Relationship of Wood Surface Energy to Surface Composition

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The wood cell wall is composed of cellulose, lignin, hemicelluloses, and extractives. Thus, the surface energy of the wood material must be some combination of the surface energies of these components. The influence of extractives on wood surface chemistry can be important in diverse industrial applications, such as coating, pulping, and wood-based composites. In this study, pine wood meal was subjected to heating, washing with toluene, and extraction with acetone/water, dichloromethane, and ethanol/benzene. The surface properties and composition were then determined by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and inverse gas chromatography (IGC). The dispersive component of the surface free energy, the enthalpy, the entropy, and the acid/base interactions were calculated from IGC measurements and compared to the surface composition as revealed by XPS. Heating and washing with toluene altered surface properties only slightly. Extraction of wood meals with acetone/ water, dichloromethane, and ethanol/benzene appeared to partially and selectively remove most extractives from the wood, resulting in an increased dispersive component of the surface energy, increased acidity, and increased basicity. The surface energy appeared to be related to the distribution of surface oxygen-containing functional groups.

1. Introduction

A substantial amount of research has addressed the influence of extractives on the adhesive properties of wood. In conventional wood composites bonded with phenol−formaldehyde resins, inferior bonding strength has been attributed to the presence of extractives on the surface.[1,2] As early as 1959 it was recognized that the migration of very small amounts of saturated fatty acid extractives to the wood surface could significantly alter wood surface properties.[3] Hemingway' demonstrated that only 400 ppm of saturated fatty acid would achieve a packed monolayer on a wood surface. Various surface treatments, such as heat,' solvent extraction,[5] and plasma treatment! have been studied in an effort to control surface properties.

Although the importance of wood surface chemical structure and the impact of small molecules on surface properties have long been appreciated, investigations have just begun to focus on establishing the surface structure−property relationships. Dynamic contact angle measurements have been used to define changes in wood veneer wettability with extractive content of the surface.' The relationship of paper surface composition to surface energy was studied by Etzler and Connors.[8]

Recently, issues associated with the recovery and reuse of waste materials have prompted consideration of alternative material systems as well. Wood-filled thermoplastic composites have been identified as a promising outlet for recycled lignocellulosic fiber because they offer favorable strength/weight ratios, toughness, and reduced abrasiveness compared with inorganic fillers. Research on the development of lignocellulosic fiber/thermoplastic polymer composites has focused on their poor interfacial properties and has renewed interest in the surface properties of these natural fibers as components in composite systems.

In contrast to the case of conventional wood composites that rely on thermosetting polymers to bond the individual wood elements, adhesion to thermoplastic matrices is limited to specific secondary interactions that are established across the phase boundary. As such, interfacial properties are likely to be much more sensitive to small variations in surface energetics, which are impacted by a number of inherently present variables. Adsorbed impurities, either from various gases or process contaminants, have been shown to negatively impact interfacial properties in polystyrene/fiber composites.[9] Surface chemical properties of lignocellulosic fibers are also partly determined by the relative proportion of exposed lignin and carbohydrate.[10] Extracellular compounds including terpenes and fatty acids, which can comprise as much as 12% (by weight) of certain wood species" also may dramatically influence the surface properties of these

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† Current address: Temple-Inland Forest Products Corp., Diboll, Texas.
(1) Christiansen, A W. *Wood Fiber Sci.* **1990**, *22* (4), 441.
(2) Hancock, W. V. Forest *Prod J.* 1992. 12 (9), 452.
(3) Swanson, J. W.; Cordingly, S. *TAPPI* 1959, *42* (10), 812.
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materials, such as wetting.[12] Grafting of polymer chains onto the wood surface has also been studied as a way of altering the surface energy.[13] Adhesion of wood fibers to polyethylene was studied by Chtourou et al.[14]

This paper reports the influence of several different treatments on the chemical composition (bulk and surface) and properties of wood particles. In addition, the relationships between surface structure and surface energetics are explored.

2. Experimental Section

2.1. **Treatment of Wood Meal.** White pine wood meal, mesh size #20−60, was contributed by American Wood Fibers, Schofield, WI. About 20 gofwood meal was used for each of five treatments and for the untreated control.

