

Determination of the Acid–Base Characteristics of Lignocellulosic Surfaces by Inverse Gas Chromatography

MANDLA A. TSHABALALA

USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin 53705-2398

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ABSTRACT: The surface acid–base characteristics of samples of cellulose, pine wood, and kenaf powder were determined by inverse gas chromatography (IGC). The test substrates were packed in a deactivated glass column and the IGC probes were injected at infinite dilution. The surface acid–base parameters were expressed in terms of the acceptor K_A and donor K_D parameters, analogous to the Gutmann acceptor and donor numbers derived from the Lewis concept of acids and bases. The K_A and K_D values were calculated from the experimental values of the enthalpy of desorption, corresponding to the specific acid–base interactions, and literature values of the acceptor and donor numbers for the acid–base probes, chloroform, carbon tetrachloride, ethyl acetate, and diethyl ether. Values of K_A and K_D suggest that the surfaces of cellulose, pine wood, and kenaf powder that have been washed by extraction with toluene/ethanol (2 : 1, v/v) are amphoteric, with a relatively greater capacity to accept electrons. The effect of the washing procedure on the dispersive component of the surface energy of the pine wood and kenaf powder was also determined. It was observed that the values for the washed substrates were relatively greater than those of the nonwashed counterparts. © 1997 John Wiley & Sons, Inc.* J Appl Polym Sci **65**: 1013–1020, 1997

Key words: surface acid–base characteristics; inverse gas chromatography; lignocellulosic surfaces; pine wood; kenaf

INTRODUCTION

Acid–base characteristics of solid surfaces play an important role in the interaction of solids with liquids. Such interactions find many applications in wood-finishing processes and the production of wood-based composites. The interaction of solids with liquids is determined by the surface chemistry of the solid and the interacting liquid. It is generally recognized by many researchers that the specific chemical interactions that may occur at the solid–liquid interface are predominantly

Lewis acid–base interactions. These are interactions in which an electron pair donated by a base is shared between the acid and the base to form an “adduct.”^{1,2} Typical examples of such interactions are hydrogen bonds between water molecules and the hydroxyl groups in cellulose.³

The objective of this study was to determine the surface acid–base characteristics of representative lignocellulosic materials by inverse gas chromatography (IGC) under conditions of near-zero surface coverage of the test material by the probe molecules.⁴ Data generated in this study will find numerous practical applications, including the design of low volatile organic compound formulations for coating wood substrates, and surface modification processes for lignocellulosic fibers and their compatibilization with synthetic polymers.

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BACKGROUND

IGC has become a widely used technique to characterize the surface properties of organic and inorganic materials. This technique consists of measuring the chromatographic retention times of vapor-phase probes of known properties on a column packed with the material of interest. Acid–base probes are used to measure the acid–base characteristics of the solid surface, and saturated n -alkane probes are used to measure the dispersive component of the surface energy of interaction. In the present study, retention times of saturated n -alkane and acid–base probes injected at infinite dilution were used to calculate the dispersive component (γ_S^D) of the surface energy, the free energy of desorption (ΔG^{AB}), and the enthalpy of desorption (ΔH^{AB}) corresponding to acid–base surface interactions. Papirer's approach, as described by Shultz and colleagues^{5,6,7} was used to estimate the acceptor (K_A) and donor (K_D) parameters of the test substrates.

The fundamental parameter in the IGC measurements is the specific retention volume, V_g , defined as the volume of carrier gas required to elute a probe from a column containing 1 g of the test substrate material. V_g is related to experimental variables by the following equation^{6,8}:

$$V_g = [(t_r - t_m)F^*]/W \quad (1)$$

where t_r and t_m are the retention times of the probe and the methane marker, respectively; W is the weight, in grams, of the test material in the column; and F^* is the corrected flow rate of the carrier gas, defined as

$$F^* = F(273.15/T)JC \quad (2)$$

where F is the carrier gas flow rate, in mL/min, measured at the flow meter temperature T (K); and J and C are the correction factors for the gas compressibility and water vapor pressure of the soap solution of the bubble flow meter, respectively.

$$J = 1.5[(P_i/P_o)^2 - 1]/[(P_i/P_o)^3 - 1] \quad (3)$$

and

$$C = 1 - (P_w/P_o) \quad (4)$$

where P_w is the water vapor pressure at room

temperature; P_o is the carrier gas pressure at the column outlet; and P_i is the carrier gas pressure at the column inlet.

