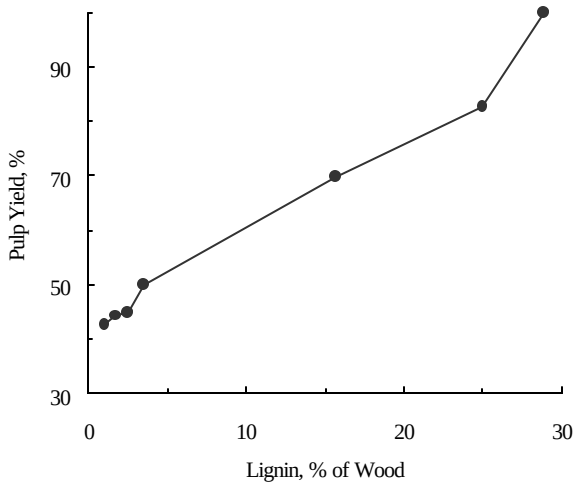

Figure 3.1A. The kraft delignification of loblolly pine showing relationship of the pulp yield - lignin content

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Subtask 3.2 Phenolic hydroxyl group (PHOH)

The lignin content was determined by Tappi standard methos, and the PHOH content was determined *in situ* by a periodate oxidation procedure (22). Figure 3.1B illustrates that this functional group increases steadily with a decrease of the pulp kappa number. This trend in consistent with previous findings (23) is rather interesting. The data suggest that the aryl ether cleavage reaction has less impact on the residual phase delignificaion, and this may be partly attributed to the residual lignin being more condensed (40).

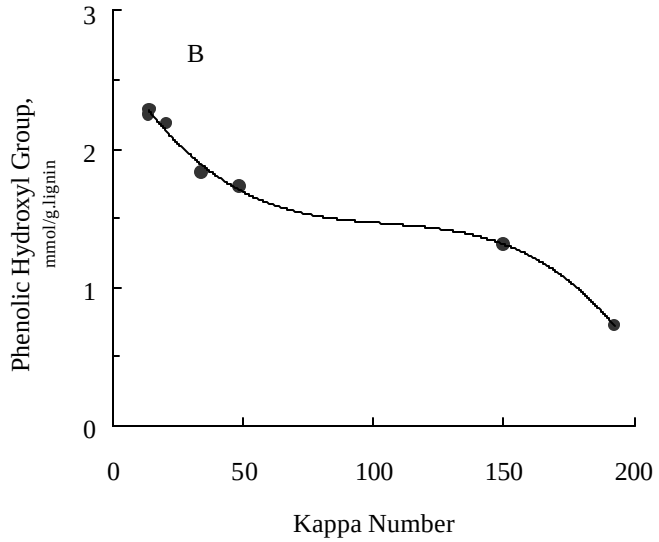

Figure 3.1B. The phenolic hydroxyl group content – kappa number relationship for a series of kraft pulps.

Subtask 3.3 Nitrobenzene oxidation (NO)

The NO oxidation of kraft pulps was conducted as discussed in Subtask 1.3. Figure 3.2 lists the major products identified including vanillin *1*, vanillic acid *2*, 5-carboxyvanillin *3*, dehydrodivanillin *4* and α-5 diguaiacylketone aldehyde *14*. The formation of vanillin and the α-5 diguaiacylketone aldehyde is of special interest. The vanillin was largely derived from the uncondensed, while the α-5 diguaiacylketone aldehyde was from the α-5 DPM units.

Figure 3.3 illustrates that the yield of vanillin plus vanillic acid decreased steadily with a decrease in the pulp kappa number. This suggests that kraft pulping steadily increased its content of C_5 –substituted units in the residual lignin. Interestingly, we have detected the formation of α-5diguaiacylketone aldehyde *14* in all the kraft pulp samples indicating the presence of the α-5 condensed units. This confirms that the α-5 type condensation is involved in the kraft pulping process. Also, the apparent yield of product *14* varied with the pulp kappa number, and was appreciably reduced for the low-kappa number pulps as indicated in Figure 3.4. Thus, it appears that the α-5 DPM units may be degraded or transformed into other structures on extended cooking as discussed in Subtask 2.1. Since the product yield was very low (< 1%), it would be very difficult for a quantitative evaluation.

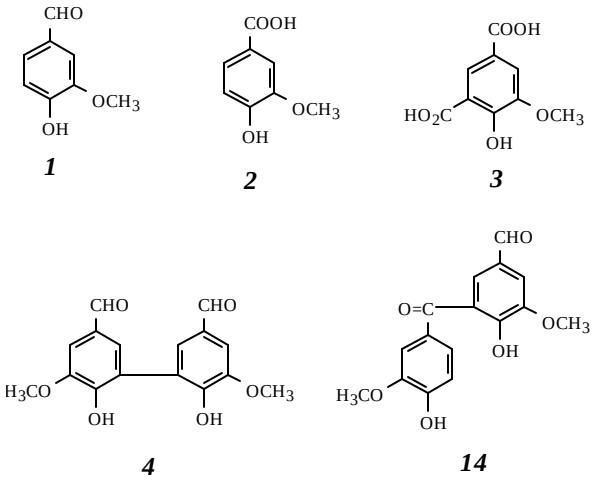

Figure 3.2. Products identified from NO of kraft pulps

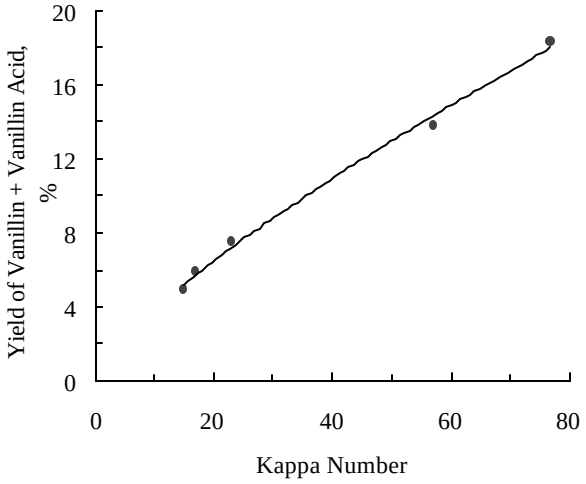

Figure 3.3. The yield of vanillin plus vanillic acid from NO for a series of kraft pulps.

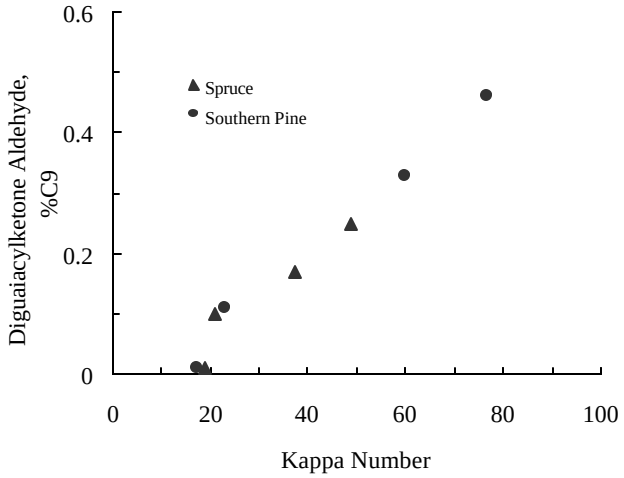

Figure 3.4. The yields of α-5diguaiacylketone aldehyde in NO of kraft pulp as related to the kappa number.

To our surprise, we were unable to detect the 5,5-divanillinmethane (*21X* of Fig. 1.7) among the NO products of kraft pulps. This may suggest that the residual lignin contain little of the 5,5'-DPM units. However, there is a possibility that the 5,5'-DPM structures present in the residual lignin were very resistant to NO, and could not be converted into the 5,5'-divanillin methane product.

Subtask 3.4 Combined NO and PMO of kraft pulps

On PMO of the softwood kraft pulps, we were unable to detect those products (*3b*, *4b*, and *5b*) expected from the 5 and 5,5'-DPM structures (Figure 1.10). Similarly, these products were not detected using a combined NO and PMO procedure. These observations, however, does not imply these DPM units were totally negligible in the kraft pulp, as this technique can detect only those DPM units of the phenolic type. Also, the reactivity of these phenolic DPM units may be hindered by the nature of side chain as discussed earlier.

Subtask 3.5 Preparation of periodate-treated kraft pulps

As noted earlier, periodate oxidation is very useful for determination of the PHOH content of residual lignin *in situ*. The kraft pulp samples were treated with periodate at 4°C for 24 h to selectively the phenolic lignin component (41). These periodate-treated samples were used to reveal the chemical nature of the etherified lignin structures.

Subtask 3.6 Characterization of periodate-treated kraft pulps

On NO of periodate-treated kraft samples, we also detected the formation of the α-5 diguaiacylketone aldehyde *14* as in the untreated sasmples. This suggests that some of the α-5 condensed units in the residual lignin were etherified. The generation of these etherified condensed units, however, involves more than the commonly accepted quinonemethide reaction, which as, indicated in Fig. 1.1, would yield totally the phenolic type structures.