Heat treatment. Wood meal was heated in an oven at 140 °C for 2 h, weighed, and then stored in sealed plastic bags.

Toluene Wash. Wood meal was stirred with *300* mL of toluene in a beaker for 5 min. The toluene was removed by rotary evaporation at 45 °C under vacuum supplied by a water tap aspirator. The dried wood meal was weighed and then sealed in plastic bags for later use.

Dichloromethane Extraction. Wood meal was equally divided into six parts, packed into six extraction thimbles, and extracted with refluxing dichloromethane for 4 h in Soxhlet extractors. The extracts were combined and concentrated by rotary evaporation, air-dried, and then vacuum-dried to produce solid extracted material, which was then weighed.

Acetone/ Water Extraction. Wood meal was equally divided into six parts, packed into six extraction thimbles, and extracted with refluxing acetone/water (1/1, v/v) for 4 h in Soxhlet extractors. The extracts were combined and concentrated by rotary evaporation, air-dried, and then vacuum-dried to produce solid extracted material, which was then weighed.

Ethanol/Benzene Extraction. Wood meal was equally divided into six parts, packed into six extraction thimbles, and extracted first with refluxing ethanol/benzene (1/1, v/v) for 4 h in Soxhlet extractors and then with ethanol alone for 4 h, and then washed with distilled water. The extracts were combined and concentrated by rotary evaporation, then air-dried, and then vacuum-dried to produce solid extracted material, which was then weighed.

2.2. **FTIR** Analysis. For each treated and untreated wood meal sample, a KBr disk of about 13-mm diameter and l-mm thickness was prepared by mixing 1.0−1.5 mg of wood meal sample or extracted material with 200 mgof KBr and pulverizing the mixture in a micro-macro pellet apparatus for 5 min under vacuum. A Nicolet DXB-20 FTIR spectrometer was used to collect the spectra, and 60 scans were used for each sample.

2.3. **XPS** Analysis. For each treated and untreated wood *meal* sample, a disk 13 mm in diameter and l-mm thick was prepared by pulverizing in a micro-macro pellet maker apparatus for 5 min under vacuum. Samples were analyzed with a Surface Science model SSX-100 ESCA spectrometer. An aluminum X-ray anode was used with a quartz monochromator and a 600 μm spot size. Charge neutralization was conducted on all samples with an electron flood gun and a Ni screen stabilized at ground potential 0.5 mm above each sample. Deconvolution of the spectral peaks was performed on all samples with the Surface Science software.

2.4. **IGC Measurements.** The probe liquids used for IGC were purchased from Aldrich Chemical Co., Milwaukee, WI. They were of chromatographic grade and were used as received. The

Table 1. Characteristics of IGC Probes

probe	a (Å²)	$\gamma_L{}^d$ (mJ/m²)	AN (kcal/mol)	DN (kcal/mol)
n-hexane	51.1	18.4	0	0
n-heptane	57	20.3	0	0
n-octane	63	21.3	0	0
n-nonane	69	22.7	0	0
n-decane	75	23.4	0	0
n-undecane	81	24.5	0	0
Acidic				
CH_2Cl_2	31.5	27.6	20.4	0
C_6H_6	46	26.7	8.2	0.1
$CHCl_3$	44	25.9	23.1	0
Amphoteric				
acetone	42.5	16.5	17.0	12.5
methyl acetate	36.5	24.6	10.7	16.5
Basic				
ether	47	15.0	3.9	19.2
THF	45	22.5	8.0	20.1

probes and their physical properties[15−18] are listed in Table 1. Retention data were obtained with a Hewlett-Packard 5890 gas chromatograph and integrator equipped with dual hydrogen flame ionization detectors maintained at 250 °C to ensure flash vaporization of probe vapors. Prepurified nitrogen was used as the carrier gas at a flow rate of 20 mL/min. Methane was used as a reference gas to determine the dead volume. Appropriate corrections for the pressure drop along the column were made on the basis of the pressure at the injection and outlet ports.

All wood meal samples were dried overnight at 100-103 °C before IGC measurements. The extractive percentages were calculated on the basis of the oven-dried weights. The wood meal samples were packed into standard 6-mm (¼ in.) gas chromatography columns. Retention times were the hverage of at least five injections for each sample and condition. All experimenta were performed across a temperature range of from 45 to 65 °C at 5 °C intervals; injections were less than 0.1 μL to ensure a valid approximation of infinite dilution of the probe vapor.