The interaction of neutral probes, such as saturated n -alkanes, with the substrate material is predominated by the van der Waals dispersive forces of interaction. It has been shown that under conditions of infinite dilution of the injected probe vapor, the dispersive component γ_S^D of the total surface energy of the substrate is related to V_g by the following equation:

$$RT \ln V_g = 2N(\gamma_S^D)^{1/2}a(\gamma_L^D)^{1/2} + C^t \quad (5)$$

where R is the gas constant; T is the column absolute temperature; N is Avogadro's number; a is the surface area of the probe molecule; and γ_L^D is the dispersive component of the surface energy of the probe.

A plot of $RT \ln V_g$ versus $2Na(\gamma_L^D)^{1/2}$ should give a straight line with slope $(\gamma_S^D)^{1/2}$.

The interaction of polar probes with the substrate involves both dispersive and acid–base interactions. The free energy of desorption, ΔG^{AB} , corresponding to acid–base surface interactions, may be related to V_g by the following equation:

$$RT \ln(V_g/V_g^{\text{ref}}) = \Delta G^{AB} \quad (6)$$

where V_g is the specific retention volume of a polar probe and V_g^{ref} is the specific retention volume of a corresponding reference n -alkane.

Equation (6) suggests that values of $RT \ln V_g$ plotted versus $2Na(\gamma_L^D)^{1/2}$ for polar probes should fall above the straight line obtained by plotting $RT \ln V_g^{\text{ref}}$ versus $2Na(\gamma_L^D)^{1/2}$ for the reference n -alkane probes. The difference in the ordinates between the point corresponding to the specific polar probe and the reference line gives an estimate of the value of the free energy of desorption corresponding to the specific acid–base interactions.

The free energy of desorption corresponding to the specific acid–base interactions may be related to the enthalpy of desorption, ΔH^{AB} by the following equation:

$$\Delta G^{AB} = \Delta H^{AB} - T\Delta S^{AB} \quad (7)$$

where ΔS^{AB} is the entropy of desorption corresponding to the specific acid–base interactions.

A plot of $\Delta G^{AB}/T$ versus $1/T$ should yield a straight line with slope, ΔH^{AB} . The enthalpy of

desorption corresponding to the specific acid–base interaction is related to the acceptor and donor parameters, K_A and K_D , of the substrates by the following expression:

$$\Delta H^{AB} = K_A DN + K_D AN \quad (8)$$

where DN and AN are the donor and acceptor numbers, respectively, of the acid–base probe as defined by Gutmann.⁹

A plot of $\Delta H^{AB}/AN$ versus DN/AN should yield a straight line with slope K_A and intercept K_D .

EXPERIMENTAL

Apparatus and Measurement

A Hewlett Packard 5880ATM gas chromatograph equipped with a flame ionization detector was used for the IGC experiments. The injector and detector temperature zones were set at 300°C. The oven temperature ranged from 40 to 100°C. Nitrogen was used as the carrier gas, at a flow rate that ranged from approximately 30 to 50 mL/min. The exact flow rate at each oven temperature was measured with a soap-bubble flow meter. The column inlet pressure at each oven temperature was measured with a portable pressure gauge equipped with syringe needle for insertion through the injection port septum. The column outlet was at atmospheric pressure, which was obtained from a barometer. The soap-bubble flow meter was at room temperature, which was obtained from a thermometer held close to the flow meter. The retention time of each probe and the methane gas marker were determined from their peak maxima as indicated by the HP 5880A integrator.

Test Materials

The test materials used as column packing in the present study were wood powder from eastern white pine (*Pinus strobus*) and kenaf powder (*Hibiscus cannabinus*). Cellulose powder, 20- μ m particle size (Aldrich Chemicals), was used as the reference material.

Probes

The IGC probes used in the present study were chromatography grade solvents (Sigma-Aldrich). The probes were used without further treatment.

Their physicochemical properties are listed in Table I. Methane gas, 1,000 ppm in nitrogen (Aldrich Chemicals), was used as the marker.

Procedure

The test material was packed in a deactivated glass column 1.2 m (4 ft) long with a 4-mm internal diameter (Alltech Associates). The column was rinsed with methanol and acetone and dried by aspirating with air before it was packed with the test material. The test material was prepared by grinding in a Wiley mill to 60/80 mesh size. The cellulose powder was used without further treatment. For preparing a washed sample, the test material was first ground to 30 mesh size, and extracted for 24 h in a Soxhlet apparatus with toluene/ethanol (2 : 1, v/v) to remove extractives such as waxes, fats, some resins, and possibly some portions of wood gums.¹⁰ After processing in the Soxhlet apparatus, the washed sample was rinsed with ethanol before drying to a constant weight in a vacuum oven at 40°C. At the end of the drying period, the sample was ground to 60/80 mesh size before packing in the column for IGC measurements.

