Surface modification of lignocellulosic fibers using high-frequency ultrasound

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Abstract

Enzymatic and chemical oxidation of fiber surfaces has been reported in the literature as a method for producing medium density fiberboards without using synthetic adhesives. This work focuses on modifying the surface properties of wood fibers by the generation of free radicals using high-frequency ultrasound. A sonochemical reactor operating at 610 kHz is used to sonicate the aqueous suspensions of thermomechanical pulp fibers (TMP). TMP is analyzed using FTIR-transmission, FTIR-ATR spectroscopy and inverse gas chromatography (IGC). The non-conjugated carbonyl groups in TMP are represented by the peak area ratio A_{1736}/A_{1511} in the FTIR-transmission spectra and by A_{1728}/A_{1509} in the FTIR-ATR spectra. The increase in these ratios suggests that there is an increase in the number of non-conjugated carbonyl groups in TMP after sonication. To further investigate, sonication of the hydrolytic lignin was also carried out and analyzed using UV, UV-ionization and FTIR-transmission spectroscopy. The changes in the surface properties of the fibers are analyzed using IGC which showed an increase in the surface free energy of fibers. The effect of operating parameters such as power of ultrasound and sonication time is also studied.

Introduction

The conventional process for the manufacture of wood composites involves the addition of synthetic resins such as urea–formaldehyde to the wood fibers, which is then hot-pressed to form fiberboards. Currently efforts are underway to develop processes to manufacture fiberboards without the addition of resins owing to environmental concerns (i.e. release of formaldehyde from the fiberboard furniture from resin degradation, etc.). An alternative is to use free radical treatment of the surface of wood fibers by physical or chemical means, to enhance the fiber adhesion for

pressing (Qian et al. 2004). The treatment of wood fibers with enzymes such as laccase or peroxidase produces lignin radicals on fiber surface, which results in increased bonding strength in fiberboards (Lund and Felby 2001, Felby et al. 2002). Free radicals can also be generated by the treatment of wood particles with Fenton's reagent (Widsten et al. 2003) (H_2O_2/ $FeSO_4$) and irradiation of wood particles with γ-radiation (Supe et al. 1993).

In this work, the modification of surface properties of wood fibers with ultrasound is examined. When an aqueous suspension is treated with ultrasound, cavitation is induced in the liquid,

decomposing water into free radicals. (Petrier et al. 1994)

$$H_2O \rightarrow \bullet H + \bullet OH$$

Seino et al. (2001) and Yoshioka et al. (2000) used electron spin resonance (ESR) methods to trap and characterize unstable radicals which were generated by the treatment of lignin solutions in DMSO with ultrasound irradiation at 45 kHz and 100 W. They concluded that the α–O–4 or β–O–4 linkages in lignin are homolytically cleaved by the ultrasonic irradiation. Pranovich et al. (1998) studied the sonochemistry of monomeric lignin model compounds at 20 kHz frequency and reported the formation of various products as a result of the hydroxyl radical attack on the aromatic ring. Tan et al. (1985) studied the behavior of lignin under the action of ultrasonic irradiation at 19 kHz and at a very high power of 1200 W concluding that there is a formation of carbonyl groups upon ultrasonic treatment.

Researchers have employed ultrasound in the extraction of lignin (Sun et al. 2002a; Sun and Tomkinson 2002a) and hemicelluloses (Sun et al. 2002b; Sun and Tomkinson 2002b; Ebringerova and Hromadkova 2002) from lignocellulosic feedstocks such as wheat straw, to achieve higher extraction yields. The treatment of cellulosic fibers with ultrasound has also been studied by several researchers. A review (Willems 1962) describes the use of ultrasound in pulp and paper technology for various processes like debarking, defibration, beating, impregnation and penetration, pulping, bleaching, stock preparation and grafting. Laine et al. (1977) studied the influence of ultrasonic irradiation at 23 kHz on the physical and chemical properties of pulp fibers, reporting an increase in the fiber wall porosity and a slight increase in the carbonyl group content of the fibers due to the oxidation of carbohydrate hydroxyls.

Although ultrasound at lower frequencies produces more violent cavitation, the effects are highly localized. On the other hand, cavitation is less violent at higher frequencies owing to shortened life time of cavitation bubbles. However the shortened bubble life time leads to a greater number of free radicals and hence more cavitational effects. The shortened bubble life time allows the free radicals to escape the cavitation sites to bulk mixture facilitating the bulk reaction (Thompson and Doraiswamy 1999). Ultrasound at higher frequencies is found to be effective for oxidation reactions. Entezari et al. (1994) found that the rate of sonochemical oxidation of iodide at 900 kHz was 31 times greater than that at 20 kHz. Petrier et al. (1994) and Berlan et al. (1994). have compared the rates of oxidative degradation of phenol in aqueous solutions over a range of ultrasound frequencies and found that the treatment at higher frequencies is more efficient. Additionally ultrasound operation at higher frequencies is quiet (i.e., noise free) which is advantageous for the scale-up and industrial utilization. So far, the high frequency ultrasound has not been applied to wood fibers.

This paper examines the effect of 610 kHz ultrasound on the surface properties of thermomechanical pulp (TMP), and on a hydrolytic lignin.

Experimental

Materials

TMP was produced from loblolly pine by pressure refining at 5.5 bar of steam pressure. Hydrolytic lignin and potassium bromide (KBr, 99 + %, FTIR grade) were purchased from Aldrich. The molecular probes for inverse gas chromatography, n-hexane, n-heptane, n-octane, and n-nonane (all analytical grades) were obtained from Aldrich. Argon (ultra high purity grade, 99.999%) was obtained from BOC gases. Deionized water, ethanol (95% pure), NaOH and HCl were obtained from Fisher.