2.5. **IGC Data Analysis.** Thermodynamic values for the adsorption of known probes on a solid packed into a chromatography column may be obtained from the retention times of the probes. The theory relating IGC data to thermodynamic functions has been developed by several groups over a period of years (reviewed by Schreiber and Lloyd9 and will not be repeated here. The theory is employed by converting the retention time to a retention volume,

$$V_N = jF(t_r - t_0) \qquad (1)$$

where V_N is the net retention volume, j is the correction factor for gas compressibility,[20] F is the carrier gas flow rate, t_r is the retention time of the probe, and t_0 is the retention time of a marker probe (in our case, methane).

V_N is related to the thermodynamic functions by[16]

$$\Delta G_A° = -RT \ln(V_N P_0 / SgB_0) \qquad (2)$$

where $\Delta G_A°$ is the free energy of adsorption of the probe on the stationary phase surface, T is the column temperature, R is the

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gas constant, P_0 is the reference partial pressure of the probe, S is the specific surface area of the stationary phase, g is the weight of the stationary phase, and B_0 is the reference state of the bidimensional spreading pressure of the adsorbed probe film on the stationary phase. Equation 2 can be rewritten as

$$\Delta G_A^\circ = RT \ln V_N + \text{constant} \tag{3}$$

where the constant depends upon the chromatographic column and the reference state chosen.

Fowkes[21] first suggested that the surface energy can be considered as the sum of the energies arising from a variety of sources. The more important sources for the systems under investigation here are the dispersive component, arising from London, van der Waals, and Lifshitz forces, and the acid/base component, arising from both Lewis acid/base interactions and hydrogen bonding.[5] We assume that the alkane probes have no acid/base character and thus interact with the surface only through dispersive forces.

The plot of ΔG_A° for an homologous series of alkanes versus the carbon number of the alkane is a straight line. The slope of this line is the free energy of an incremental methylene group on the stationary phase ($\Delta G_{A(CH_2)}^\circ$). This value can be used to relate the tree energy of adsorption to the London component of the surface energy of the stationary phase by an equation proposed by Dorris and Gray:[22]

$$-\Delta G_{A(CH_2)}^\circ / Na_{CH_2} = 2(\gamma_{(CH_2)}\gamma_s^d)^{1/2} \tag{4}$$

where N is Avogadro's number, a_{CH_2} is the area of an adsorbed methyl group, equal to 0.06 nm^2, $\gamma_{(CH_2)}$ is the surface. energy of a methylene group, equal to 36.6 mJ/m^2 at 293.15 K (although this number is not universally accepted), and γ_s^d is the dispersive component of the surface free energy of the stationary phase.

Information on the acid/base. properties of the stationary phase can be gained with an approach described by Schultz and Lavielle.[16] In addition to obtaining the V_N values for an homologous series of alkanes, we also measured V_N for acidic and basic probes. We used benzene, CH_2Cl_2, and $CHCl_3$ as acidic probes and diethyl ether, methyl acetate, and THF as basic probes. Acetone is an amphoteric probe and was also included in our studies.[21] The equation used to relate retention volume to surface energy is[16]

$$RT \ln V_N = 2N(\gamma_s^d)^{1/2}a(\gamma_l^d)^{1/2} + \text{constant} \tag{5}$$

where a is the cross-sectional area of the probe on the surface (a reported quantity), γ_L^d is the dispersive component of the surface tension of the probe (equal to the total surface tension for alkanes), and entropic contributions are neglected. Plotting $RT \ln V_N$ versus $a(\gamma_L^d)^{1/2}$ yields a straight line for the homologous alkane series. The acidic and basic probes will deviate from this line. The ordinal deviation from the alkane line is defined as the specific interaction parameter (ΔG_{sp}°)[14]

$$\Delta G_{sp}^\circ = RT \ln \frac{V_N}{V_N^{ref}} \tag{6}$$

where V_N^{ref} is the value of V_N on the alkane line at the value of $[a(\gamma_L^d)^{1/2}]$ corresponding to the acidic or basic probe.