RESULTS AND DISCUSSION

Preliminary Experiments

Preliminary experiments were performed on the cellulose powder to determine the optimum chromatographic conditions for reproducible measurements of the retention times of the probes. The chromatographic peak shape of each probe had to be as symmetrical as possible. Thus it was established that in order to obtain peak shapes with an acceptable asymmetry factor of unity at 10% of the peak height, it was sufficient to draw only 0.1 μ L of the head space probe vapor into a 1- μ L syringe from a 3-mL vial containing approximately 1 mL of the probe liquid at room temperature. To obtain an infinitely dilute aliquot of the probe vapor, it was necessary to purge the syringe with several syringe volumes of air before injecting into the column. It was established that 1 μ L of 1,000 ppm of methane gas in nitrogen gave a sharp, narrow peak of approximately 7 area counts at an attenuation of 2⁰ and a threshold of zero. These integrator conditions were used for all the chromatographic measurements in the pres-

Table I Physicochemical Properties of the IGC Probes Used in the Present Study^{5,6,7,8}

Probe	a (Å) ²	γ_L^D (mJ m ⁻²)	AN	DN (kcal/mol)	M_w	Specific Character
<i>n</i> -Hexane	51.5	18.4	0	0	86.18	neutral
<i>n</i> -Heptane	57	20.3	0	0	100.21	neutral
<i>n</i> -Octane	63	21.3	0	0	114.23	neutral
<i>n</i> -Nonane	69	22.7	0	0	128.26	neutral
<i>n</i> -Decane	75	23.4	0	0	142.29	neutral
Chloroform	44	25.9	23.1	0	119.38	acid
Diethyl ether	47	15.0	3.9	19.2	74.12	amphoteric
Ethyl acetate	48	16.5	9.3	17.1	88.11	amphoteric
Carbon tetrachloride	46	26.8	8.6	0	153.82	acid

ent study. Thus it was assumed that the condition of “near-zero surface coverage” of the test material in the column was satisfied and any peak tailing could be ascribed to the existence of heterogeneous adsorption sites on the test material.

Dispersive Component of the Surface Energy

The values for the dispersive component, γ_S^D of the surface energy are summarized in Table II. Plots of γ_S^D as a function of temperature for the substrates used in this study are shown in Figure 1. All of the substrates showed a negative temperature coefficient in the temperature range 40 to 60°C. Reidl and Kamdem¹¹ reported a similar temperature dependence for unmodified chemithermomechanical pulp. In the present study, the temperature dependence was determined in the temperature range 40 to 100°C. While cellulose and pine wood showed a negative temperature coefficient over this entire range, the kenaf appeared to deviate somewhat from this trend. As shown in Figure 1, the temperature coefficient for the washed kenaf changed to positive in the temperature range 60 to 80°C. Other than the possi-

bility of an outlier, it is also possible that after equilibrating overnight at an oven temperature of 80°C the washed kenaf surface suffered a compositional change that resulted in this apparently anomalous behavior.

As seen in Figure 1, washing the pine wood and kenaf powder by extraction in a Soxhlet apparatus with toluene/ethanol had the effect of increasing their respective γ_S^D values toward that of the cellulose powder.

Free Energy of Desorption, ΔG^{AB} , and Enthalpy of Desorption, ΔH^{AB}

Values of the free energy of desorption, ΔG^{AB} , corresponding to surface acid–base interactions, are summarized in Table III. These values were calculated according to eq. (6) for the respective substrates at different column oven temperatures. The corresponding values of the enthalpy of desorption, ΔH^{AB} determined from the plots of $\Delta G^{AB}/T$ as a function of $1/T$, are given in Table IV. The carbon tetrachloride probe showed a negative acid–base free energy and enthalpy of desorption on the cellulose. This suggests that the acid–

Table II Dispersive Component, γ_S^D , of the Surface Energy of Lignocellulosic Particles at Different Temperatures

Material	γ_S^D (mJ m ⁻²)				
	40°C	50°C	60°C	80°C	100°C
Cellulose	48	—	44	40	36
Washed wood	49	46	43	35	34
Nonwashed wood	37	35	33	30	30
Washed kenaf	42	38	34	44	27
Nonwashed kenaf	40	35	34	30	27