Apparatus

Sonication is carried out in a high-frequency sonochemical reactor (Ultrasonic Energy Systems, Sonochemist 300C) operating at 610 kHz and at varying powers. A photograph of the reactor is shown in Figure 1. It consists of a 450 ml glass vessel attached to a transducer. An acoustic window separates the reactor contents from the outside coolant. The ultrasonic waves reach inside the

reactor through the acoustic window. The other end of the vessel has a concave focusing acoustic-mirror which is used to concentrate the ultrasonic waves in the vessel.

A schematic of the experimental setup is shown in Figure 2. The sonochemical reactor (R) containing a suspension of the substrate material in distilled water, is submerged in a polycarbonate tank (W) filled with water. The tank is partitioned into two sections: the reactor section and control sample section. The reactor temperature is measured by a thermometer (T), and cooled using a chiller (Cole-Parmer, Model C1283-60) dipped in the water bath to remove heat produced during sonication, thereby maintaining a temperature of 20 °C. The temperature in the control section was also maintained at 20 °C, with a temperature controller (TC) (Fisher, Isotemp Model 730). Argon is bubbled continuously into both the reactor and control vessels.

Procedure

4.5 g of TMP was suspended in 450 ml of distilled water (1% consistency) by stirring. The suspension was sonicated at 100 and 200 W for 3 h each, after which the pulp was filtered and air-dried. The control sample was treated in the identically manner, except for the exposure to ultrasound. The TMP samples were analyzed using FTIR-transmission, FTIR-ATR spectroscopy and IGC.

To study the effect of ultrasound on lignin, 4 g hydrolytic lignin was suspended in 400 ml distilled water, and 4 drops of 1 N NaOH, and stirred. The mixture was sonicated at 200 W for 5 h at 20°C, and then lignin was precipitated out by adding 10 ml of 0.1 N HCl. The precipitate was filtered under vacuum, washed with water, air-dried and later ground into fine powder and stored for analysis. Exactly the same procedure was followed for the control sample in the absence of ultrasonic
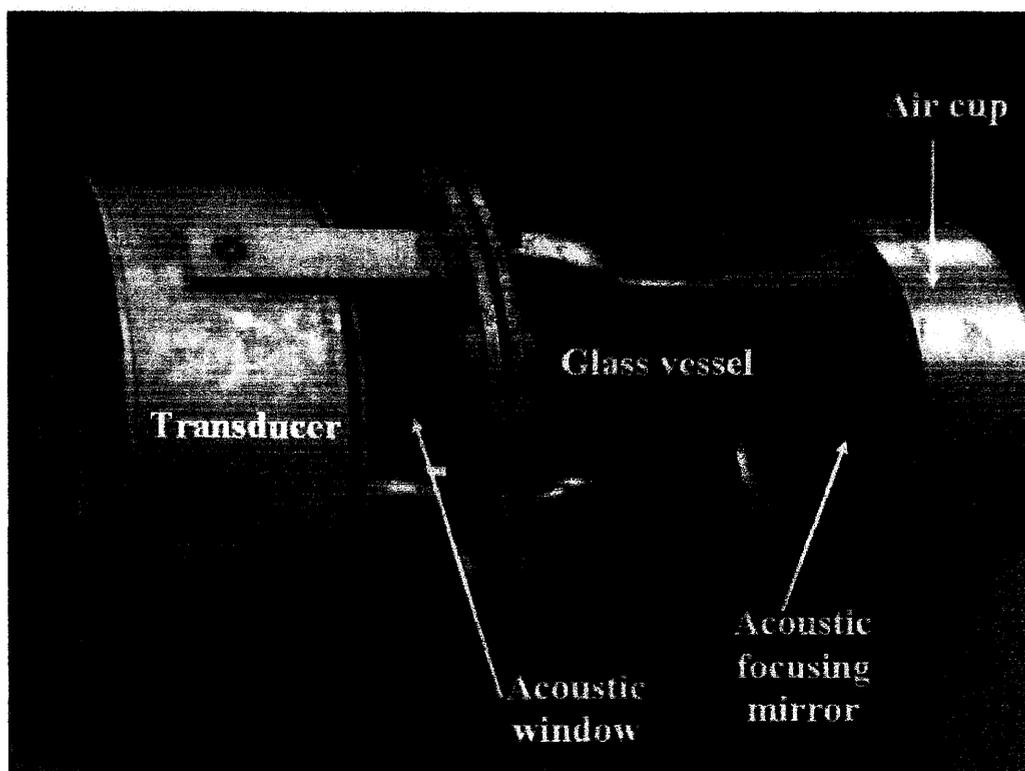

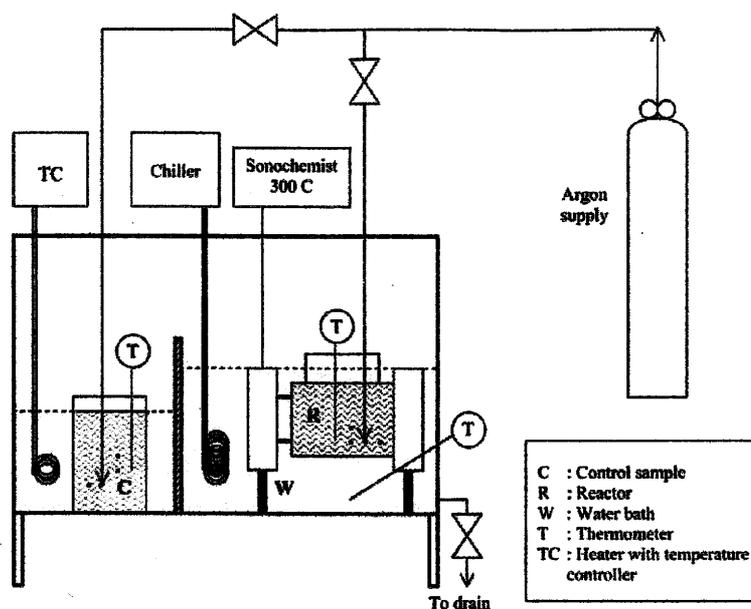*Figure 1.* Photograph of the sonochemical reactor operating at 610 kHz.

