

## **RF-O<sub>2</sub> PLASMA SURFACE MODIFICATION OF KRAFT LIGNIN DERIVED FROM WOOD PULPING**

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### **ABSTRACT**

The RF O<sub>2</sub>-plasma treatments show significant changes in the nature and relative ratio of surface atoms in kraft lignin compounds. The comparisons between the treatments and the measured results reveal that the oxidation response of a kraft lignin can be predicted quite well by changing the external plasma parameters. The XPS measurements show that low power and prolonged reaction time are sufficient, to significantly alter the chemical structure of lignin.

The nonequivalent, High Resolution (HR), C<sub>1s</sub> XPS analyses reveals the diversity of oxygen-based functionalities. Besides the characteristic lignin functionalities, the existence of a newly formed -COO group can be noted. It has been suggested that the increase of -COO concentration is related to the diminution of C-C & C=C, C-O-C & C-OH, and O-C-O groups on the lignin structure.

**KEY WORDS:** Kraft lignin, xps, cold plasma, functionalities, oxidation, surface modification

### **INTRODUCTION**

Second after cellulose, lignin is the most abundant natural polymer in the plant kingdom. It is an amorphous structure of phenylpropane units. However, it does not have a single repeating unit like cellulose, but instead consists of a complex arrangement of substituted aromatic phenolic units (Fengel and Wegener 1984, Sjoström 1993).

An increasing concern for the environment has given pressure to research on easily available raw materials. The introduction of very strict regulation on the pulp and paper industry, especially in developed countries, has led to extensive investigations being made in reducing waste disposal to the environment (Biermann 1993, Casey 1980).

As lignin is derived from chemical pulping processes (e.g. kraft), as waste, its abundance has made it a potential candidate for a variety of purposes. However, the recovery of chemicals after pulping is important for the process efficiency and conservation of environment. In this way, some environmental problems, such as air, water, and soil contamination resulting from toxic delignification derivatives, can be avoided to some degree (Biermann 1993, Smook 1994).

Lignosulfonate products, which are obtained either directly from sulfite black liquors or by sulfonation of acid-precipitated kraft black liquor, have already been reported as being used in

various areas including; fertilizer components (Garcia et al. 1996), rubber products (Kosikova et al. 2003), cement (Kamoun et al. 2003), binder for composites (Cetin and Ozmen 2003), and other types of products (Fengel and Wegener 1984). However, some of the drawbacks are very high recovery costs and a complicated process. Moreover, the target markets for lignin are not attractive enough to cover the full cost of the recovery process. Hence, only a small portion of commercial lignin is currently produced as a coproduct of the paper industry.

The research for using lignin in various applications has been extensively investigated in recent years. Among these, the most promising technologies are adhesives (El Mansouri et al. 2007, Cetin and Ozmen 2003) and the emulsifying field (Gundersen et al. 2001), as they can provide high modifications with low environmental impact.

Although, extensive research has already been reported on the conventional modification of lignin-based products for some applications, there is limited information concerning the use of lignin in glow discharge processing.

In this study, it is aimed to bring some element of comprehension to the plasma process of recovered kraft lignin from wood pulping. Hence, the radio frequency (RF) O<sub>2</sub>-plasma technique for lignin modification was investigated. This is of capital importance for understanding the anisotropic properties, for modeling of the chemical structure in polymer and other industries. To better understand the type of reactions formed after RF O<sub>2</sub>-plasma treatments, the surface atomic composition with various functionalities were evaluated with the help of X-ray Photoelectron Spectroscopy (XPS).

## MATERIAL AND METHODS

Indulin At is a purified form of kraft lignin; it is completely free of all carbohydrates and extractive substitutes and is ideal for using in a wide range of polymeric applications. Typical physical and chemical characteristics of the lignin utilized in this study are as follows (Anon.);

- Physical form: Free-flowing brown powder
- Solid material content: 97 % lignin
- Bulk density: 26 lbs/ft<sup>3</sup>
- Moisture content: 5%
- Fire point: 198°C
- Specific gravity: 1.3 g/cm<sup>3</sup>

The O<sub>2</sub> gas was purchased from Liquid Carbonic Co. (Illinois, USA) with a purity of 99%.