Subbtask 3.7 (New) Ozonation

On ozonation of a softwood kraft pulp, we have detected the formation of products *26* and *27* (Fig. 1.12), indicating the presence of α-5 condensed units in the residual lignin. This is consistent with the results of NO analysis discussed earlier. Although the combined yields of these two products were low (1.2%), the actual content could be significantly higher, when considering a low efficiency of the dimer conversion (Subtask 1.5), and a reduced reactivity of a pulp substrate.

Implications

The presence of α-condensed DPM units in the residual kraft lignin has been confirmed by the formation of the characteristic oxidation products in NO and in ozonation. On the other hand, we could not detect the presence of 5,5'-DPM condensed structures in the residual lignin. Thus, our results suggest that alkaline condensation reactions may be largely limited to the α-5 type. Also, there is an indication that these structural moieties may not be entirely phenolic or may be associated with a rather condensed side chain unit rendering them not responsive to the degradation process.

As noted earlier, each of three analytical methods developed in this study has its limitations, and can only detect certain types of the DPM condensed units. It continues to be a challenge to devise a viable technique for determining the total content of DPM condensed units in the residual lignin *in situ*.

TASK 4

Determine the Reactivity of Kraft Residual Lignin *in Situ*

We have determined the delignification behavior of kraft pulps toward a series of non-chlorine bleaching agents including alkali-O_2, chlorine dioxide, hydrogen peroxide, and ozone delignification. Also, we have examined a new task on delignification with a laccase-mediator-system (LMS).

In this study, a major emphasis is to understand the relative reactivity of the phenolic and etherified lignin components. As noted earlier, the phenolic content of residual lignin can be readily determined *in situ* by the periodate oxidation procedure. On the other hand, a quantitative determination of the DPM units in the residual lignin has been difficult to achieve as discussed in Task 3.

Subtask 4.1 Alkali-O_2 delignification

Figure 4.1 illustrates the rate of O_2 delignification for a southern pine EMCC kraft conducted at 100°C, and its influence on the PHOH content of residual lignin. It is evident that the initial rapid delignification was closely related to a removal of the phenolic units, and a significant portion of these structures still remained under typical O_2 delignification conditions. These data support the general contention (42) that O_2 delignification is largely associated with the removal of phenolic units. However, the slow delignification phase appears to involve also the oxidative degradation of etherified structures as discussed later of this section.

Also, the O_2-delignification was determined for a series of conventional kraft pulps with kappa number in the 15-80 range using similar conditions at 100 °C for 1 h, and this would have completed the rapid delignification phase. As indicated in Figure 4.2, the apparent O_2 delignification increased significantly with decreasing kappa number of the unbleached pulps. Thus, the apparent reactivity of residual lignin toward O_2-delignification improves with an extended kraft cooking.

The influence of O_2 bleaching on the characteristics of residual lignin was determined in terms of the phenolic hydroxyl group (PhOH) content, NO products and the response to neutral sulfonation reaction.

4.1.1 Phenolic hydroxyl group (PHOH)

Figure 4.3 shows the influence of O_2-delignification on the PHOH content - kappa number relationship for a series of kraft pulps. Both the un- and O_2-delignified samples display a similar pattern. As indicated, the low-kappa number pulp has a significantly higher PHOH content than the high-kappa number sample. Although the apparent PhOH content of unbleached pulps has a direct impact on O_2-delignification (Figure 4.4), the overall reactivity of this functional group appears to be slightly lower for the low-kappa number pulps. It should be noted that under typical O_2 bleaching conditions, the apparent phenolic content of O_2-bleached residual lignin was reduced by about 40-45%. The nature of the remaining less reactive phenolic structures is still not fully understood.

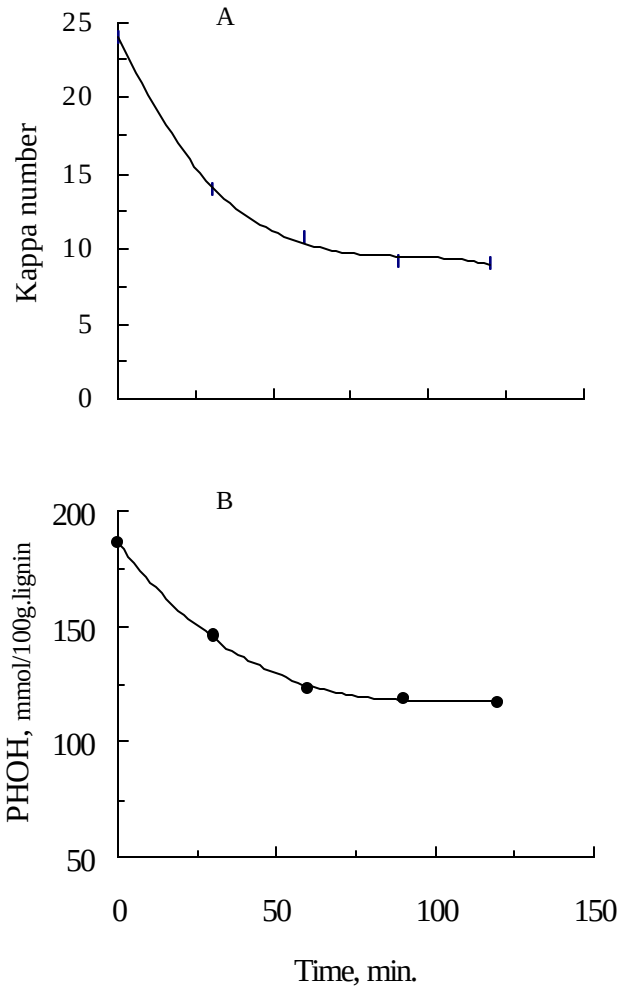

Figure 4.1. The rate of O_2 delignification for a southern pine EMCC kraft conducted at 100°C (A), and its influence on the PHOH content of residual lignin.

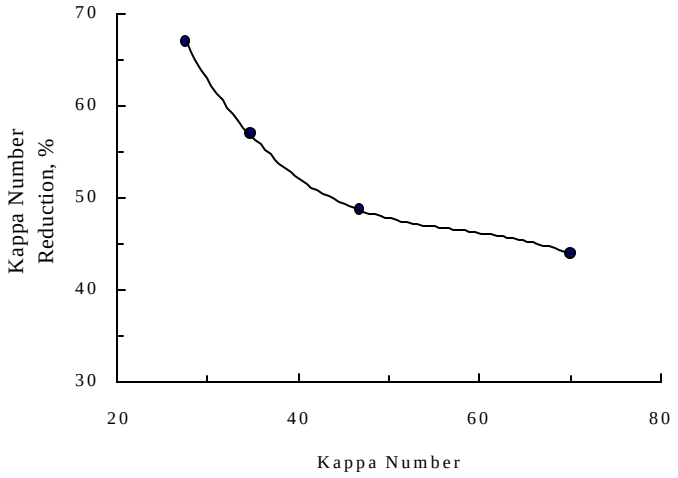

Figure 4.2. Percent O_2 delignification of kraft pulps as related to kappa number of the unbleached Kraft samples.

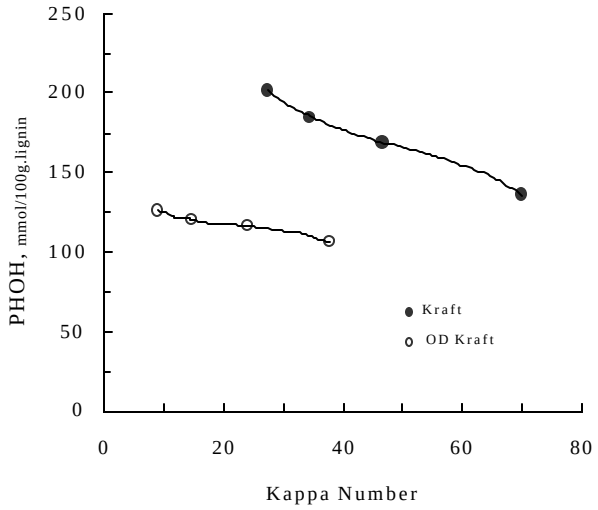

Figure 4.3. The influence of O_2 delignification on the PHOH - kappa number relationship for a series of kraft pulps.

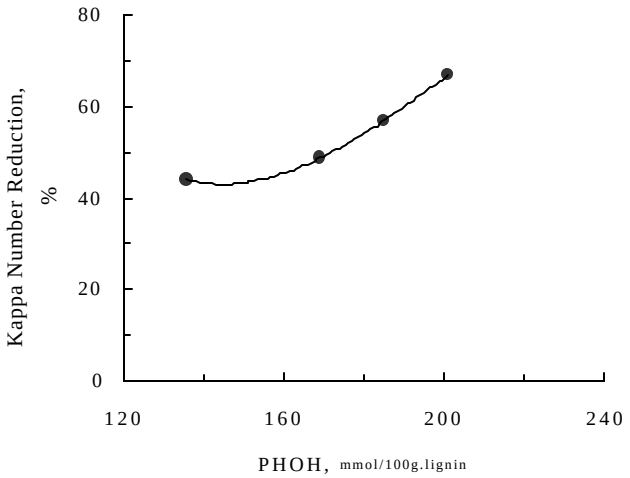

Figure 4.4. The influence of PHOH content on O_2 delignification for a series of kraft pulps.