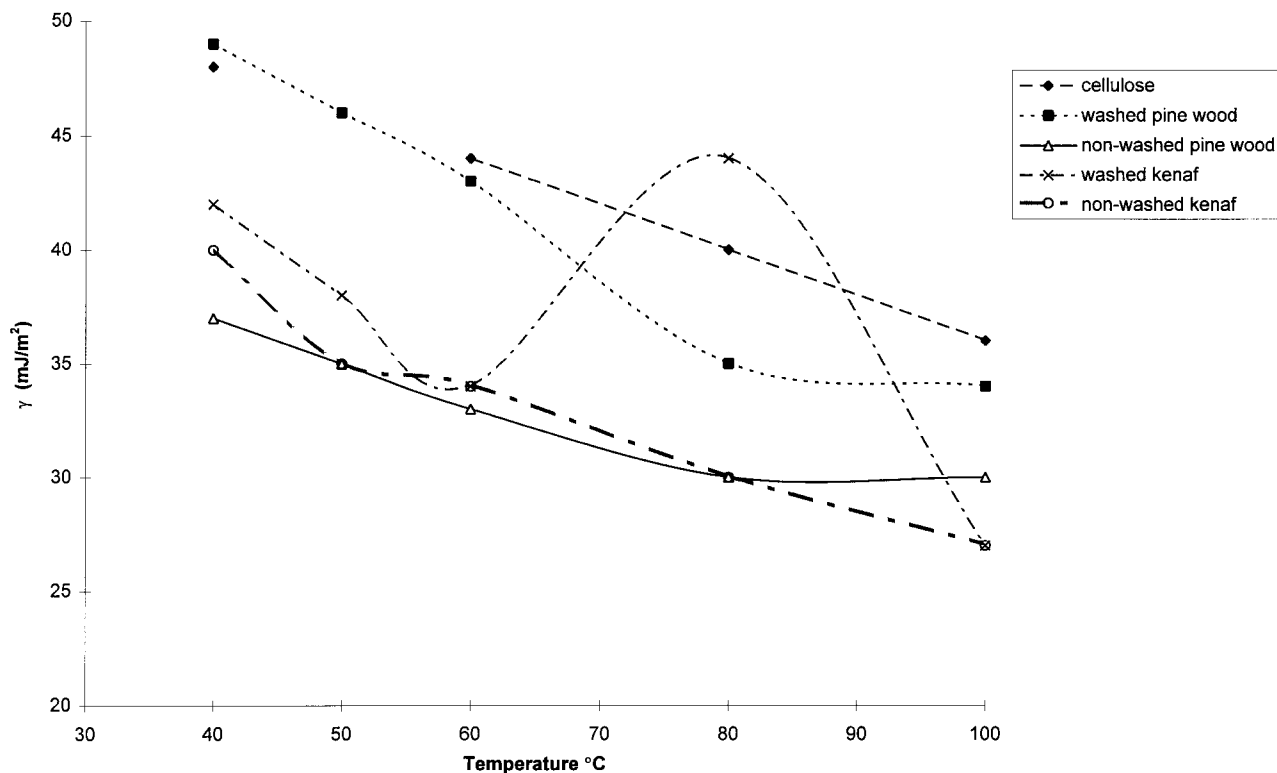


Figure 1 Plots of γ_s^D as a function of temperature for cellulose, washed pine wood, washed kenaf, nonwashed pine wood, and nonwashed kenaf particles.

base interaction between cellulose and the carbon tetrachloride probe is not favorable to adsorption. Considering that carbon tetrachloride is acidic ($AN = 8.6$) and the cellulose substrate used in this study was found to have an acidic characteristic ($K_A = 0.24$), this result is not surprising. Kamdem and associates¹² also reported a negative acid–base free energy of desorption for carbon tetrachloride on extracted birch wood meal.

Plots of $\Delta H^{AB}/DN$ as a Function of DN/AN

Plots of $\Delta H^{AB}/AN$ as a function of DN/AN for the test substrates used in this study were almost linear, as shown in Figure 2. Qualitatively, the nonwashed wood particles showed relatively lower acid–base characteristics than did washed wood and cellulose. A similar trend was observed in the case of nonwashed kenaf compared with washed kenaf and cellulose. Chtourou and co-workers¹³ obtained similar results in their study of polyethylene pulp and wood pulp fibers.