Plasma treatments were carried out in a 13.56 MHz RF rotating plasma reactor. In this special installation, the reactor is capable of treatment of powdery lignin substrates. Because of the rotation, fresh surfaces of the samples are constantly brought out, leading to uniform surface treatments. The reactor is composed of a cylindrical shaped Pyrex glass chamber (4) provided with two removable stainless steel caps. The RF power (1) is transmitted to the reactor through two outer copper electrodes (2, 3); with one of them connected to the RF power supply, and the other to the ground. The gases are supplied to the reactor through several metallic chemical reservoirs (10). The gas flow is controlled by flow meters (9). The vacuum inside the reactor is quickly achieved through a vacuum pump (7). A liquid nitrogen trap (5) is used to protect the pump from the reactive plasma species. The desired flow rate and pressure, monitored by a vacuum gauge (8), can be established in the reactor. The schematic diagram of the rotating plasma reactor is presented in Fig. 1.

The experimental conditions and parameters used in this study are;

- RF power source and power level: 13.56 MHz, 50-350 Watts
- Treatment time: 1-9 minutes
- Base pressure: 30-100 mTorr
- Pressure in the absence of plasma: 150-450 mTorr
- Oxygen flow rate: 2-15 sccm
- Temperature: room temperature.

Survey and high resolution XPS multiplex spectra were taken with a Perkin-Elmer PHI 5400 Spectrometer (MgX-ray source; 15 kV, and 300 W; 45°). XPS survey spectra were collected in the range of 0-1000 eV binding energy, with a resolution of 1.0 eV. The pass energy of the electron energy analyzer was set at 89.45 eV. The high resolution XPS multiplex spectra were collected for all elements identified from the survey scan (C<sub>1s</sub>, O<sub>1s</sub>). The energy resolution of the multiplex scan was 0.05 eV with a pass energy of 35.75 eV. The surface atomic composition was calculated with the provided system software-based peak intensity corrected for atomic sensitivity factors.

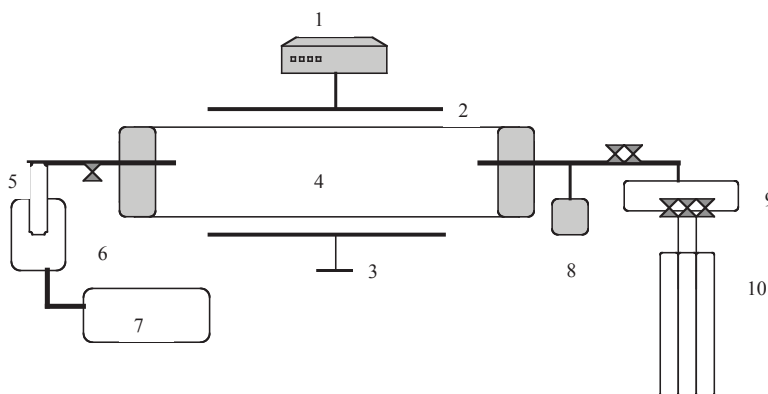


Fig. 1: Schematic diagram of the RF rotating plasma reactor system.

1- power source (13.56 MHz); 2- powered electrode, 3- grounded electrode, 4- Pyrex glass chamber; 5- trap; 6- liquid nitrogen reservoir; 7- vacuum pump; 8- MKS vacuum gauge (baratron); 9- flowmeters and controller; 10- gas or chemical tanks

## RESULTS AND DISCUSSIONS

The surface atomic composition of Indulin AT lignin (kraft), after oxygen plasma treatment, are presented in Table 1. As hydrogen is not included (not detected by XPS), lignin has carbon and oxygen elements, which are characteristic of its structure, as seen in Figure 2 a. However, the relative surface atomic composition exhibits 73.2% carbon and 26.8% oxygen. These are in good agreement with the results reported by Toriz and his group. They found 72.8% carbon and 26.6% oxygen for kraft lignin (Toriz et al. 2004). It is well known that the chemical composition and types of lignin vary, depending on the species and isolation process (Sarkanen and Ludwig 1971). Hence, it is important to note that the determinations of all depolymerized lignin compounds are very complicated and not intend to evaluate. Moreover, it was proposed by Sjostrom (1993) that several hundreds of lignin degradation compounds can be found in black (waste) liquor and some of them

are presented in Fig. 2 b. Having this information, it is reasonable to use Indulin AT lignin as a model for modification under RF-O<sub>2</sub> glow discharge treatments.