4.1.2. Nitrobenzene Oxidation

O_2 delignification has a noticeable effect on the yield of vanillin plus vanillic acid from NO of the un- and O_2 - delignified kraft pulps. As indicated in Fig. 4.5, the yield changes, expressed as percentages of the un-delignified pulp residual lignin, varied considerably ranging from a10% decrease to a 25% increase for the 80 and 15 kappa number pulps, respectively. The observed yield reduction may be resulted from a preferential removal of he the uncondensed units. On the other hand, the yield increase is likely resulted from the formation of vanillin-producing moieties during the O_2 delignification process. Also, the content of α-5DPM units was substantially reduced after the O_2 delignification. All these observations are consistent with the behavior of phenolic DPM model dimers, which were very reactive in alkali - O_2 as illustrated in Figure 2.1.

4.1.3. Response to Neutral Sulfite Treatment (**New**)

Since fiber sulfonation under neutral or slightly alkaline conditions is generally limited to the phenolic units of lignin, which are capable to form the quinonemethide intermediates (43), it may be used to reveal the nature of phenolic lignin units. In neutral sulfite treatment of the wood lignin (at pH 7.5 and 140 °C for 1 h), an nearly quantitative sulfonation of the phenolic units was observed previously for a variety of wood species (44), indicating little condensation occurring at the benzylic position. Similar analysis has been extended to the kraft and O_2-bleached pulps.

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Figure 4.6 illustrates that the sulfonate group content, when compared at similar kappa number, was substantially higher for the O_2-bleached than for the kraft pulp. This is a rather interesting phenomenon especially in considering that the O_2-bleached pulp had a significantly lower PhOH content than the kraft pulp (Fig. 4.3). It follows that O_2 bleaching must have generated additional sites capable to undergo sulfonation under slightly alkaline conditions. The enhanced sulfonation of O_2-bleached pulps in sulfite treatments, based on lignin model compound reactions (43), may be ascribed to the sulfitolytic cleavages of etherified β-aryl ether structures containing an α-carbonyl group. This finding supports the concept that the oxidation of etherified units was involved in O_2 bleaching.

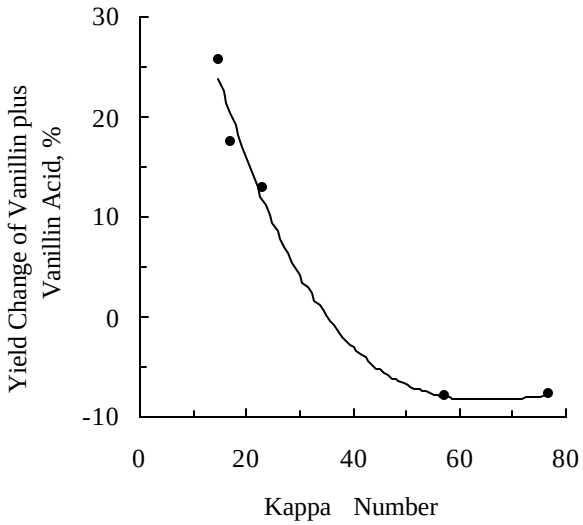

Figure 4.5. The influence of O_2 delignification on the yield of vanillin plus vanillic acid in nitrobenzene oxidation as related to kappa number of the unbleached samples.

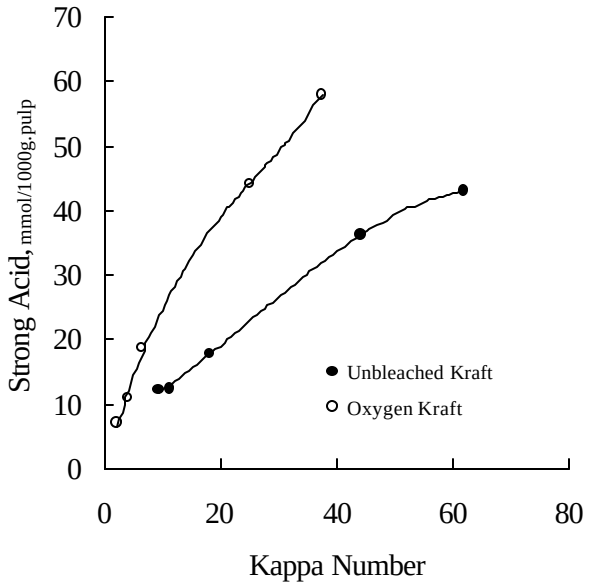

Figure 4.6. A comparison of kraft pulps before and after the O_2 delignification in response to neutral sulfite treatments.

Subtask 4.2 Chlorine Dioxide

The chlorine dioxide delignification of kraft pulps was conducted using different chemical charge (0.5-8% of active chlorine on pulp) at 70 °C for 1 h. During these treatments, practically all the chlorine dioxide was consumed except small amounts of residual chlorine dioxide were detected in the experiment with 8 % chemical charge. The delignification as illustrated in Figure 4.7A is directly related to the chlorine dioxide charge up to approximately 4% level.

Figure 4.7B shows the relationship between the chlorine dioxide delignification and the degradation of phenolic units in the residual lignin as measured by the periodate oxidation method (22). This analytical procedure, based on methanol formation, excludes the detection of catechol units. Accordingly, the catechol-types resulting from demethylation reactions would be accounted as loss of phenolic hydroxyl groups in the present study.

It is evident that the chlorine dioxide delignification displays two distinct phases. The initial delignification up to approximately 30 % level was closely related to degradation of the phenolic structures, whereas further delignification appears to be also involved in the oxidation of etherified structures. Interestingly, about 20 % of the phenolic structures in the residual kraft pulp were fairly resistant to the chlorine dioxide action.

On NO of the chlorine dioxide treated samples, we could not detect the presence of α-5 DPM units for the sample at 50% delignification. In consistent with the lignin DPM model dimer reactions, these units were reactive, and practically degraded under typical chlorine dioxide bleaching conditions.

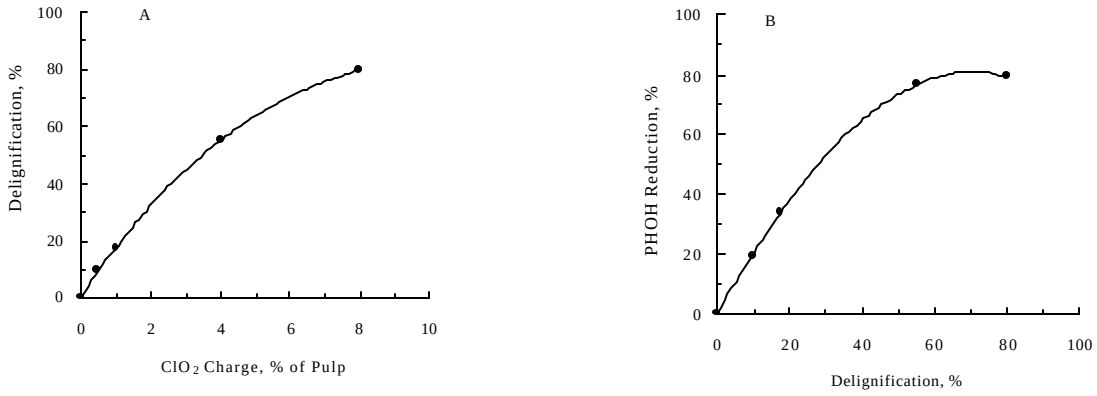

Figure 4.7. The influence of ClO_2 charge on delignification of the kraft pulps (A), and of delignification on the PHOH content of residual lignin (B).

Subtask 4.3 Hydrogen peroxide

The peroxide delignification was conducted with a chemical charge of 3% H_2O_2 and 2% NaOH at 10% consistency and at 90°C for two h. Figure 4.8 illustrates that the peroxide delignification increases with a decrease of the unbleached kraft kappa number. This phenomenon is similar to that of the O_2 delignification (Fig. 4.2), and suggests that the apparent delignification with peroxide was higher for the low kappa pulps.

Figure 4.9 shows the influence of peroxide delignification on the PHOH content of residual kraft pulps. It is evident that the peroxide delignification was accompanied by a significant reduction of this functional group. The extent of this reduction, however, was appreciably lower than that observed in the O_2 delignification process (Fig. 4.3). Thus, it appears that the perioxide delignification also involves the oxidative degradation of certain reactive etherified units. The nature of residual lignin in peioxide - delignified kraft pulps, as revealed in the NO products, was slightly different from that of the O_2 - delignified samples, and contained little of the vanillic acid-producing structural units.