Figure 2. Apparatus used for sonication of lignin and TMP at 610 kHz.

irradiation. The lignin samples were analyzed using UV and FTIR-transmission spectroscopy.

Later TMP was sonicated in a series of experiments at the power levels of 100, 150, 200 and 250 W for 1 and 3 h each and analyzed using FTIR-ATR.

Analyses

UV spectroscopy

100 mg lignin was dissolved in 100 ml ethanol (95% pure). 5 ml of the aliquot was diluted to 100 ml using deionized water, which was then analyzed using a UV spectrophotometer (Spectronic, Genesys 2) against a blank solution prepared by diluting 5 ml of 95% ethanol to 100 ml using deionized water.

The lignin samples were also analyzed under alkaline conditions (Goldschmid 1954; Wexler 1964; Sarkanen et al. 1967a) which results in the ionization of the phenolic groups and the UV spectra exhibits bathochromic shifts of the characteristic peak at 280 nm.

100 mg lignin was dissolved in 100 ml ethanol (95% pure). 5 ml of the aliquot was mixed with

5 ml of 1 N NaOH, which then was diluted using 100 ml using deionized water. The blank solution was prepared by adding 5 ml of 0.1 N HCl to the 5 ml of aliquot followed by dilution to 100 ml using deionized water. The alkaline solution of lignin was analyzed against the acidic solution of lignin using quartz cuvettes which were covered to prevent evaporation.

The UV spectroscopy experiments were run in triplicates, with the observed variation of less than 5%.

FTIR-transmission

The FTIR-transmission spectra of the material were obtained using Perkin Elmer, Spectrum 2000 spectrophotometer. The material was added to KBr at 1 wt.% concentration. The mixture was finely ground in a mortar and pestle and a disc was prepared using 100 mg of the ground mass in a pellet maker. The pellet was scanned from 4000 cm^{-1} to 600 cm^{-1} with 64 scans, a resolution of 4.0 cm^{-1}, an interval of 1 cm^{-1}, with triangular apodization. A disc made with 100 mg of pure KBr was used as a background scan.

FTIR-ATR

In order to detect the changes on the surface of TMP upon sonication, a Nicolet (Avatar model) FTIR spectrometer was used to obtain attenuated total reflectance (ATR) spectra. The TMP samples were scanned in the range of $4000-600$ cm^{-1} using the same settings as for the transmission spectra and air as background.

Areas under the peaks of both FTIR-transmission and FTIR-ATR spectra were determined using Spectrum software (Perkin Elmer, version 1.10) by sloping baseline method. In order to obtain a difference spectrum of hydrolytic lignin, the absorbance spectrum was normalized to the peak at 1515 cm^{-1} due to aromatic ring vibrations in lignin to compensate for concentration differences.

Both IR spectroscopy experiments were run in triplicates, with the observed variation of less than 10%.

Inverse Gas Chromatography (IGC)

The air-dried TMP samples were packed in a stainless steel 316 column (Alltech, 1/4" OD, 0.21" ID, 21" length). The quantity of TMP packed in the column (1.5–1.6 g) was found by difference. Table 1 shows the properties of the probes used in IGC study. IGC measurements were performed using a gas chromatograph (HP 5790) equipped with a flame ionization detector. The detector and injector temperatures were maintained at 200 and 150 °C, respectively to ensure flash evaporation of probe vapors. Helium was used as the carrier gas with a flow rate of 15 ml/min, measured using a soap-bubble flow meter. Methane was used as an inert marker probe to determine the dead volume in the column. A very small volume of vapor probes (~0.1 µl) was injected into the column with a Hamilton syringe to ensure a valid approximation of infinite dilution of the probe vapor and the condition of near zero coverage. All peaks were

Table 1. Properties of the molecular probes used in IGC.

Probe	A(Å^2)	γ_l^D(mJ/m^2)
n-hexane	51.5	18.4
n-heptane	57.0	20.3
n-octane	63.0	21.3
n-nonane	69.0	22.7

found to be symmetrical and their retention time was determined with an integrator connected to the GC. Each injection was repeated at least 3 times so as to get reproducible retention time and the average value was used in the calculations. The analysis was done at 3 different oven temperatures: 45, 60, and 75 °C. The oven was allowed to equilibrate for one hour between temperature changes.

IGC Data analysis

The net retention volume V_N is related to the retention time by: (Felix and Gatenholm 1993; Kamdem et al. 1993; Jacob and Berg 1994; Kazayawoko et al. 1997; Liu et al. 1998; Dutschk et al. 2001)

$$V_N = F \cdot (t_r - t_0)$$

where, F is the flow rate of the carrier gas, t_r is the retention time of the individual probe and, t_0 is the retention time of practically non-adsorbing probe (methane). The dispersive interactions arise from London, Van der Waals and Lifshitz forces between the adsorbent and a series of alkanes. Based on the retention volumes (V_N), the dispersive interactions were determined using the methods of Schultz and Lavielle (Sarkanen et al. 1967b; Liu et al. 1998) and Dorris and Gray (Kamdem et al. 1993; Liu et al. 1998; Colom et al. 2003). Assuming a very low adsorbate concentration, the former technique calculates the dispersive component of the surface energy according to the relationship

$$RT \ln(V_N) = 2N(\gamma_s^D)^{1/2} a(\gamma_l^D)^{1/2} + C$$

where R is the gas constant, T is the temperature in degrees Kelvin, N is Avogadro's number, a is the area occupied by the adsorbate, γ_l^D is the dispersive component of the surface energy of the adsorbate, and C is a constant. Since $RT \ln(V_N)$ varies linearly with $a(\gamma_l^D)^{1/2}$, γ_s^D can be determined from the slope of the plot of $RT \ln(V_N)$ versus $a(\gamma_l^D)^{1/2}$.