The V_N values are then obtained for a series of temperatures, and the van't Hoff equation[23] is used to derive the specific enthalpy of adsorption (ΔH_{sp}°),

$$\frac{\partial(R \ln V_s^\circ)}{\partial\left(\frac{1}{T}\right)} = -\Delta H_{sp}^\circ \tag{7}$$

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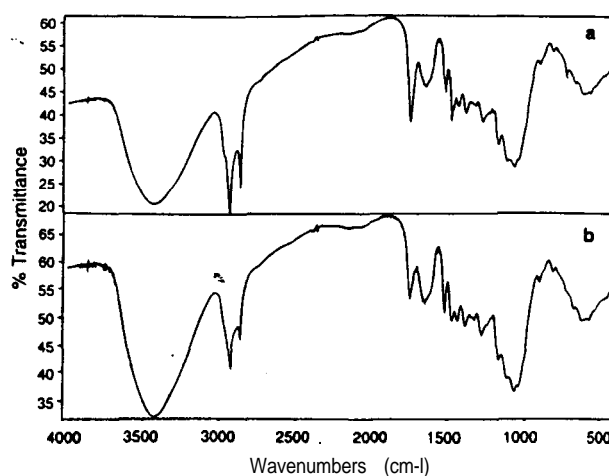

Figure 1. FTIR spectra of (a) untreated wood meal and (b) heat-treated wood meal.

Following Saint-Flour and Papirer,[24] we used the four-parameter equation originally developed by Drago[25] to describe acid/base interactions. We may then write

$$\Delta H_{sp}^\circ = K_A \cdot DN + K_D \cdot AN \tag{8}$$

where K_A and K_D are the acceptor and donor parameters of the stationary phase, respectively, and AN and DN are the (known) Gutmann acid and donor numbers of the probe. Equation 7 may be rearranged to[16]

$$\frac{\Delta H_{sp}^\circ}{AN} = K_A\frac{DN}{AN} + K_D \tag{9}$$

This gives a linear plot with a slope of K_A and an intercept of K_D.

3. Results and Discussion

No significant weight loss was observed with either heat treatment or the toluene wash. Weight loss upon extraction varied with the extraction solvent: acetone/water extraction removed 6.30%. dichloromethane 11.62%, and ethanol/benzene 7.82% of the solids by weight. The effects of the extractions on surface composition were further investigated with FTIR and XPS analysis.

3.1. FTIR. The FTIR spectra of wood meal after heat treatment (Figure 1B) had changed considerably from that of untreated wood meal (Figure 1A). Both the aromatic and aliphatic C-H stretches around 2800 cm^{-1} were reduced compared to the hydroxyl peak around 3400 cm^{-1} and the C-O stretch at 1000-1100 cm^{-1}. This may indicate that some hydrocarbon compounds had been lost to volatilization. In addition, the carbonyl peak at 1740 cm^{-1} was reduced in comparison to both the 3400 and 1000−1100 peaks and the aromatic stretch at 1600-1700 cm^{-1}, indicating a loss of this functionality from the surface. The peak at 730 cm^{-1} was greatly reduced after heat treatment. This may indicate the reaction of the alkene functionality present in the untreated wood meal during heat treatment.

The FTIR spectra of the toluene-washed sample (not shown) showed little change from the untreated sample. The FTIR spectra of the extracted samples (not shown) showed only reduced and broadened C-H stretches in comparison with the untreated and heat-treated samples. Differences between the various extractions were not

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Table 2. Summary of XPS Spectral Parameters

	peak	control	heat	toluene wash	dichloromethane	ethanol/benzene	acetone/water
Cl	BE	280.99	*280. 96*	280.93	281.1	281.21	281.19
	fwhm[a]	1.66	1.58	1.67	1.7	1.72	1.75
	area (%)	87.71	85.75	87.55	51.33	51.40	54.33
C_2	BE	282.9	282.71	282.85	282.79	282.89	282.85
	fwhm	1.26	1.2	1.27	1.69	1.59	1.62
	area (%)	7.15	7.83	7.82	42.26	40.08	36.70
C_3	BE	285.12	284.98	284.98	284.69	284.65	284.67
	fwhm	1.59	1.78	1.6	1.36	1.76	1.91
	area (%)	5.15	6.42	4.63	6.41	8.53	8.97
O_1	BE	528.75	528.45	528.56	529.04	529.21	529.04
	fwhm	2.05	1.77	1.9	2.01	2.08	1.98
	area (%)	100	81.13	91.35	100	100	97.62
O_2	BE	ND[b]	529.61	529.84	ND	ND	529.96
	fwhm	ND	1.26	1.2	ND	ND	0.83
	area (%)	ND	18.87	8.65	ND	ND	2.31
C/O	atom/atom (%)	79.8/20.2	82.5/17.5	79.9/20.1	66.7/33.3	65.7/34.3	65.8/34.2