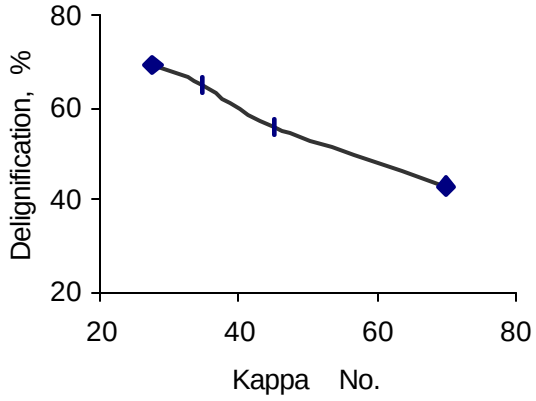

Figure 4.8. The peroxide delignification of kraft pulps as related to the kappa number of the unbleached samples.

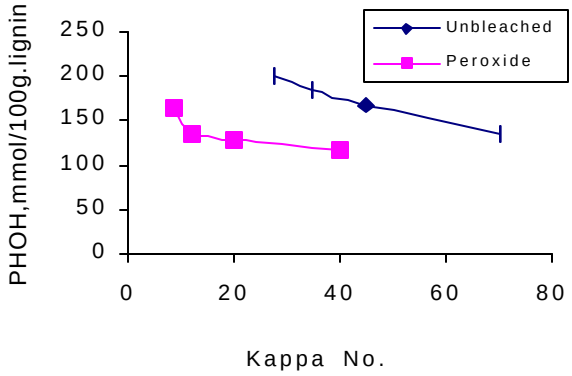

Figure 4.9. The influence of peroxide delignification on the PHOH content – kappa number relationship of kraft pulps.

Subtask 4.4 Ozone

The ozone treatment of kraft pulps was conducted in a low consistency (1 %), because the limitation of ozone concentration we can generate. Figure 4.10A illustrates that the delignification of kraft pulp based on the apparent O_3 consumption displays two discernible phases.

Interestingly, the initial delignification resulted in a slight increase in the phenolic hydroxyl group content of residual lignin (Fig. 4.10B). This observation seems to suggest that the degradation of etherified units is an important reaction in ozonation. Also, the initial ozonation was shown to have little influence in the vanillin yield on NO of the residual lignin. The latter product generally serves as an estimation of the uncondensed lignin units. Thus, the reactivity of condensed lignin structures toward ozone appears to be quite comparable to that of uncondensed units.

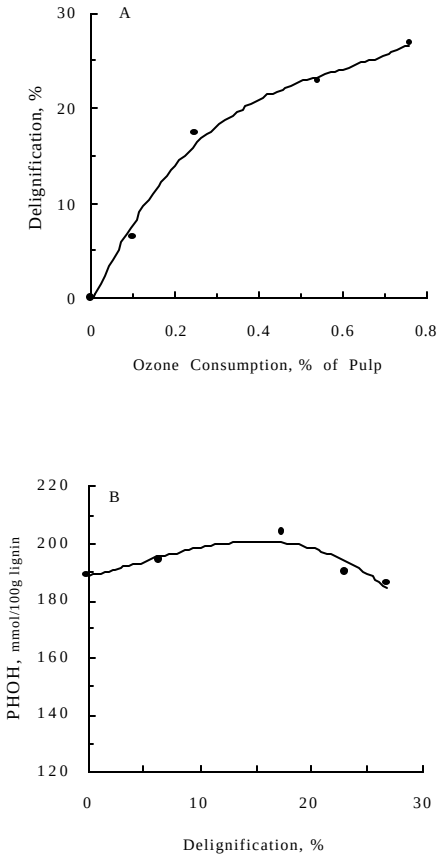

Figure 4.10. The influence of O_3 charge on the delignification of kraft pulps (A), and of delignification on the PHOH content of residual lignin.

Subtask 4.5 (New) Laccase-Mediator-System

The enzyme-assisted delignification of kraft pulps by laccase from *Botrytis cinerea* was conducted in two stages, and evaluated by the kappa number reduction after an initial laccase treatment in the presence of HOBT as mediator (39). These experiments were conducted under atmospheric conditions for 5 days (EMS) as well as after a subsequent alkaline treatment at 80 °C for 1 h (EMS-E). The kraft sample examined was a softwood EMCC (extended modified continuous cooked) pulp (at a kappa number of 28).

Figure 4.11 illustrates that the initial LMS delignification of kraft pulp is accompanied by a significant decrease in PHOH content of the residual lignin. This functional group reached a steady level at a later stage of delignification. This pattern suggests that the LMS delignification reactions were not entirely attributed to the removal of existing phenolic units. Interestingly, the subsequent alkaline extraction (LMS-E) resulted in an apparent increase in the phenolic hydroxyl group content, which was probably derived from the aryl ether cleavages. Thus, some alkali-labile aryl ether units were generated during the LMS stage. In this regard, the introduction of α-carbonyl groups is known to facilitate the β-aryl ether cleavages in alkali (45).

Also, our data supports a previous report by Blaakshin *et al*. (46) that a prior methylation of pulp to block the phenolic hydroxyl groups has little influence on the LMS delignification process. Thus, the LMS delignification is unique in the mechanism involved and unlike most delignification systems does not depend heavily on the degradation of phenolic units.

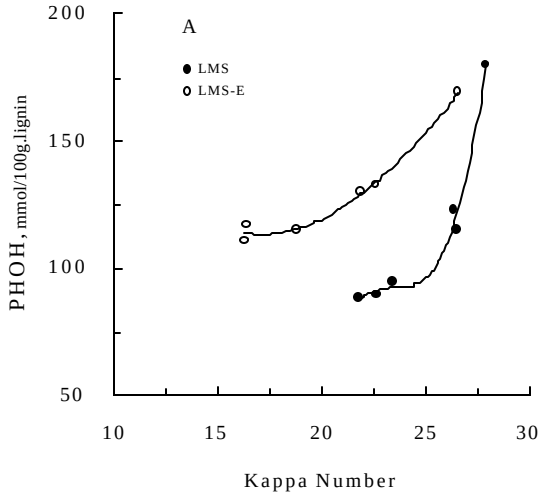

Figure 4.11. The influence of laccase-assisted delignification of unbleached kraft pulp (A) on the phenolic hydroxyl group content (PHOH) after initial enzyme treatment (LMS), after the alkali extraction (LMS-E).

Implications

The results of Task 4 provide further insights into the delignification behavior of softwood kraft pulps toward O_2, chlorine dioxide, peroxide, ozone, and laccase-mediator system. The relative reactivity of the phenolic and non-phenolic components varied widely among these non-chlorine agents. In O_2 and ClO_2 bleaching, the oxidative degradation of phenolic structures appears to be largely responsible for the delignification reaction. In ozonation, the reactivity of etherified units seems to be quite comparable to that of the phenolic structure. Also, it is capable to degrade both the uncondensed and condensed units.

On the other hand, the laccase-assisted delignification is unique in the mechanism involved,and unlike most chemical bleaching systems does not depend heavily on the degradation of phenolic lignin units.

Judging from the behavior of phenolic DPM dimers being very sensitive to an alkali /O_2-treatment resulting in the formation of monomeric and oxidative coupling products, these transformations are also likely to involve in the O_2-bleaching of kraft pulps. This contention is consistent with the characteristics of O_2-bleached pulps. The O_2-delignification efficiency has been shown to increase significantly with a decrease in the unbleached pulp kappa number, and is closely related to the phenolic hydroxyl group content of kraft pulps.

O_2 delignification, although removed a significant amount of the phenolic units, resulted in an apparent increase in response to neutral sulfonation for the O_2-bleached pulp. Also, it showed a significant increase in the yield of vanillin plus vanillic acid for the low-kappa number pulps on nitrobenzene oxidation analysis

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The present data further support the contention that the presence of diphenylmethane-type structures is a contributing factor to the low reactivity of residual kraft lignin toward O_2 delignification.

TASK 5

Determine the Impact of Pulping Conditions On the Nature of Residual Lignin

Subtask 5.1 Preparation of Modified kraft pulps

In this task, the main objective was to determine the influence of alkaline pulping conditions on the nature of residual lignin. The pulps prepared include conventional kraft, high sulfidity (40%) kraft, soda, and soda-AQ (anthraquinone), and neutral sulfite-AQ pulp samples. An EMCC kraft sample was kindly provided by then Ahms

Figure 5.1 illustrates a typical kraft delignification of softwood chips conducted in a batch digester at 170°C using a 25% sulfidity and 18% active alkali charge. The delignification rate, as generally observed, proceeded very slowly below the 30 kappa number level.. As indicated, the kraft delignification rate remained essentially unchanged by using a higher sulfidity (40 vs. 25%) while maintaining a constant active alkali charge.