This method of determining γ_s^D has been criticized because of uncertainties associated with changes in the surface area of the adsorbate due to interaction with the adsorbent (Felix and Gatenholm 1993). Given this, a second calculation

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was performed using the semi-empirical equation of Dorris and Gray (Kamdem et al. 1993; Liu et al. 1998; Colom et al. 2003).

$$\gamma_s^D = \frac{1}{\gamma_{(-CH_2-)}} \cdot \left[\frac{\Delta G_{(-CH_2-)}}{2 \cdot N \cdot a} \right]^2$$

where, $\gamma_{(-CH_2-)}$ is the surface tension of a methylene group (35.6 mJ/m^2 at 293.15 K) and $\Delta G_{(-CH_2-)}$ is the free energy of a methylene group. $\Delta G_{(-CH_2-)}$ is obtained from the slope of the plot of $RT \ln(V_N)$ versus the number of carbon atoms in a series of n-alkanes.

Results and discussions

The FTIR-transmission spectra of the control and sonicated sample of TMP are shown in Figure 3. The IR bands are due to various functional groups in wood (Sarkanen et al. 1967b; Colom et al. 2003) and lignin (Faix 1991; Hortling et al. 1997; Nada et al. 1998). For example, the peak at 1736 cm^{-1} is due to C=O stretching vibrations of non-conjugated carbonyls in lignin while the peak at 1511 cm^{-1} corresponds to the aromatic ring vibrations in lignin. It is clear from Figure 3 that there are no new peaks and the peak positions have remained unchanged as a result of sonication. Since there are not any visible differences in the intensities of various bands, the areas under the peaks were measured by using the sloping base line method as shown in Figure 4. The ratio of the area under the peak at 1736 cm^{-1} to the area under the peak at 1511 cm^{-1} (A$_{1736}$/A$_{1511}$) is a measure of the number of non-conjugated carbonyls present. It can be seen (Table 2) that the value of A$_{1736}$/A$_{1511}$ has increased from 0.993 for the control sample of TMP to 1.141 for TMP sonicated at 100 W for 3 h. The value has further increased to 1.166 for TMP sonicated at 200 W for 3 h. There was no difference in the peak area ratios corresponding to other peaks. Thus, it can be concluded that there is an increase in the number non-conjugated carbonyls in TMP as a result of ultrasonic treatment, which is possibly due to the oxidation of lignin present in TMP fibers.

Figure 5 shows the FTIR-ATR spectra of the control and sonicated samples of TMP. The peak at 1728 cm^{-1} is due to non-conjugated carbonyls

in lignin while the peak at 1509 cm^{-1} corresponds to aromatic ring vibrations in lignin. The area under the peaks was calculated using sloping baseline method as shown in Figure 6. The ratio of the area under the peak at 1728 cm^{-1} to the area under the peak at 1509 cm^{-1} (A$_{1728}$/A$_{1509}$) is used as a measure of the degree of surface oxidation of TMP. It can be seen from Table 2 that value of A$_{1728}$/A$_{1509}$ has increased from 0.429 for the control sample of TMP to 0.486 for TMP sonicated at 100 W for 3 h and to 0.578 for TMP sonicated at 200 W for 3 h. There was no difference in the peak area ratios corresponding to other peaks. This shows that there is an increase in the number of non-conjugated carbonyls present on the surface of TMP which is due to oxidation of lignin, mainly present at the surface.

Both ATR with typical penetration depth of 100 nm and transmission infrared spectroscopy are basically measure bulk fibers, when the surface changes are only a few nanometer deep. For example, volume in the depth of 1 nanometer is only about 0.1% of the volume in the depth of 1000 nm, in the case of a perfectly flat fiber. However the fibers are not perfectly flatly on the ATR crystal. A number of fibers are curved away from the crystal surface, which will cause more fiber surface to be in the path of ATR measurement.

To confirm that lignin gets oxidized as a result of sonication, the control and sonicated samples of hydrolytic lignin were analyzed using UV and FTIR-transmission. The UV spectra comparing the control and sonicated samples of hydrolytic lignin are shown in Figure 7. The peak at 279 nm indicates the presence of non-conjugated phenolic hydroxyl groups in hydrolytic lignin (Goldschmid 1954; Wexler 1964; Sarkanen et al. 1967a). The absorbance value at 279 nm (Table 3) has decreased from 0.769 for the control sample of hydrolytic lignin to 0.673 for the sonicated sample, which shows that there a decrease in the number of non-conjugated phenolic hydroxyl groups as a result of sonication which is in agreement with the findings of Tan et al. (1985)