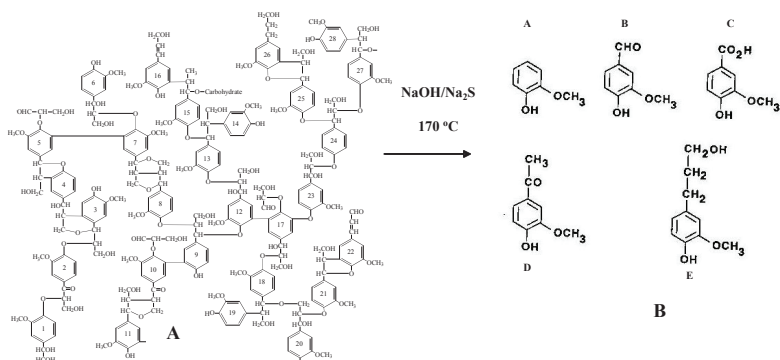


Fig. 2.: A: proposed lignin structure; B: Depolymerized some lignin compounds; a: guaiacol, b: vanillin, c: vanillic acid, d: acetovanillone, e: dihydroconiferyl alcohol

The marked effect of plasma external parameters on oxygen incorporation is clearly evident in Tab. 1. Even the 50 W and 5 min level was effective for implanting extensive oxygen (36.1%) on the surface. This value represents an approximately 35% oxygen increase on the surface when compared to the untreated sample. A longer treatment time generally results in higher oxygen concentration. In Table 1, one may also observe that similar amounts of oxygen are implanted at 100 and 200 W, at the different treatment times. These comparisons between the treatments and the measured results reveal that the oxidation response of a lignin can be predicted quite well by external plasma parameters.

Tab. 1: Atomic concentration of Indulin lignin determined by XPS after RF O<sub>2</sub>-Plasma treatment

Power (Watts)	Pressure (mTorr)	Time (min)	C (%)	O (%)
0	0	0	73.2	26.8
50	300	5	63.9	36.1
100	200	3	66.2	33.8
200	300	5	66.8	33.2
300	200	7	71.9	28.1
350	300	5	68.1	31.9

Foerch and co-workers proposed that the O/C ratio of a plasma-treated polymeric surface might be used as an indication for the surface modification process (Foerch et al. 1994). As, quantifications of XPS data allowed determination of oxygen-to-carbon (O/C) atomic ratios; this could be useful to investigate the interactions in the plasma process at various conditions and effects of oxygen implantation on lignin.

As seen in Fig. 3, the plasma-mediated oxidation process was extremely intense in low energy exposure, followed by a slightly decreasing shape as the energy increased. The highest O/C ratio of 0.56 was obtained at a lower energy (50 W) and further power effects decreased with oxygen incorporation. It seemed as if the increase of the oxygen was inversely related to power. This was probably because of the ablative effects of the high energy glow discharge environments. It was reported by Yasuda that oxygen containing plasma species could cause oxidative ablation, which was influenced by operational parameters of discharge (Yasuda 1985).

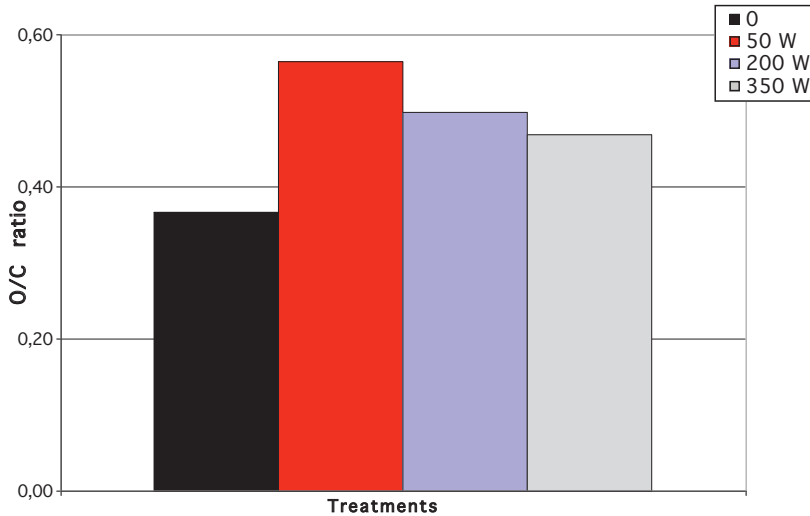


Fig. 3: Effect of RF-power on the surface O/C ratio in  $O_2$ -plasma treated lignin compounds

Yasuda has also speculated that the mechanism of reaction tends to occur predominantly with free radicals at low energy levels, but if the energy increases to higher levels, the mechanism becomes ionic. However, both reaction mechanisms are always present in the RF-plasma. Moreover, interactions between the plasma and substrates are very complicated and do not allow a simple explanation of the reaction mechanism to be used for an evaluation of the lignin surface oxidation/deoxidation processes.