On the other hand, the delignification rate of soda, soda-AQ, and NS-AQ cooks was significantly lower than that of kraft, especially for the NS-AQ, which was conducted at an even higher temperature (180 vs. 170°C).

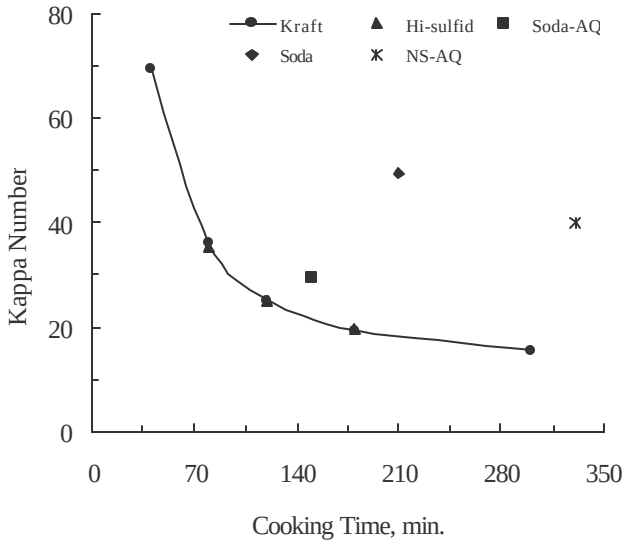

Figure 5.1. The influence of pulping conditions on the rate of alkaline delignification at 170 °C 180°C for the NS-AQ cook).

Subtask 5.2 Phenolic hydroxyl groups

The phenolic hydroxyl group (PHOH) content of the pulp residual lignin was determined *in situ* by periodate oxidation method based on methanol formation (22). As illustrated in Figures 5.2 and 5.3, alkaline cooking conditions have a noticeable influence on the PHOH – kappa number relationship of the unbleached kraft pulps. In general, the PHOH content of residual lignin increased steadily with a decrease in the unbleached pulp kappa number. The increase of this functional group is especially pronounced with kappa number below the 30 level.

Compared to the reference kraft at similar kappa number, a slightly lower PHOH content was observed for the high-sulfidity pulp while higher values were obtained for other alkaline pulps (soda, soda-AQ, and NS-AQ). Since PHOH are essential to lignin dissolution in alkali, a higher content of this functional group in the residual lignin may be partly related to the residual lignin being more condensed. Interestingly, this contention is in line with a general trend that the tendency of alkaline lignin condensation reactions would increase in the order of: high sulfidity < reference kraft < NS-AQ < soda-AQ < soda cooks

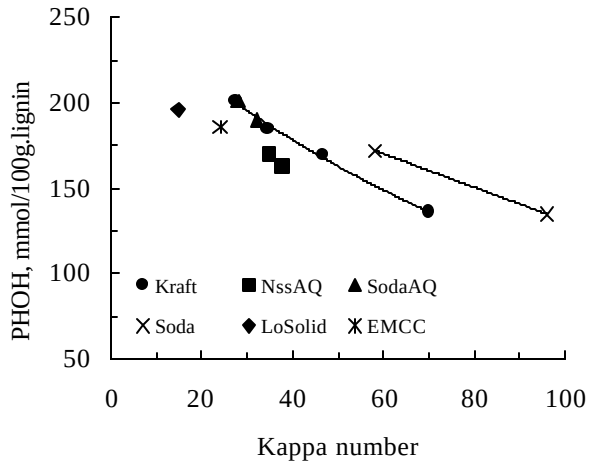

Figure 5.2. The influence of alkaline cooking conditions on the PHOH content of residual lignin as related to kappa number of the unbleached pulps.

Subtask 5.3 Characterization of total condensed units

The sulfidity in kraft pulping was found having a noticeable influence on the characteristics of residual lignin. Compared with a reference kraft at similar kappa number, a high sulfidity (40%) pulp lignin appears to be less condense, as indicated by a slightly higher yield of vanillin (Figure 5.4) and a lower yield of the α-5 diguaiacylketone aldehyde (Figure 5.5) from the NO analysis. Also, the high sulfidity pulp was more responsive to a neutral sulfite treatment, and this suggests the residual lignin being less substituted at the benzylic positions.

Similarly, compared with a reference kraft at similar kappa number, the residual lignin of a neutral-anthraquinone (AQ) pulp was shown to give an appreciably higher yield of vanillin in NO analysis. Thus, it appears that sulfite ions significantly reduced the condensed structures in the residual lignin.

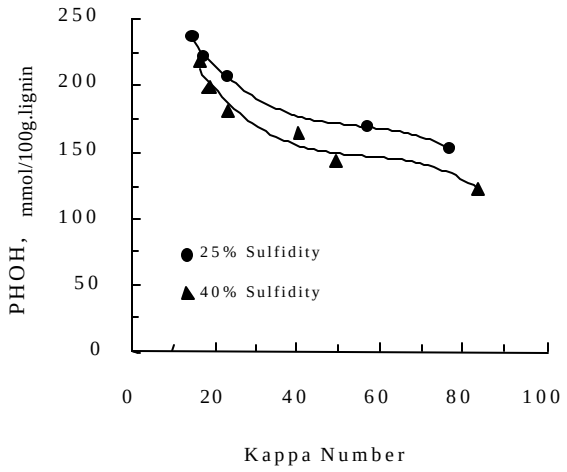

Figure 5.3. The influence of sulfidity on PHOH content of the residual lignin as related to kappa number of the kraft pulps.

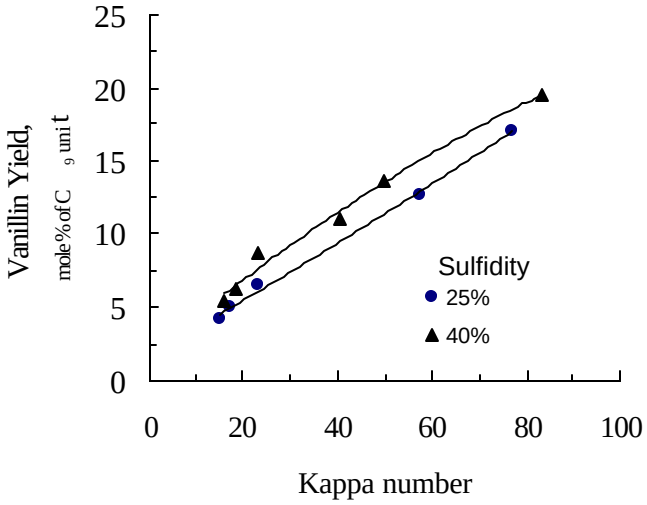

Figure 5.4. The influence of sulfidity on the yield of vanillin in NO oxidation of the kraft pulps.

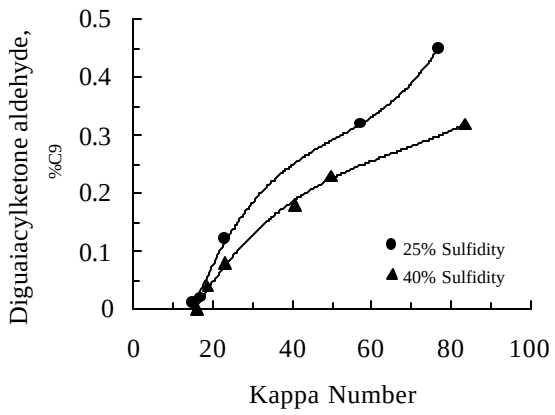

Figure 5.5. The influence of sulfidity on the yield of α-5 diguaiacylketone aldehyde in NO of the kraft pulps

Subtask 5.4 Preparation of periodate-treated modified kraft pulps

The periodate-treated modified karaft pulps were similarly prepared as indicated in Subtask 3.5. These samples included EMCC, soda, soda-AQ, and NS-AQ pulps.

Subtask 5.5 Characterization of periodate-treated modified kraft pulps

The periodate-treated modified kraft pulps were characterized by the NO method (Subtask 3.3) mainly to detect the formation of the α-5 diguaiacylketone aldehyde *14* from the α-5 DPM units. Interestingly, this product was detected in all the modified kraft samples indicated in Subtask 5.4. This further confirms the involvement of the α-5 type condensation in alkaline cooking. The extent to which these lignin condensation reactions may be varied with cooking conditions is still difficult to quantity due to the limitation of the NO method discussed earlier.

However, we observed an interesting trend on the vanillin yield of periodate-treated modified kraft pulps, which are largely derived from the uncondensed lignin units. Comparing pulps at similar kappa number, the vanillin yield decreases in the order of NS-AQ > EMCC > kraft > soda-AQ > soda. This trend parallels to a increasing tendency of lignin condensation reactions. Thus, the modification of etherified lignin structures varies considerably with the cooking conditions.

TASK 6

Determine the Impacts of Alkaline Pulping Conditions on the Reactivity of Residual Lignin

The Task 6 was to examine the response of modified kraft and alkaline pulps to non-chlorine agents with emphasis on the O_2 delignification. The kraft samples included two series of batch-cooked spruce pulps using different sulfidity and one EMCC sample. The other alkaline pulps were soda, soda-AQ (anthraquinone), and neutral sulfite-AQ pulp samples.