The UV-ionization spectra of the control and sonicated samples of (Figure 8) have two peaks (at 249 and 295 nm) which correspond to the phenolic hydroxyl groups in lignin. The peak at 295 nm is characteristic of the non-conjugated phenolic hydroxyl groups (Goldschmid 1954; Wexler 1964;
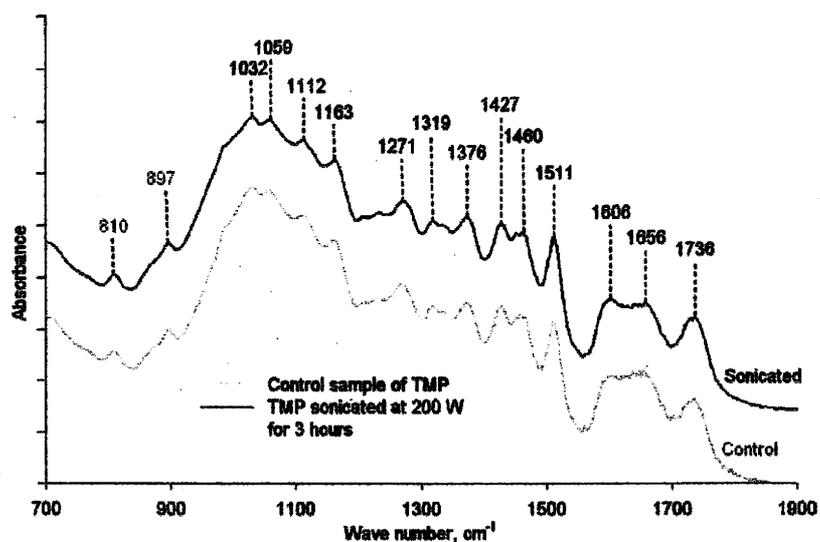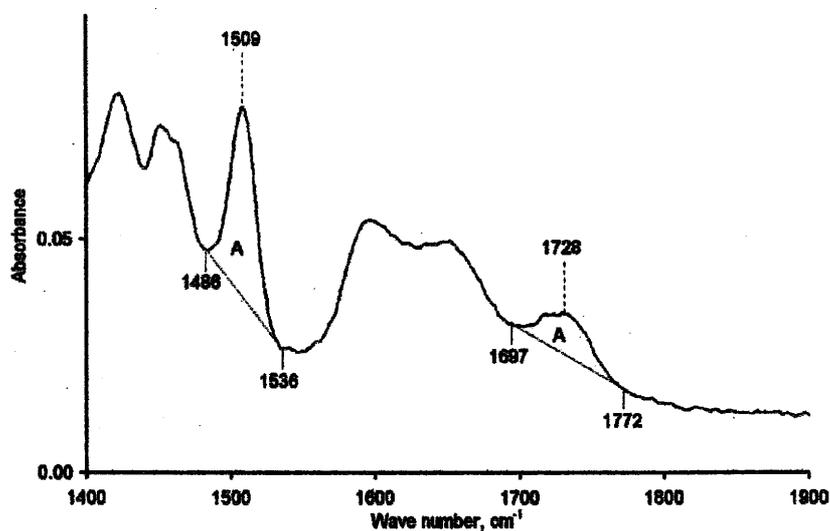
Figure 3. FTIR-transmission spectra of TMP.

Figure 4. Sloping baseline method to calculate the area under the peaks of the FTIR-transmission spectrum of TMP.

Table 2. FTIR-transmission/ ATR area data for TMP samples.

Sample	FTIR-transmission A_{1736}/A_{1511}	FTIR-ATR A_{1728}/A_{1509}
Control sample of TMP	0.993	0.429
TMP sonicated at 100 W for 3 h	1.141	0.486
TMP sonicated at 200 W for 3 h	1.166	0.578
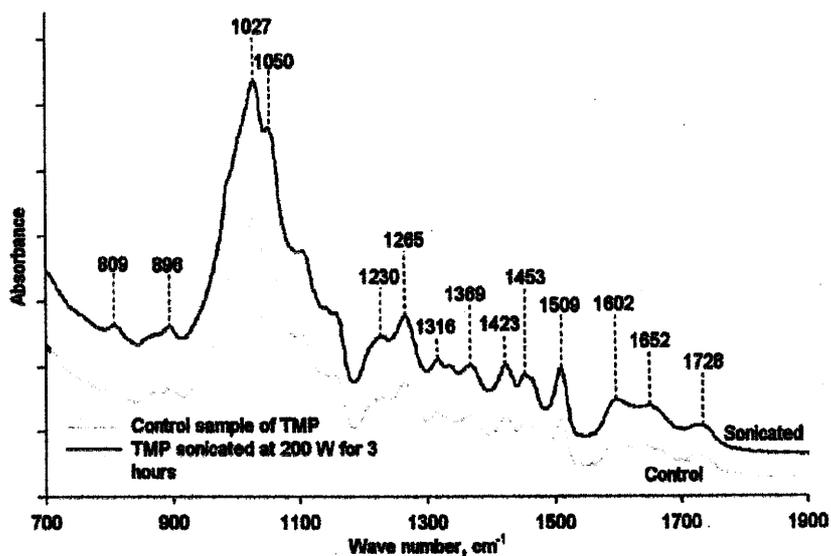
Figure 5. FTIR-ATR spectra of TMP obtained using air as background.
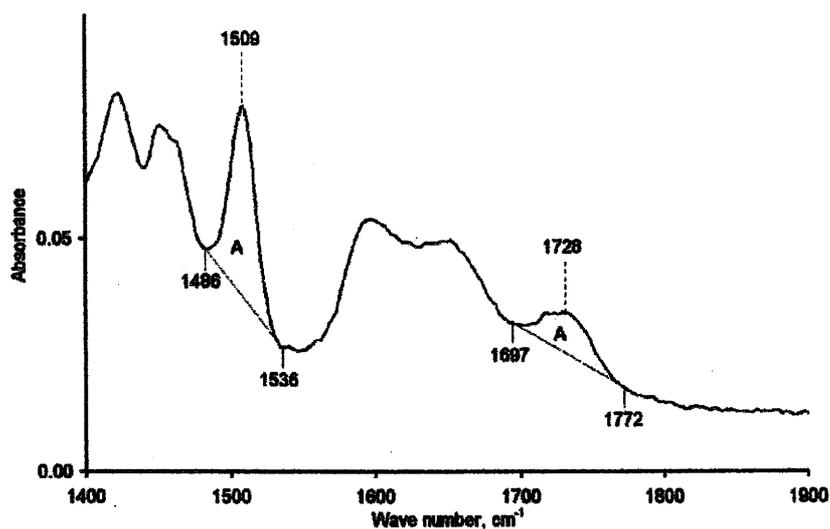
Figure 6. Sloping baseline method to calculate the area under the peaks of the FTIR-ATR spectrum of TMP.