Fig. 4 clearly reveals prolonged exposure affects the increasing oxygen on lignin. The highest O/C of 0.53 responding to the oxygen content of 34.7% was found at the 9 min treatment. It appeared that the oxygen implantation was positively related to the reaction time. The surface atomic concentration recorded by XPS measurements clearly revealed that low power and prolonged reaction time were sufficient to significantly alter the surface of lignin (Tab. 1, Figs. 3 and 4). This might be attributable to high fragmentation following ablating/etching effects at higher powers; although for longer times, the extent of the modification was similar to that obtained at a shorter exposure time.

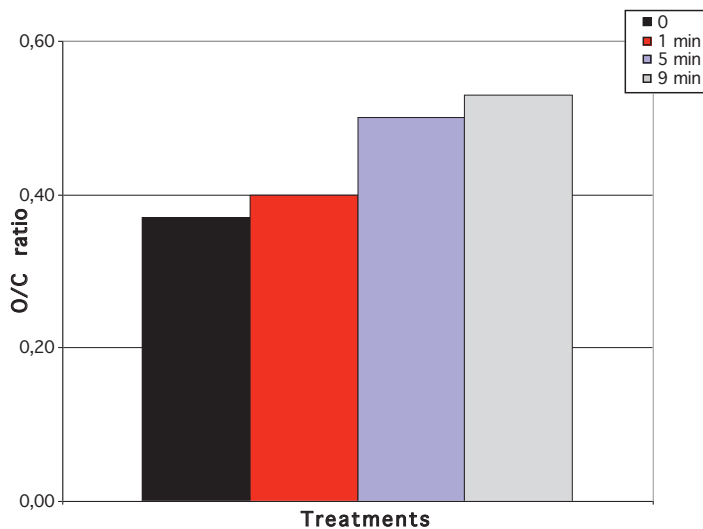


Fig. 4: Effect of treatment time on the surface O/C ratio in  $O_2$ -plasma treated lignin compounds

The pressure seems to contribute to the control of relative surface oxygen concentrations to some level (Fig. 5). A positive correlation is also observed with conditions where pressure is at 200 W and treatment was for 5 min. The highest O/C of 0.58 (O: 36.6%) was found at the highest pressure level of 450 mTorr.

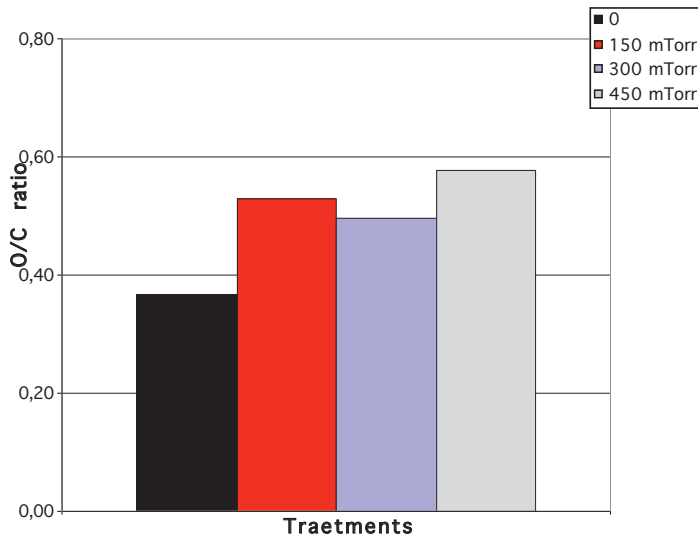


Fig. 5: Effect of pressure on the surface O/C ratio in  $O_2$ -plasma treated lignin compounds

It was speculated by Denes and his co-workers that the bond energies of the atoms of organic structures were variable and less than the energy range of the glow discharge species (0-20 eV),

such as; electrons, ions, metastables, and UV/visible (Denes et al. 2005). Considering the lignin structure, it has C-H, C-C, C=C, and C=O functionalities (Fig. 2), with bond energies ranging from 3.3 to 11.2 eV (Lide 1995). Hence, RF O<sub>2</sub>-plasma is intense enough to dissociate almost all chemical bonds involved in recovering kraft lignin structures and to create free radical species, as well as, the ring opening process.