Subtask 6.1 O_2 Delignification

The O_2 delignification was conducted with a charge of 2.5% NaOH and 0.5% $MgSO_4$ at 10% consistency and 100°C under 100 psi of O_2 for 1h. These reaction conditions would have completed the rapid delignification phase. Figures 6.1 and 6.2 illustrate that alkaline pulping conditions have a significant influence on the O_2 delignification efficiency as indicated by the percent kappa number reduction. In general, the O_2 delignification efficiency increased with decreasing kappa number of the unbleached pulps. Thus, the apparent reactivity of the pulp residual lignin toward O_2 delignification improves with extended kraft cooking. Comparing the reference kraft at similar kappa number, a slightly higher O_2 delignification was for the soda pulps, and lower for other alkaline (high-sulfidity, EMCC, soda-AQ and NS-AQ) pulps.

As indicated earlier (Fig. 4.4), the extent of O_2 delignification for a series of kraft pulps is closely related to the PHOH content of the residual lignin. This contention can also be extended to a variety of modified kraft and soda pulps as reflected in their PHOH content (Figs. 5.2 and 5.3) and their response to O_2 delignification (Figs. 6.1 and 6.2)

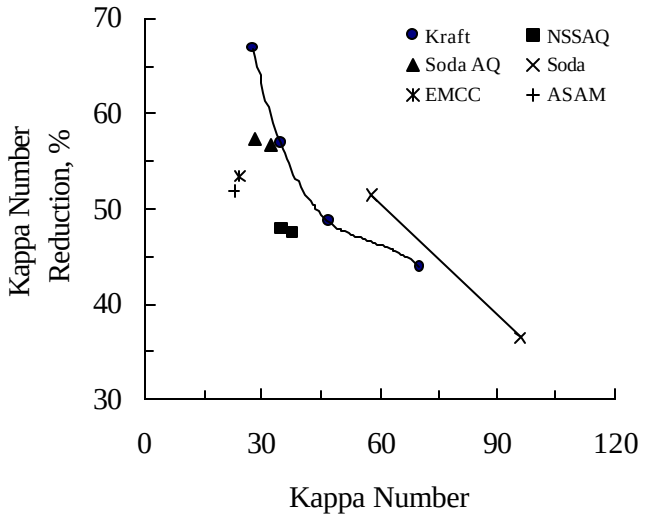

Figure 6.1. The influence of cooking conditions on the O_2 delignification of alkaline pulps.

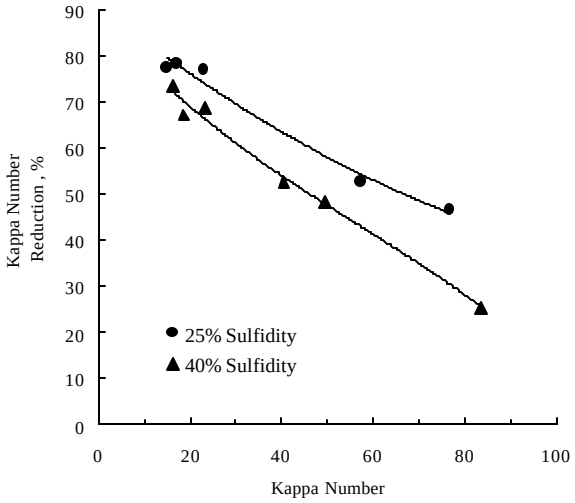

Figure 6.2. The influence of sulfidity in O_2 delignification of kraft pulps.

Subtask 6.2 Chlorine Dioxide

Figure 6.3 illustrates chlorine dioxide delignification for a series of softwood kraft, soda-AQ, and NS-AQ pulps. The reactions were conducted using a 0.1 kappa factor of ClO_2 charge at 70°C for 1 h. As indicated, the extent of chlorine dioxide delignification under similar conditions was shown to increase slightly with decreasing kappa number of the unbleached samples. Also, the response of modified pulps (soda-AQ and neutral sulfite-AQ) to the chlorine dioxide delignification was very comparable to that of kraft pulps, when comparing at similar kappa number.

Subtask 6.3 Alkali Peroxide

Figure 6.4 shows the peroxide delignification for a series of kraft soda, and NS-AQ pulps. The reactions were conducted with a chemical charge of 3% H_2O_2 and 2% NaOH at 10% consistency and at 90°C for two h. As indicated, the kappa number of the unbleached samples has significant effects on the delignification, and a similar response was observed for the modified pulps (soda and neutral-AQ) when compared at similar kappa number. In general, the low kappa number pulps were more responsive to the alkali peroxide delignification than the high kappa number pulps.

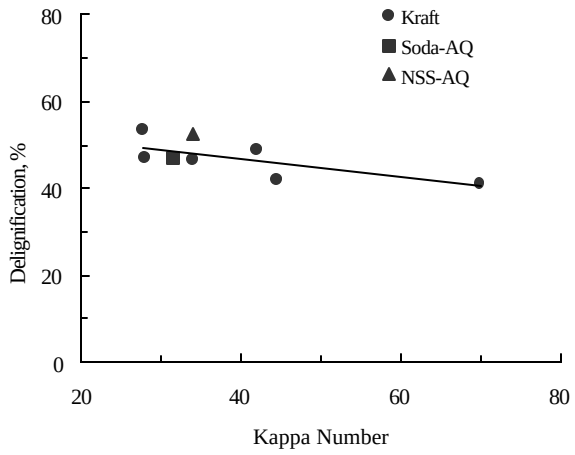

Figure 6.3. The chlorine dioxide delignification for a series of kraft and modified alkaline pulps.

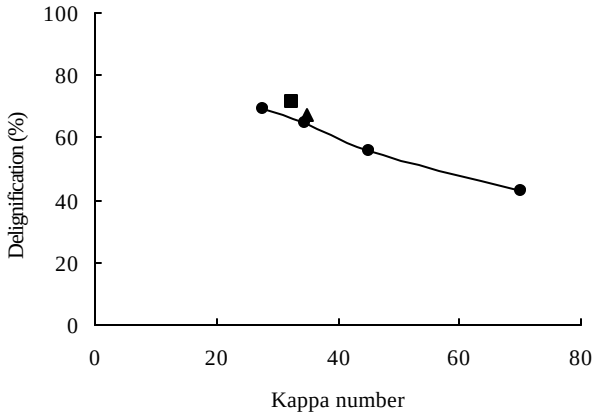

Figure 6.4. The alkali peroxide delignmification for a series of kraft •, soda-AQ ■, and NS –AQ ▲ pulps.

Subtask 6.4 Ozone

We have examined the delignification behavior of a NS-AQ and a reference kraft pulp under similar ozonation conditions. These two samples have a similar lignin content (5.7 vs.5.2 %), and display a two-phase delignification (Figure 6.5). As indicated, the initial rapid delignification of the NS-AQ pulp was appreciably higher than that of the kraft sample. Also, a significant amount of the residual lignin was very resistant to the ozone degradation.

In view of the importance of O_2 delignification in pulp bleaching, we have examined the ozonation behavior of an O_2-delignified kraft and compare to that of the kraft sample. Figure 6.6 illustrates that the O_2-bleached pulp was very responsive to ozonation resulting in a higher delignification than the kraft sample for a given O_3 consumption (Fig. 4.10). Also, the O_3 delignification of O_2 pulp was accompanied by a noticeable increase in the PHOH content of residual lignin. The increase of this functional unit is likely attributed to the oxidative cleavage of aryl ether structures. It follows that certain functional groups generated in the O_2 delignification process are very labile to the ozone degradation.

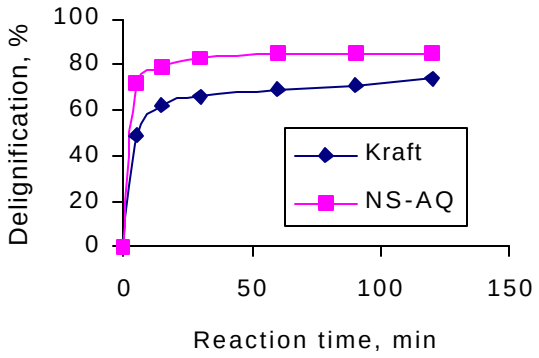

Figure 6. 5. The ozone delignification rate of an NS-AQ and a reference kraft pulps.