Sarkanen et al. 1967a). Table 3 shows the absorbance values of various peaks. The absorbance at 249 nm has decreased from 0.579 to 0.442 and the absorbance at 295 nm has decreased from 0.298 to 0.204 as a result of sonication which confirms that there is a decrease in non-conjugated phenolic hydroxyl groups after sonication.

The normalized FTIR-transmission spectra of the control and sonicated samples of hydrolytic lignin are shown in Figure 9. Here, the peak at

1700 cm^{-1} corresponds to C=O stretching vibrations in non-conjugated carbonyls in lignin. It is evident from Figure 12 that there are no new peaks and there is no change in the position of peaks as a result of ultrasonic irradiation of the hydrolytic lignin. To compare the intensities of bands in the region of interest, a difference spectrum was obtained as shown in Figure 10. It can be seen that there is a considerable increase in the intensity of absorption in the region from 1680 to 1800 cm^{-1}, which corresponds to C=O stretching vibrations in non-conjugated carbonyls. The area under the peaks was calculated by the sloping baseline method (Figure 11) for quantification purpose. The value of A_{1700}/A_{1515} increases from 1.310 for the control sample to 1.562 for the son-

icated sample which confirms that there is an increase in the non-conjugated carbonyl groups present in lignin as a result of sonication. Combined UV and FTIR results suggest that the oxidation of hydroxyl groups in lignin have taken place to form carbonyl groups after sonication.

IGC analysis was carried out to study the effect of sonication on the surface properties of TMP fibers. Table 4 shows the dispersive components of the surface free energy γ_s^D of the control and sonicated samples of TMP evaluated using the two methods. It can be seen there is an increase in the value of γ_s^D as a result of sonication. It shows that the surface of TMP fibers has become more wettable after sonication, which is in accord with the spectroscopic results that found increased levels of
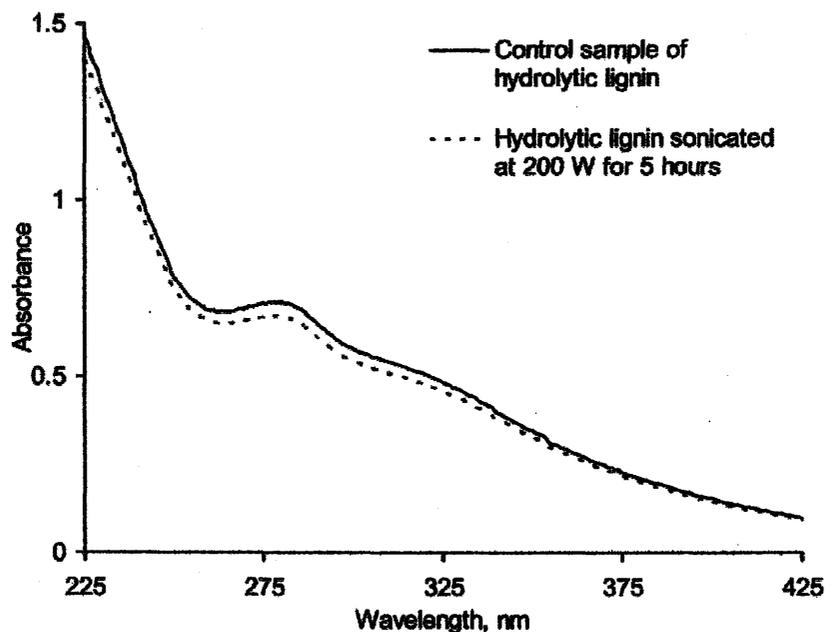

Figure 7. UV spectra of hydrolytic lignin.

Table 3. UV spectroscopy data for hydrolytic lignin samples.

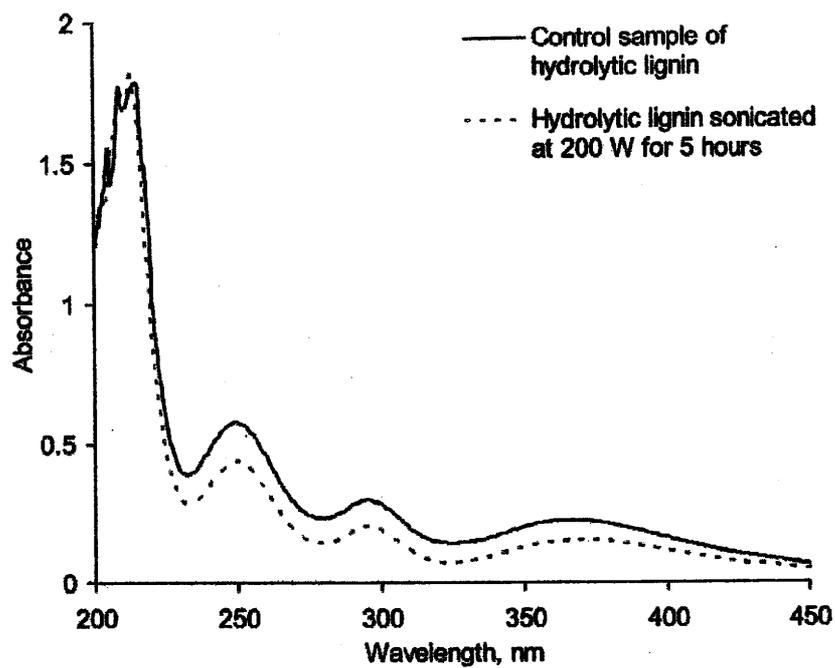| Technique	Wavelength (nm)	Absorbance	
		Control sample of hydrolytic lignin	Hydrolytic lignin sonicated at 200 W for 5 h
UV	279	0.769	0.673
UV-ionization	366	0.224	0.154
	295	0.298	0.204
	249	0.579	0.442
	215	1.785	1.841