Sabharwal and co-workers reported very extensive free radical formation in the lignin structure under argon plasma environment (Sabharwal 1993). This may also occur for oxygen, which is a high energy source and very reactive under plasma environment. Hence, free radical formation in the lignin is possible in several ways: hydrogen abstraction from polymer chains, and bond scission by electron bombardment. Apparently the oxidation of plasma treated lignin is probably on account of free radical formation followed by oxygen incorporation. Storm and Carlson investigated the oxygen plasma caused oxidation reactions on the paper surface and primarily on lignin (Storm and Carlson 1992). The results found in this study also indicate that extensive oxidation proceeds under RF-O<sub>2</sub> exposure of lignin compounds.

The nonequivalent High Resolution (HR) C<sub>1s</sub> XPS analyses give additional insight into the chemical structure of the treated lignin. They clearly reveal the diversity in oxygen based functionalities. Besides the characteristic C-C & C=C (285 eV), C-O-C & C-OH (286.7 eV), and O-C-O (288 eV) functionalities, the existence of a newly formed -COO (288.8 eV) group can be noted. It is important to note that assigning the resolved HR C<sub>1s</sub> XPS peaks with nonequivalent positions should be considered as being only suggestive.

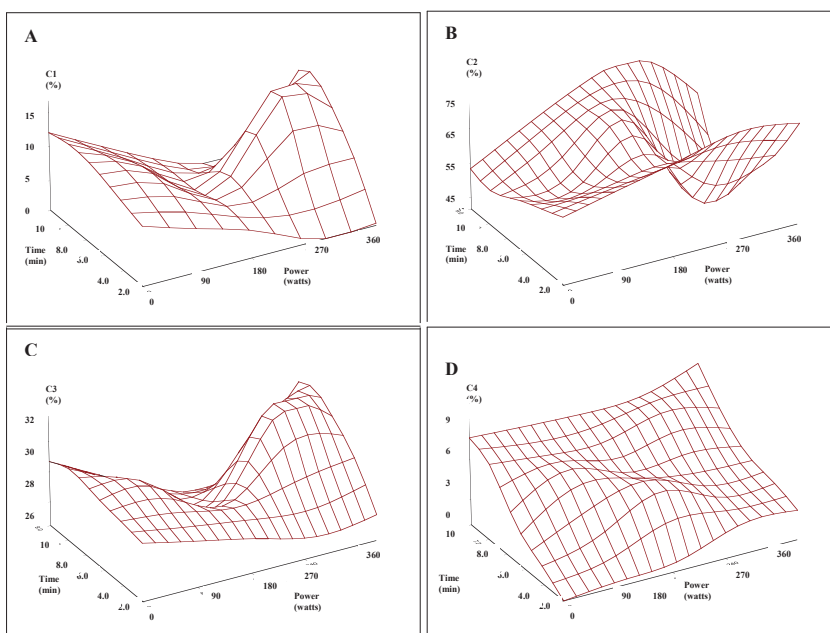


Fig. 6: Treatment time and power effects on surface functionalities of RF-O<sub>2</sub> plasma treated lignin (a: C-C & C=C, b: C-O-C & C-OH, c: O-C-O, d: -COO)

The newly formed and modified functionalities were determined with high-resolution (HR-C<sub>1s</sub>) XPS spectra and results plotted as function treatment time and power (Figure 6 a-d). Significant modifications could be noted in the nature and surface areas of the nonequivalent HR C<sub>1s</sub> spectra. A considerable increase in C-C & C=C groups can be identified at the high power and prolonged plasma exposure. These indicate that lignin exposed to O<sub>2</sub>-plasma environments for long periods of time can generate intense deoxygenation reactions (Fig. 6 a). Similar results were also observed for O-C-O groups (Fig. 6 c). Data resulting from the C-O-C & C-OH (Fig. 6 b) are consistent with observations noted in Figure 6a, and in good agreement with the decrease in the C-O-C & C-OH groups especially at a shorter time. However, the decrease of C-O-C & C-OH functionalities at the prolonged exposure time, such as; above 5 min can be attributed to the plasma-induced cleavage of various linkages within the lignin compounds, followed by recombination and grafting of the new oxygen functionalities. Figure 6d clearly reveals that power and exposure time have a close relationship generating -COO groups. It is significant to observe the increasing those in HR C<sub>1s</sub> are appears to generate intensive free radicals then react with oxygen atoms to induce an oxidation reaction. It suggests that the relative increase in -COO concentration is related to diminution of C-C & C=C, C-O-C & C-OH, and O-C-O concentrations.