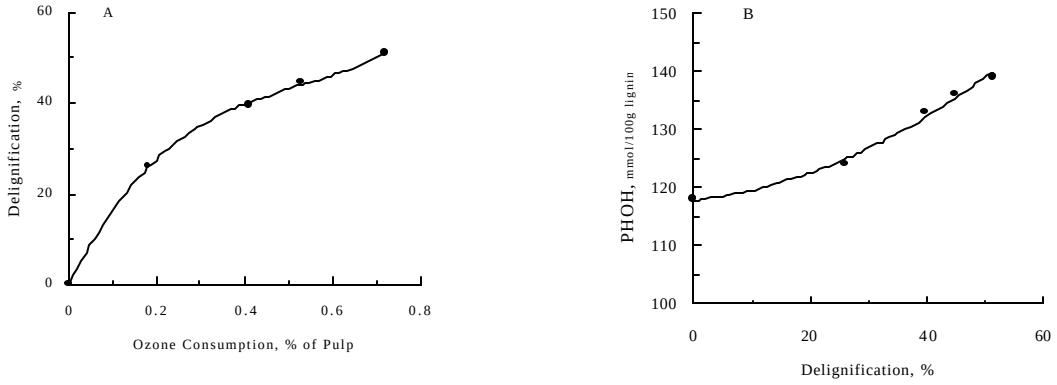

Figure 6.6. The influence of O_3 charge on the delignification of O_2 -delignified kraft pulps (A), and of delignification on the PHOH content of residual lignin.

Subtask 6.5 (New) Laccase-Mediator-System (LMS)

We have examined the influence of O_2 bleaching on the delignification with a LMS process, and the procedure was similar to that described in Subtask 4.5. Interestingly, the O_2 –delignified pulp was more responsive to the LMS process resulting in a higher delignification than the kraft pulp. Also, a similar delignification pattern was observed for both the O_2 –delignified (Figure 6.7) and the original kraft (Figure 4.11) samples with respect to changes of the PHOH content in the residual lignin. These findings further support the contention that the degradation of etherified structures is a key mechanism in the overall LMS delignification process.

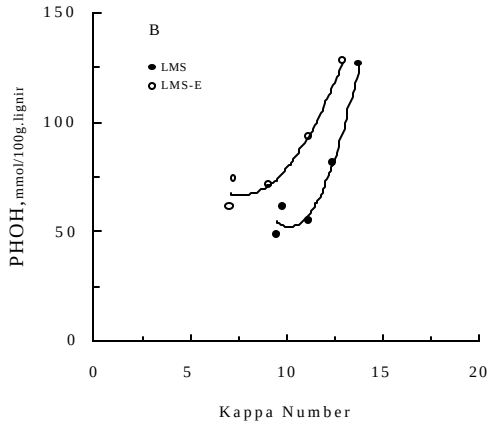

Figure 6.7. The influence of laccase-assisted delignification of the O_2-delignified kraft pulp (B) on the phenolic hydroxyl group content (PHOH) after in itial enzyme treatment (LMS), after the alkaline extraction (LMS-E).

TASK 7 (NEW)

Determine the Significance of Benzylic Oxidation in Delignification Reactions

Although O_2 delignification is generally accepted as being attributed to the removal of phenolic units, approximately 50% of these functional units were still remained after bleaching (Figs. 4.1 and 4.3). However, our recent results suggest that the oxidative degradation of etherified structures is also an important reaction in O_2 bleaching. As discussed earlier, the residual lignin of O_2-bleached kraft pulps, as compared to that of the unbleached samples, has a lower phenolic unit content (Fig. 4.3), and was more responsive to neutral sulfite treatments resulting in a higher sulfonation (Fig. 4.6) and a higher aryl ether cleavage reactions. These enhanced chemical reactions, based on lignin model dimers reaction (43), may be ascribed partly to the sulfitolytic cleavages of etherified β-aryl ether structures containing an α-carbonyl group. Also, laccase is well known for its ability in mediating the benzylic oxidation of etherified lignin model compounds, but its contribution to the pulp delignification has not been clearly defined.

In view the importance of benzylic oxidation in the overall bleaching process, we have initiated this new task to evaluate the reactivity of etherified structures in O_2 bleaching and in LMS delignification process.

Subtask 7.1 O_2 Delignification

We have examined the behavior of etherified lignin β-aryl ether model dimers and methylated kraft pulps under O_2 delignification, as only limited information are available on this subject (42,47).

7.1.1. Lignin model dimers reactions

The reactivity of an etherified lignin β-ether model dimer (I), and the corresponding oxidized dimer at the α position (II) (Figure 7.1) toward O_2-alkali was determined primarily to understand their degradation patterns. They were prepared according to the published procedure (46), and the reactions were conducted in a Quantum reactor under an O_2 pressure of 90 p.s.i. at 100°C to simulate the O_2 bleaching conditions. Table 7.1 summarizes the results on the formation of structurally significant products.

Dimer I was found to be not entirely stable toward O_2-alkali (0.5 M NaOH) at 100°C. After 1h treatment, approximately 20% of the dimer were reacted resulting in the formation of guaiacol (7%) and veratric acid (5%). These two products were likely derived from the β-ether and the C_α-C_β cleavages, respectively

Table 7.1. Structurally significant products from the treatments of lignin β-ether model dimers in alkaline oxygen solution [a]

Dimer [b]	Unreacted Dimer, %	Products [b], mol %	
		1	*2*
I	78.8	6.7	5.2
II	< 0.1	7.9	0.1

[a] Conducted in 0.5 M (dimer I) or 0.06 M (dimer II) NaOH at 100°C under 90 psi O_2 pressure for 1 h.
[b] Referred to Fig. 7.1.

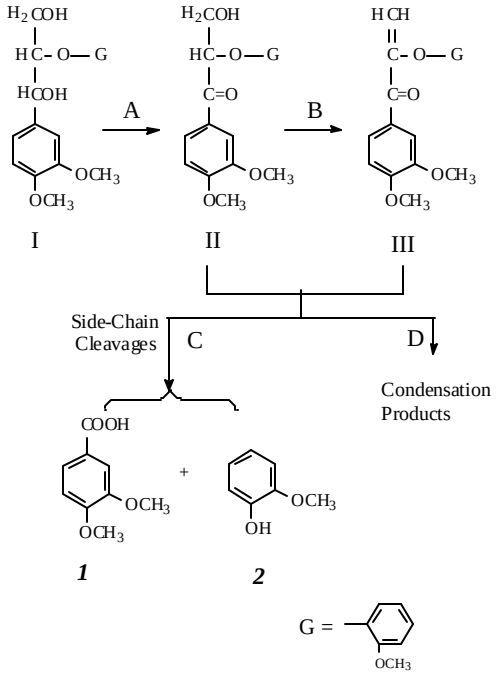

Figure 7.1. A proposed scheme for the degradation of an etherified lignin β-ether model dimer.

The reaction products from the O_2-alkali treatment of dimer II was separated into a chloroform soluble fraction containing mainly the aromatic type products, an aqueous fraction of aliphatic acid, and an insoluble precipitate of condensed products. Thus, the chemical transformation of dimer II under O_2 bleaching conditions is quite complex and involves a variety of processes ranging from degradation to condensation as illustrated in Figure 7.1.

Reaction B represents an alkali-catalyzed β-elimination of dimer II to yield enone III. This elimination reaction was previously reported (48) to occur readily in alkali (0.3 M NaOH at 30°C) with exclusion of air. We observed a similar behavior in a dilute alkali (0.06 M NaOH) under O_2 bleaching conditions. Gierer *et al*. (48) also reported that dimer II and enone III condensed readily in alkali to yield dimeric products (Reaction D). Reaction C involves the side-chain cleavages including both the C_α-C_β and C_1-C_α linkages, and may account largely for the formation of veratric acid and guaiacol.

Preliminary results indicate that the enone dimer III was more reactive than dimer II toward O_2-NaOH treatments, and gave a higher yields of guaiacol and veratric acid. The latter product suggests that the oxidative cleavage of the C_α-C_β linkage is a dominant process.

7.1.2 Reactivity of methylated kraft pulp

In order to understand the reactivity of etherified structures in O_2 bleaching, we have determined the delignification behavior of methylated kraft pulps, in which the PHOH were blocked by reacting with dimethyl sulfate.

Premethylation has been shown having a significant influence on the O_2 delignification process. As expected, the methylated sample was fairly stable under typical O_2 bleaching conditions resulting in little delignification . This is consistent with the general concept that O_2 delignification is largely attributed to the removal of phenolic structures. However, the degradation of etherified units is also involved as revealed from analysis of the products formed in the bleaching effluent.

Figure 7.2 illustrates that bleaching of the unmodified kraft pulp gave significant amounts of vanillin and vanillic acid, whereas only noticeable amounts of veratric acid were found in the delignification of the methylated pulp. The latter acid, as noted earlier, represents a C_α-C_β cleavage product of the etherified units containing α-carbonyl groups (Fig. 7.1). A similar behavior was also observed in O_2 bleaching of a methylated O_2-prebleached sample. The latter sample gave a considerably higher yield of veratric acid than the methylated kraft pulp. These results confirm that the benzylic oxidation of etherified units is significant under O_2 bleaching conditions.