[a] Full width at half maximum. [b] Not determined.

evident in the FTIR spectra. The greater discrimination available with XPS was used to further differentiate these samples.

3.2. **XPS Surface Characterization.** The C_{1s} carbon and O_{1s} oxygen peaks obtained for each sample were deconvoluted (Table 2). The assignment of the deconvoluted C_{1s} peak for lignocellulosics has reached a general consensus in the literature.% Our spectra deconvoluted to three peaks. The C_1 peak corresponds to carbon bound to hydrogen or itself, C-H, or C-C bonds; the C_2 peak corresponds to carbon singly bound to oxygen, C-O; and the C_3 peak to carbon doubly bonded to oxygen, C=O, or to two oxygens, O-C-O. The oxygen O_{1s} peak deconvoluted to two peaks. We assigned O_1 to correspond to singly bonded and O_2 to doubly bonded oxygens.

The O/C ratio was calculated from the deconvoluted peaks.[26] The samples fell into two groups based on the O/C ratios. The first group consisted of the untreated, heat-treated, and toluene-washed samples, with O/C ratios between 0.16 and 0.21. The second group consisted of the extracted samples with O/C ratios between 0.41 and 0.43. A comparison of O/C ratios as a function of weight loss upon extraction showed that differences in O/C ratios among extracted samples were much less than the differences in O/C ratios between the extracted and unextracted groups (Figure 2). In addition, the ratio for the extracted materials was intermediate between the theoretical values for lignin and cellulose.[27] The O/C ratios for the untreated, heat-treated, and toluene-washed wood meals were lower, however, which indicates the presence of low O/C extractable compounds on their surfaces. We also concluded that the toluene wash was apparently ineffective in removing extractives from the wood surface.

The O/C ratio was similar for all three extractions, which suggests that most of the surface extractables had been removed and that the remaining surfaces were composed of only cellulose, hemicelluoses, and lignin. Although these materials might be expected to have similar surface energies, IGC studies revealed important differences.

3.3. **Dispersive Component of the Surface Energy.** Values for the dispersive component of the surface free energy (γ_s^d) were obtained from the retention volumes of alkane probes and eq 4. The extracted samples showed higher γ_s^d values than did the untreated, heat-treated, and toluene-washed samples (Figure 3). When γ_s^d at 50 °C was plotted against the XPS O/C ratio, a correlation

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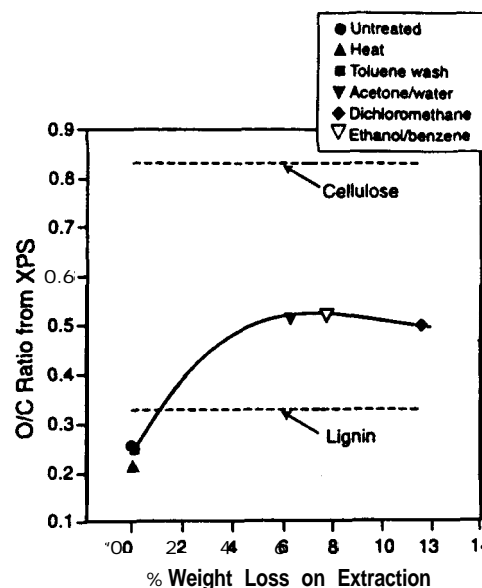