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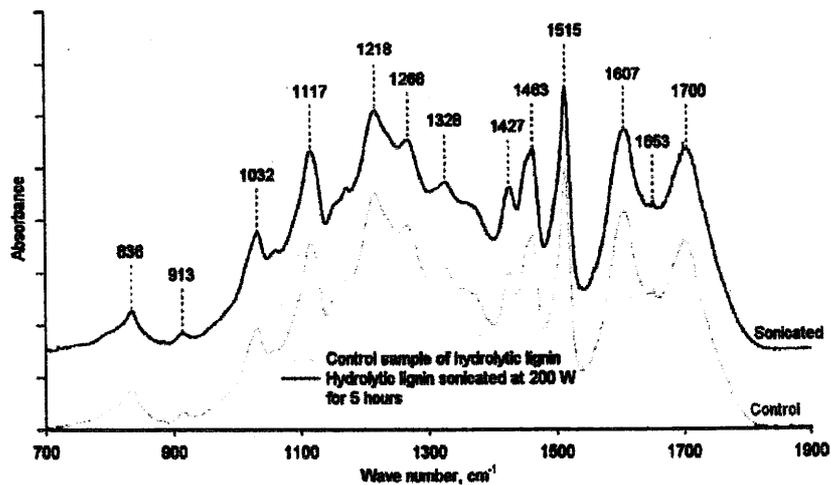Figure 8. UV-ionization spectra of hydrolytic lignin.

Figure 9. FTIR-transmission spectra of hydrolytic lignin.

oxidation upon treatment with ultrasound. It is also found that the results are consistent between the two methods used for calculating the γ_s^D.

FTIR-ATR was employed to study the effect of the ultrasound power on the degree of surface oxidation of TMP fibers. The peak area ratio
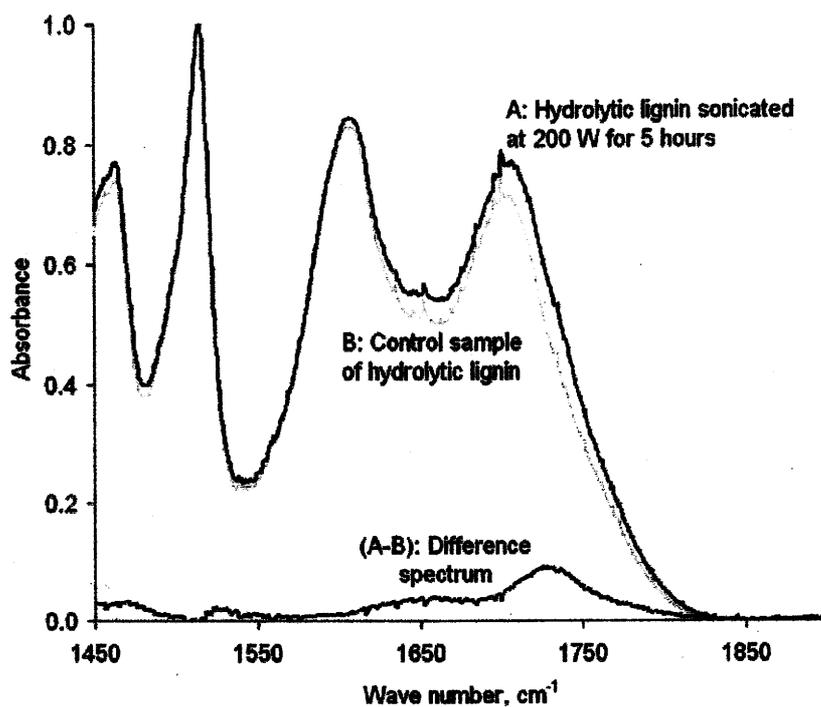
Figure 10. Difference spectrum (FTIR-transmission) showing an increase in the absorption in the band near 1700 cm^{-1} upon sonication.

A_{1728}/A_{1509} was used for quantification purpose. Figure 12 shows the plot of A_{1728}/A_{1509} obtained from the FTIR-ATR spectra of TMP fibers soni-cated for 1 hour versus ultrasound power, indicating that value of A_{1728}/A_{1509} increases linearly with ultrasound power. Figure 13 shows the
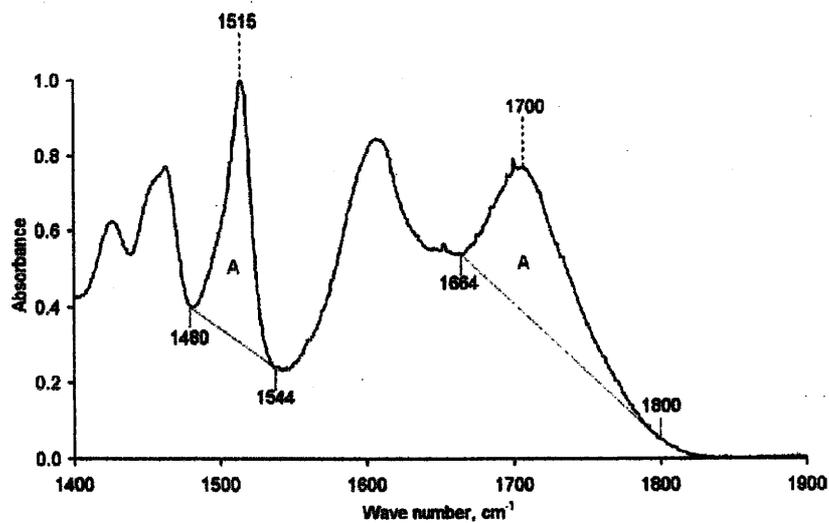