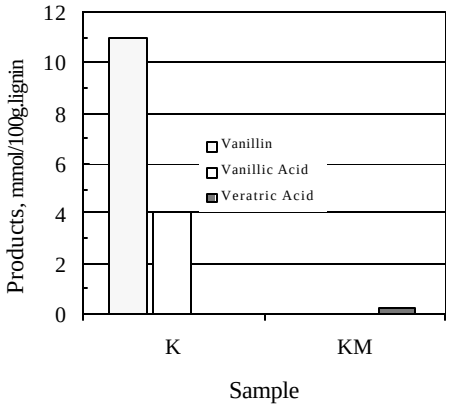

Figure 7.2. Influence of pre-methylation on the formation of vanillin, vanillic acid, and veratric acid in O_2 delignification of kraft pulps.

7.1.3. Role of NO_2 Pretreatment in O_2 delignification

Although the NO_2 pretreatment of kraft pulps is well known for its enhancement in O_2 delignification (49), there are still no general agreements on the detailed mechanism involved (50-52).We have examined the NO_2 treatment of a methylated and borohydride reduced kraft pulp (24 kappa number) using a 20% NO_2 charge at 50°C for 45 min. Interestingly, the O_2 delignification of this treated sample resulted in a significant delignification (~20%), and formation of veratric acid (Fig. 7.3). The latter acid, as noted earlier, represents a C_α-C_β cleavage product of the etherified units containing α-carbonyl groups (Fig. 7.1). These observations confirm that the benzylic oxidation is an important reaction in the NO_2 treatment, and it could be used to enhance the O_2 delignification process.

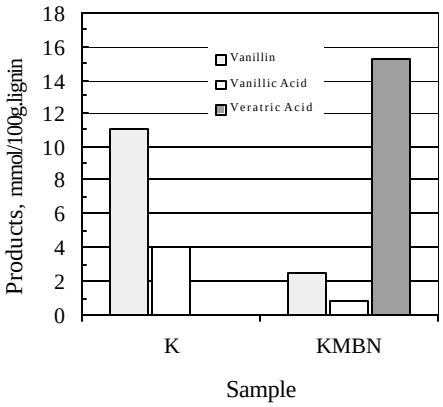

Figure 7.3. Influence of pre-methylation (M), borohydride reduction (B) and NO_2 treatment (N) on the formation of vanillin, vanillic acid, and veratric acid in the O_2 delignification of kraft pulps.

Subtask 7.2 Laccase-Mediator- System (LMS)

As discussed in Tasks 4.5 and 6.5, the LMS delignification delignification of the kraft (Fig. 4.11) and the O_2 delignified (Figure 6.7) samples is very unique, and seems to involve a significant contribution from the degradation of the etherified structures. The major objective of this subtask was to confirm the latter hypothesis and to further understand the delignification mechanism of the laccase-assisted delignification process.

7.2.1. Delignification of a pre-methylated kraft pulp

To further understand the reactivity of etherified structures toward the laccase treatment, we have determined the delignification behavior of a pre-methylated kraft pulp, in which the phenolic hydroxyl groups (PHOH) were blocked by reacting with dimethyl sulfate. As indicated in Table 7.2, the pre-methylated sample (No. 4) was very responsive to the LMS process resulting in a higher delignification than the unmethylated sample (No. 1). This finding clearly demonstrates that the degradation of etherified structures is an important reaction in the LMS process. A similar observation was also reported by Balakshin *et al*. (46).

7.2.2. Formation of Side-Chain Cleavage Products

We have further analyzed the effluents in the LMS-E stage for simple aromatic products. As shown in Table 7.2, only vanillic acid was detected from delignification of the unmodified kraft sample (No. 3), whereas veratric acid was the major product from the methylated sample (No. 6), in addition to small amounts of vanillic acid. The veratric acid was likely derived from the C_α-C_β cleavage of etherified units containing α-carbonyl groups as indicated in Reaction C for a β-aryl ether dimer (Figure 7.1). This finding further confirms the involvement of benzylic oxidation, and also the significance of side-chain cleavages in the LMS delignification process.

Table 7.2. The influence of premethylation (M), on the laccase (L) and the subsequent alkali (E) treatments in delignification of kraft pulp (K) and in the formation of simple aromatic products

Sample		Kappa No.	Products, mmol/100g pulp	
No	Type		Vanillic acid	Veratryl acis
1	K	28.0	-	-
2	KL	23.5	-	-
3	KLE	16.9	7.9	-
4	KM	19.2	-	-
5	KML	13.8	-	-
6	KMLE	6.1	8.6	35.0

Implications

The present study confirms our earlier hypothesis that the oxidation of etherified units is involved in both the O_2 and in the LMS delignification process. The initial oxidation is likely to occur mainly at the benzylic position, which is then followed by a variety of both degradation and condensation reactions (Fig. 7.1). Attempts to further understand the nature of these reactions and the controlling factors involved may provide a strategy for improving these delignification processes.

Concluding Remarks

This project provides considerable insights into the nature of kraft residual lignin, and its reactivity toward a series of the non-chlorine agents, especially the O_2 delignification system. Our major findings and their potential applications in kraft pulping and pulp bleaching are briefly outlined in the following.

1. Alkaline lignin condensation reactions

The analytical techniques developed in this project provide a direct means to detect the DPM condensed units of residual lignin *in situ* based on the formation of products characteristic of the parent unit. These methods include NO, PMO, and ozonation. Each of these procedures has its limitation, and is suitable for a qualitative determination. However, it continues to be a challenge to devise an improved technique for a quantitative determination of the content of different condensed units present in the residual lignin *in situ*.

Our results confirm that in kraft pulping, the alkaline condensation reactions may be largely limited to the α-5 type, whereas the 5,5'DPM type is not significantly involved. This finding is consistent with a recent report based on the analysis of isolated residual lignin by the ^{13}C NMR technique (46). Interestingly,, we have shown that a portion of the α-5 DPM units present in the kraft pulps may be etherified, and the formation of these structures can not be explained by the generally accepted mechanism to involve only the QM intermediate (Reaction C of Fig. 1.1). These etherified DPM units are likely a significant factor contributing to the low reactivity of residual lignin. Thus, the nature of condensed units present in residual lignin appears to be more complex than we generally perceive.

2. Role of phenolic hydroxyl group (PHOH)

Our results clearly suggest that the PHOH content of residual lignin determined *in situ* by the periodate method is closely related to the tendency of lignin condensation under the prevailing pulping conditions as illustrated in Figure 5.2, and is also closely related to the O_2 delignification process (Fig. 4.4). We consistently observe that the content of this functional group in residual lignin like the condensed units increases steadily with the kraft delignification. Interestingly, Roost *et al.* (53) reported recently that the kappa number of kraft pulps has a significant influence on bleachability toward a TCF sequence with a high response for the high kappa number pulps. This further imply the importance of condensed units in pulp bleachability.

3. Reactivity of residual lignin

We have demonstrated that the reactivity of kraft residual lignin varies considerably toward non-chlorine bleaching agents in terms of the phenolic and etherified components. For example, the initial O_2 and chlorine dioxide delignification were closely related to degradation of the phenolic units. In ozonation, the degradation of the phenolic and etherified structures was comparable. On the other hand, the lacasse-assissted deignification does not depend on the degradation of the phenolic units. It follows that the overall pulping and bleaching efficiency can be optimized by a proper combination of the pulping conditions and bleaching sequence.

4. Improved alkaline delignification

Our results clearly showed that the benzylic oxidation is a key process to degrade the etherified lignin structures, which account for the bulk of wood and residual lignin. Also, this type of reaction can be used to enhance the O_2 delignification process as reflected in a NO_2 pretreatment. It follows that an ideal pulping process would consist of a mild oxidation stage followed by a simple alkali extraction. We have been interested in this conceptual approach and hopefully will be able to pursue this subject further in a near future.

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LIST OF PUBLICATIONS

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B. Refereed Publications

1. Xu, H. and Lai, Y.-Z., " Reactivity of Lignin Diphenylmethane Model Dimers. 1. Nitrobenzene Oxidation", *Holzforschung,* **52**: 51-56 (1998).

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D. Abstracts

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E. Presentations

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2. Lai, Y.-Z., 'The Reactivity of Lignin Condensed Model Dimers Under Mild Alkali – O_2 Conditions", Presented at the 9th International Symposium on Wood and Pulping Chemistry, Montreal, June-12, 1997.

3. Yang, R., "Direct Measurement of the Methoxyl Group Content with Gas Chromatography in Aqueous Solution", Presented at Spotlight on Research '98 Graduate and Undergraduate Research Symposium, SUNY College of Environmental Science and Forestry, April 14, 1998.

4. Lai, Y.-Z., "Attempts to Further Characterize the Structural Changes of Residual Lignin in O_2 Bleaching", Presented at the International Pulp Bleaching Conference, Helsinki, June 1-5, 1998.

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27. Lai, Y.-Z., "On the Unique Features of Laccase-Assisted Delignification" Presented at the Empire State Paper Research Associates Fall Meeting in Syracuse, October 23-25, 2001.

E. Future Publication Plan

1. Numerous manuscripts will be prepared and submitted to refereed journals for publications.