Acid–Base Parameters K_A and K_D

The K_A and K_D values for the respective substrates were estimated from the slope and inter-

cept of the respective linear regression lines of $\Delta H^{AB}/AN$ as a function of DN/AN . These values are summarized in Table V. The K_A and K_D values for the cellulose particles used in this study compare favorably with those calculated from Berg's data for Whatman CF1 cellulose powder.¹

The washed pine wood and washed kenaf particles showed an amphoteric surface characteristic. The nonwashed wood particles had relatively no acid–base characteristics, and the nonwashed kenaf particles showed a predominantly basic characteristic. This suggests that the surfaces of nonwashed pine wood and nonwashed kenaf particles were enriched by different classes of extractives. In the case of the pine wood, these surface extractives may be predominantly waxes, and in kenaf they may be predominantly triglycerides. The waxes would be expected to have no acid–base characteristics, whereas the triglycerides would be expected to show a relatively pronounced basic characteristic.

CONCLUSIONS

The results of this study indicate that the surfaces of washed pine wood and kenaf particles are am-

Table III Free Energy of Desorption, ΔG^{AB} , of the Acid–Base Probes at Different Temperatures for Cellulose, Wood, and Kenaf Particles

Substrate/Probe	ΔG^{AB} (kJ/mol)				
	40°C	50°C	60°C	80°C	100°C
Cellulose					
Carbon tetrachloride	−1.51	^a	−1.46	−1.34	−1.32
Chloroform	1.74	^a	1.67	1.37	1.36
Diethyl ether	6.96	^a	6.13	5.28	4.61
Ethyl acetate	10.90	^a	10.03	9.44	8.78
Washed wood					
Chloroform	3.24	3.13	3.08	2.67	3.15
Diethyl ether	5.61	5.24	4.82	4.00	4.26
Ethyl acetate	10.66	10.22	9.78	8.79	9.05
Washed kenaf					
Chloroform	4.15	3.81	3.55	4.39	3.46
Diethyl ether	4.91	4.40	3.46	4.43	2.06
Ethyl acetate	10.93	10.18	9.47	10.63	8.93
Nonwashed wood					
Chloroform	2.44	2.44	2.44	2.53	2.99
Diethyl ether	1.49	1.53	1.48	1.46	1.25
Ethyl acetate	4.34	4.25	4.16	4.20	4.73
Nonwashed kenaf					
Chloroform	3.57	3.31	3.09	2.99	2.89
Diethyl ether	2.20	1.89	1.30	1.49	2.08
Ethyl acetate	7.60	6.78	6.19	5.53	4.69

^a Measurement not taken.

photic in character, with a relatively greater capacity to accept electrons. Kamdem and associates¹² reached a similar conclusion with respect to extracted wood meal from white birch wood. The surface acid–base characteristics of the nonwashed substrates is determined by the chemistry of the extractives that cover the surface. The nonwashed pine wood powder surface, for example, was covered by neutral substances, most likely waxes. On the contrary, the nonwashed kenaf

powder surface appears to have been covered with substances that had a pronounced basic character, very likely triglycerides.

The cellulose powder surface showed a predominantly acidic character, with K_A and K_D values of 0.24 and 0.01, respectively. These values appear to be consistent with the molecular structure of cellulose, where the hydrogen atoms in the hydroxyl groups act as electron acceptors and the oxygen atoms in the glycoside linkages and hy-

Table IV Enthalpy of Desorption, ΔH^{AB} , for Cellulose, Wood, and Kenaf Particles

Probe	ΔH^{AB} (kJ/mol)				
	Cellulose	Washed Wood	Washed Kenaf	Nonwashed Wood	Nonwashed Kenaf
Chloroform	4	4	5	0	7
Carbon tetrachloride	−3	^a	^a	^a	^a
Diethyl ether	19	14	16	3	3
Ethyl acetate	22	20	21	3	22

^a Measurement not taken.