Figure 11. Sloping baseline method to calculate the area under the peaks of the FTIR-transmission spectrum of hydrolytic lignin.
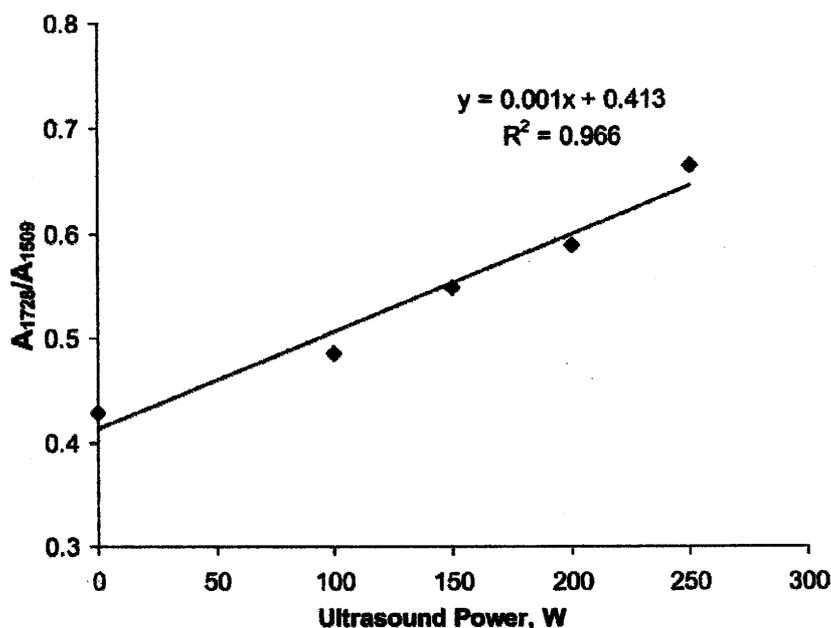
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Figure 12. Effect of ultrasound power on the area ratio A1728/A1509 of the FTIR-ATR spectrum of TMP sonicated for 1 h.

comparison of TMP samples sonicated for 1 and 3 h at various ultrasound powers. There is, however, no substantial difference in the value of A_{1728}/A_{1509} between the TMP samples sonicated for 1 and 3 h.

Conclusions

Aqueous suspensions of thermo-mechanical pulp were subjected to ultrasonic irradiations at 610 kHz frequency. FTIR transmission and ATR results show an increase in non-conjugated carbonyl groups in TMP upon sonication. To investigate this behavior, sonication of the hydrolytic lignin was carried out, which also shows an increase in the number of non-conjugated carbonyl groups coupled with a decrease in non-conjugated phenolic hydroxyl groups. The increase in non-conjugated carbonyls in TMP after sonication can attributed to the oxidation of phenolic hydroxyl groups in lignin. The increase in the surface energy of sonicated fibers, as seen from IGC analysis, suggest that the surface of sonicated TMP fibers is more active. The extent of surface oxidation of TMP increases linearly with an increase in the ultrasound power, however the results are not significantly different for the fibers sonicated for 1 and 3 h.

Acknowledgments

Table 4. Dispersive component of the surface free energy of TMP samples.

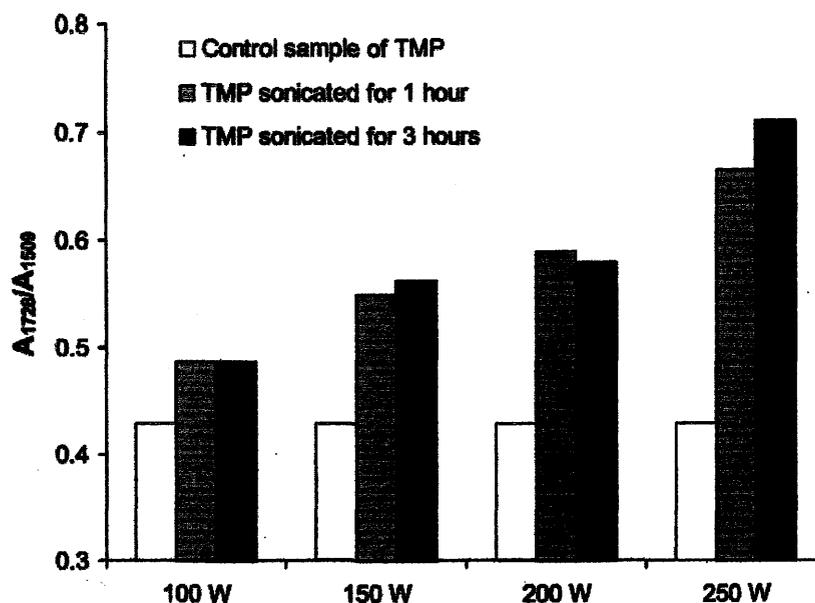| Sample	Dorris and Gray method		Schultz and Lavielle method	
	γ_s^D mJ/m^2	R^2	γ_s^D mJ/m^2	R^2
Control sample of TMP	28.5	0.9	28.6	0.9
TMP sonicated at 100 W for 3 h	29.3	1	29.4	1
TMP sonicated at 200 W for 3 h	36.0	1	31.4	1

Figure 13. Effect of sonication time on the area ratio A1728/A1509 of the FTIR-ATR spectrum of TMP at various power levels.

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