Figure 2. Surface composition as a function of weight loss upon extraction for wood meal samples.
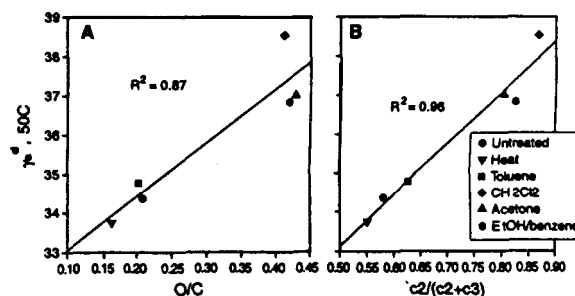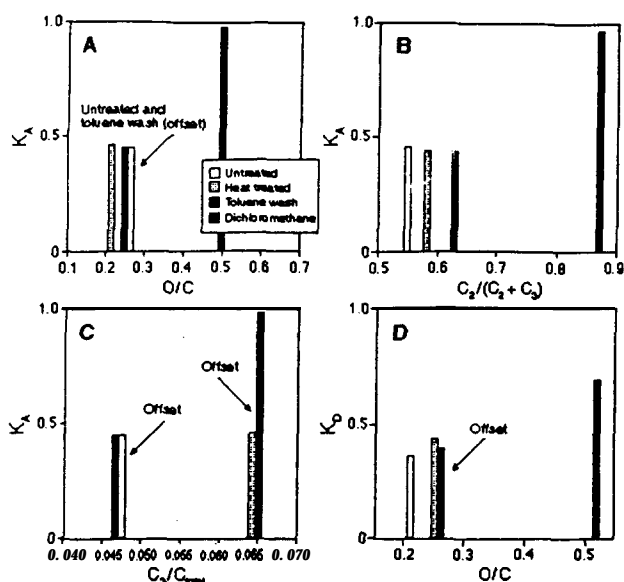

Figure 3. Dispersive component of the surface free energy for extracted and unextracted wood meal as a function of (A) oxygen/carbon surface ratios and (B) singly bound carbon-oxygen over the sum of singly, doubly, and multiply bound carbon-oxygen.

coefficient of 0.87 was obtained (Figure 3A). An improved correlation was observed when the γ_s^d values were plotted against the ratio $C_2/(C_2 + C_3)$ (Figure 3B). This ratio reflects the amount of singly bonded carbon atoms versus the sum of those that are singly and double bonded, that is hydroxyls and ether groups compared to the sum of hydroxyl, ether, carbonyl, and carboxyl groups.

The above information suggests that the extracted surfaces consist primarily of lignin, hemicelluloses, and cellulose but that slight variations in the abundance of the various oxygenated species, including unextracted

Figure 4. Acceptor parameter for treated and untreated wood *meal as a function of* **(A)** surface **oxygen/carbon** ratios, **(B)** singly **bound** carbon-oxygen over the **sum** of singly, doubly, **and multiply** bound carbon-oxygen. and **(C)** ratio of doubly and multi& bound **carbon—oxygen to total** carbon. **(D) Donor** parameter as a **function** of the ratio of surface oxygen/carbon ratios.

materials, have an important effect on the dispersive component of the surface properties. This effect may be viewed by using different variables, such as γ_s^d versus C_1/C_{total}, C_3/C_{total}, or $(C_2 + C_3)/C_1$, but $C_2/(C_2 + C_d$ appears to have the best correlation. We observed that γ_s^d increased with increasing $C_2/(C_2 + C_3)$. Why this should be so currently leads more toward speculation than to definitive answers. The error in both γ_s^d and the XPS variables associated with these measurements was estimated to be about **5—10%;** thus, any firm conclusions based on the $C_2/(C_2 + C_3)$ correlation would be unwarranted at this point. Additional research is needed to verify and elucidate these *findings.*

Other investigators have reported on the effect of surface composition on surface energy. Hammer and **Drzal**[28] found good correlation between oxygen concentration as measured by XPS and the change in polar/dispersive ratios measured by contact angles for fibers with surface treatments. Yasuda et **al.**[29,30] investigated the migration of surface moieties to the bulk phase under changing environmental conditions and found strong relationships between contact angles and XPS F_{1s} intensities for PET and nylon films. **Etzler** and **Conners**[8] found a correlation between XPS C/O ratios and the Zisman critical contact angles for treated papers.