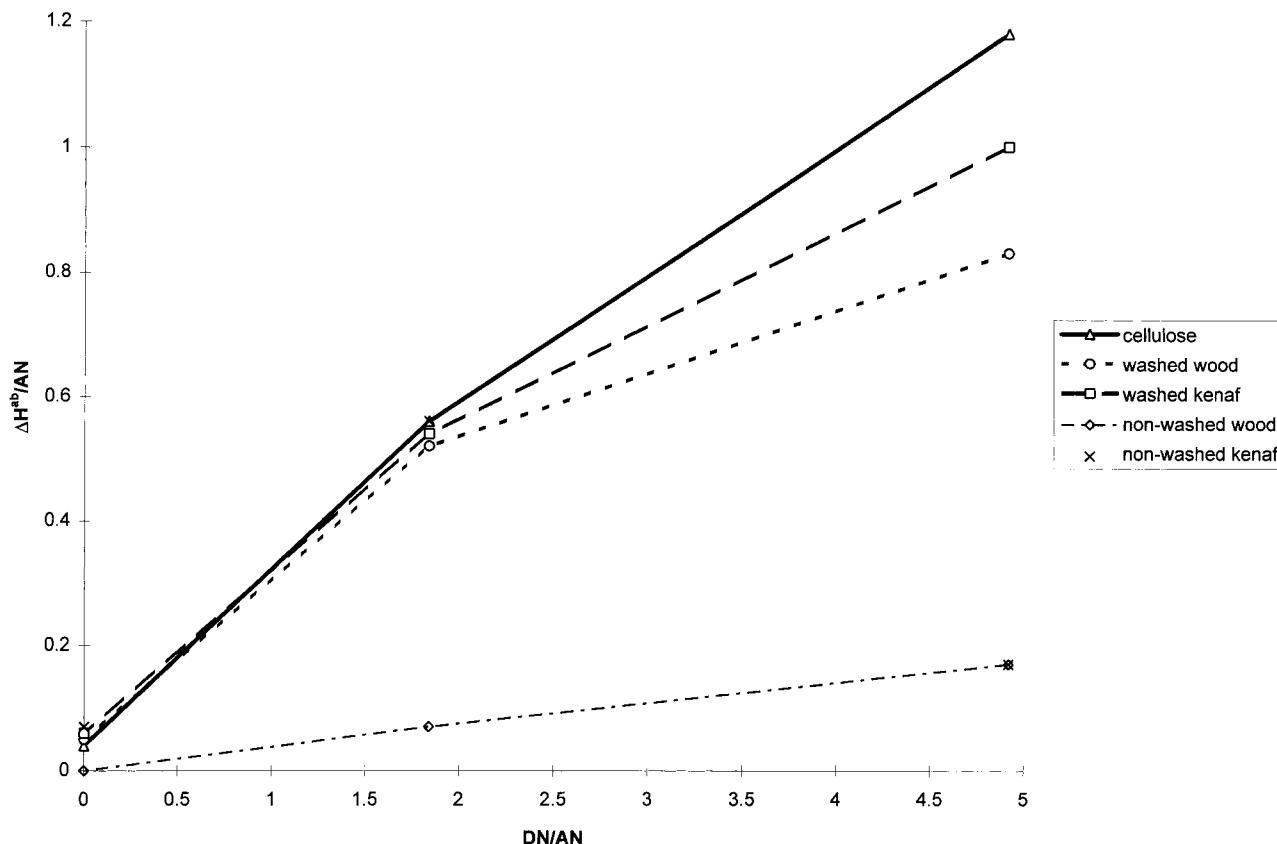


Figure 2 Plots of $\Delta H^{AB}/DN$ as a function of AN/DN for cellulose, washed pine wood, washed kenaf, nonwashed pine wood, and nonwashed kenaf particles.

droxyl groups act as electron donors. The relatively high K_A value indicates a surface that is rich in hydroxyl groups. Felix and Gatenholm¹⁴ reported almost similar acid–base behavior for cellulose fiber treated with alkenyl succinic anhydride.

The removal of extractives by treatment with toluene/ethanol had the effect of increasing the dispersive component of the surface energy of the

pine wood and kenaf particles. Indeed, when a sample of the nonwashed pine wood particles was partitioned in a diethyl ether/water solvent system, the wood particles remained at the diethyl ether/water interface. By contrast, a sample of the washed wood particles partitioned completely into the aqueous layer, similarly to the cellulose particles.

These results are of special practical importance because surface acid–base interactions may be implicated in the adhesion of coatings and finishes to wood and other lignocellulosic substrates. Fowkes¹⁵ and Fowkes and Mostafa¹⁶ demonstrated that to be true for the adsorption of model acidic and basic polymers on model acidic and basic inorganic substrates, silica and calcium carbonate, respectively. These findings illustrated that adsorption occurred only when there was an exothermic interfacial acid–base interaction.

Table V Surface Acid–Base Characteristics, K_A and K_D , for Cellulose, Wood, and Kenaf Particles

Material	K_A	K_D
Cellulose	0.24	0.01
Whatman CF1 cellulose	0.39 ^a	−0.02 ^a
Washed wood	0.15	0.11
Washed kenaf	0.18	0.11
Nonwashed wood	0.03	0
Nonwashed kenaf	0	0.26

^a Values calculated from Berg's data.¹

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