## CONCLUSIONS

The RF O<sub>2</sub>-glow discharge appears to disrupt the lignin structure to various degrees. Considerably high surface oxygen atomic concentration as well as new oxygen-based functionalities can be generated in RF O<sub>2</sub>-plasma conditions. Under certain experimental conditions, oxygen concentrations as high as 39.1% can be achieved.

However, the treatment time and pressure are more effective for lignin modification in O<sub>2</sub>-plasma environment than for power. Low power inputs with longer exposure time can result in a high degree of fragmentation.

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## REFERENCES

1. Anon. Indulin At lignin booklet, Westvaco chemical co. West virginia, USA, 1 pp.
2. Biermann, C.J., 1993: Essentials of pulping and papermaking. Academic Press Inc, San Diego, 753 pp.
3. Casey, J.P., 1980: Pulp and Paper, Chemistry and chemical technology, 3<sup>rd</sup> ed., Vol. II, John Wiley & Sons, New York, 1406 pp.
4. Cetin, N.S., Ozmen, N., 2003: Studies on lignin-based Adhesives for particleboard panels, Turk J Agric For, 27, 183-190
5. Denes, F.S., Cruz-Barba, E., Manolache, S., 2005: Plasma treatment of wood, In: Handbook of wood chemistry and wood composites, (ed. Roger M. Rowell), Ch 16, CRC, 510 pp.



6. El Mansouri, N-E., Pizzi, A., Salvado, J., 2007: Lignin-based wood panel adhesives without formaldehyde, *Holz Roh Werkst*, 65: 65-70
7. Fengel, D., Wegener, G., 1984: *Wood, Chemistry, Ultrastructure, Reactions*. Walter de Gruyter Public, Berlin, 585 pp.
8. Foerch, R., Kill, G., Walzak, M.J., 1994: Plasma surface modification of polyethylene: short-term vs. long-term plasma treatment. In: *Plasma Surface Modification of Polymers: Relevance to Adhesion*, (ed. M. Strobel, C. S Lyons and K. L. Mittal) Pp. 99, VSP BV, The Netherlands
9. Garcia, M.C., Diez, J.A., Vallejo, A., Garcia, L., Cartagena, M.C., 1996: Use of kraft pine lignin in controlled-release fertilizer formulations, *Industrial & Engineering Chemistry Research* 35 (1): 245-249
10. Gundersen, S.A., Saether, O., Sjoblom, J., 2001: Salt effects on lignosulfonate and kraft lignin stabilized O/W-emulsions studied by means of electrical conductivity and video enhanced microscopy, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 186 (3), 141-153
11. Kamoun, A., Jelidi, A., Chaabouni, M., 2003: Evaluation of the performance of sulfonated esparto grass lignin as a plasticizer-water reducer for cement, *Cement and Concrete Research*, 33: (7), 995-1003
12. Kosikova, B., Alexy, P., Gregorova, A., 2003: Use of lignin products derived from wood
13. pulping as environmentally desirable component of composite rubber materials. *Wood Research*, vol. 48: (1/2), 62-67
14. Lide, D.R., 1995: *Handbook of chemistry and physics*, 76<sup>th</sup> edition, CRC press, New York, 1302 pp.
15. Sabharwal, H.S., Denes, F., Nielsen, L., Young, R.A., 1993: Free-radical formation in jute from argon plasma treatment, *Journal of Agricultural and Food Chemistry*, 41 (11): 2202-2207
16. Sahin, H.T. Utilization of kraft lignin through plasma treatment, unpublished results, University of Wisconsin, WI
17. Sarkanen, K.V., Ludwig, C.H., 1971: *Lignins: Occurrence, Formation, Structure and Reactions*, John Wiley and Sons Inc., New York, 916 pp.
18. Sjostrom, E., 1993: *Wood Chemistry, Fundamentals and Applications*. Academic Press, San Diego, 247 pp.
19. Smook, G.A., 1994: *Handbook for Pulp and Paper Technologists*. Angus Wilde Publications, Canada, 419 pp.
20. Storm, G., Carlsson, G., 1992: Wettability of kraft pulps-effect of surface composition and oxygen plasma treatment, *Journal of Adhesion Science and Technology*, 6 (6): 745-761
21. Toriz, G., Ramos, J., Young, R.A., 2004: Lignin-polypropylene composites. II. Plasma modification of kraft lignin and particulate polypropylene, *Journal of Applied Polymer Science*, 91, 1920 pp.
22. Yasuda, H., 1985: *Plasma polymerization*, Academic press, Orlando, FL, 432 pp.

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