3.4. **Acid/Base Interactions. IGC** data for acidic and basic probes was obtained and compared with that for the alkanes (see above) to provide the specific interaction parameter AC,,," from the plot of $RT \ln V_g^\circ$ versus $a(\gamma_L^d)^{1/2}$ following eqs 5 and 6. The specific enthalpy interaction parameter (ΔH_{sp}°) was calculated from eq 7. Equation 9 was then used to calculate the K_A values for each sample. Because of experimental **difficulties,** the **ethanol/benzene-** and acetone/water-extracted samples were omitted from this analysis. The K_A values fell into two clusters when plotted against the O/C ratio of the samples (Figure 4A).

The unextracted samples showed low O/C ratios and low K_A values, whereas the **CH₂Cl₂-extracted** samples showed a higher **O/C** ratio and a higher K_A value. This was expected, since the **extractables** in wood are typically hydrophobic compounds.[11] Removing them should have increased **O/C** and exposed the more acidic oxygenated species of cellulose and lignin.

The correlation of surface energy with $C_2/(C_2 + C_3)$ was worse than that with **O/C** for the acid/base interactions (Figure 4B). This iš not surprising, as they arise from different chemical functionalities. Interestingly, the K_A values did not correlate well with C_3/C_{total} (Figure 4C). We concluded that the acidity of the surface depends on more than just carboxyl groups. The lignin contains phenolic hydroxyls, which probably contributed acidity to the surface. Other Lewis acid groups, such as aromatic rings and hydroxyls, were also present and may have also contributed to the total acidity of the surface.

The K_D values appeared to also fall into the same groups as the K_A values, with the extracted sample showing a higher K_D value than the unextracted samples as a function of **O/C** (**Figure 4D**). Correlations with other surface composition ratios were attempted, but *no* significant pattern was observed. This observation suggests that extraction reveals more highly polar groups on the surface and increases both the acidity and basicity of the wood surface.

The dispersive component of the surface free energy (γ_s^d) is a thermodynamic value, if all the assumptions and values used for the various parameters are correct. The &and& values are not fundamental but rather empirical values based upon arbitrarily defined AN and DN values. They have important comparative value but may not be combined with γ_s^d to give an approximation to the total surface energy. We can say, however, that the extractions increased the total surface energy of the wood meal, increased the dispersive component by about **10—12%,** approximately quadrupled the acceptor component, and increased the donor component by approximately 75%.

One possible interpretation of the data is that the extracted wood surface becomes more polar, with the polarity governed by the presence of an oxygenated functionality. Yet the surface energy depends not only upon the presence of oxygenated **groups** on the surface but also on the **specific** functionality as determined by the $C_2/(C_2 + C_3)$ ratio, for γ_s^d, and the O/C ratio, for K_A and K_D (other ratios also may provide good correlation for the observed data). This leads to the conclusion that the wood surface is a dynamic one, where the basic polymeric constituents of cellulose, hemicellulose, and lignin alter their configuration on the surface in response to changes in their chemical environment, with surface energy determined by complex interactions among oxygenated species.

4. **Conclusions**

FTIR suggested both an increase in extractives on the wood surface and the reaction of surface alkenes with heat treatment. **FTIR** also suggested the removal of extractives with solvent extraction. XPS showed that solvent extraction raised the O/C ratio. The difference in O/C ratio for the various extractions was small compared with the difference between unextracted and extracted samples.

ICC showed a relationship between surface composition and the dispersive component of the surface free energy (γ_s^d). The free energy increased with increasing $C_2/(C_2 + C_3)$ ratio (other ratios also correlated well). The OK ratio

(28) *Hammer, G.* E.; **Drzal,** L. T. *Appl. Surf Sci.* **1980,** *4*, 340.
(29) Yasuda, T.; Okuno, T.; Yoshida, K. *J. Polym. Sci., Part B: Polym. Phys.* **1988,** *26*, 1781.
(30) Yasuda, T.; **Miyama,** M. *Langmuir* **1992.8,** 1425.

was not the best correlated predictor of γ_s^d. The acceptor and donor components of the surface free energy increased **dramatically** after solvent extraction.

The wood surface appears to be a complicated system that responds differently to various treatments but has properties that are governed by oxygen-containing functional groups. Additional research is needed to further elucidate both the relationships among these groups and the mechanisms by which the wood surface changes in response to modification of the chemical environment.