Alcohol Adsorption on Softwood Lignin from Aqueous Solutions

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Lignin prepared by acid and enzyme hydrolysis of a softwood mixture adsors acetone, butanol, and other alcohols while showing only a slight uptake of glucose. Adsorption of butanol is independent of temperature in the range of 30-65°C. The Polanyi theory fits adsorption for the linear alcohols methanol through hexanol with values of ΔS and ΔH ranging from 2.6 to 26 J mol⁻¹ K⁻¹ and -0.6 to -8 kJ/mol. The adsorption capacity is given by Q (g alcohol/g lignin) = Kc*, where c* is the equilibrium alcohol concentration (g/mL), K = eφ exp(ΔS/RT), and eφ is the porosity of the lignin (0.23–0.42 mL/g). The value of the adsorption capacity constant K for n-butanol ranges from 1.3 to 2.7 mL/g on sorbent containing 26–72% lignin, while ethanol is 0.5–0.73, acetone is 0.62–1.0, and glucose is 0.39. Adsorption is shown to occur through combined hydrophobic and hydrophilic interactions of the alkyl and hydroxyl groups, respectively, of the adsorbate and the lignin. Consequently, for the alcohols methanol to hexanol, we present the capacity constant K = K(ΔH) + K(ΔS) as a sum of an alkyl adsorption constant (0.1–9.5 mL/g) and a hydrophobic (0.40–0.50 mL/g) contribution. This approach may be applicable to organic acids. Lignin's sorbent properties have potential to moderate product inhibition in the anaerobic acetone–butanol–ethanol (ABE) fermentation.

INTRODUCTION

Butanol fermentations are carried out under anaerobic conditions with Clostridium spp. Before 1970, butanol produced by fermentation was a major source of the alcohol in the United States. As synthetic routes were developed for producing butanol from petroleum, fermentation processes were abandoned. However, a recent analysis has suggested that if production costs of fermentation butanol can be reduced, fermentation routes using Clostridium acetobutylicum may once again be potentially competitive with rhodium-catalyzed petroleum routes based on hydroformylation of butanol from propylene. The current U.S. markets for butanol and acetone are 800 million and 1.6 billion lbs/year, respectively. The values of these products are $0.10 and $0.24 per pound, respectively ($0.66 and $0.53/kg). Because of their price and volume, butanol and acetone are considered commodities, and profitabilities are particularly sensitive to incremental changes in production costs.

Butanol is not only a product of the anaerobic C. acetobutylicum fermentation, but also the major toxic substance responsible for bringing a premature end to the fermentation at a concentration of ca. 1.5%.* It appears that butanol tolerance can be enhanced by manipulating the cell membrane's fatty acid composition. Even so, the solvent concentrations that are possible (2–3%) would still be relatively low in the context of a commercial plant. Consequently, large improvements in recovery efficiency during fermentation are needed. Simultaneous benefits include (1) recovery of butanol, (2) higher fermentation productivity, and (3) reduced downstream separation costs.

The removal of strongly inhibitory butanol from the fermentation broth will improve the productivity of the acetone–butanol–ethanol (ABE) fermentation. The major methods used for removing butanol are liquid–liquid extraction and adsorption on sorbents. Previous non-bioactive solvents tested for liquid–liquid extraction include oleyl alcohol (adsorption capacity constant K = 2–4 mL/g), polyoxyalkylene (K = 1.5–3), dibutyl phthalate (K = 1.4), inlagnolated hydrocarbon (K < 1), and freon 113 (K = 0.1). AdSORption on sorbents for adsorption of butanol from fermentation broths and pure solutions were activated carbons (K = 20), silicatite and various polymers (such as hydrophobic, cross-linked polysyrereen, cross-linked acrylic ester resin, copolymers of divinylbenzene, and styrene) (K = 2–5). To the best of our knowledge, lignin derived from biomass has not been reported as a sorbent for removing alcohol inhibitors during fermentation.

Lignin is a complex polymeric network formed by dehydrogenation of a mixture of p-hydroxycinnamyl alcohols (i.e., p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol). The hydroxyl groups, ether groups, carboxyl groups, and benzyl groups can form hydrogen bonds with the hydroxyl groups of alcohols resulting in hydrophilic interactions. The alkyl and aromatic parts of lignin can interact with the alkyl groups of alcohols through van der Waals forces (i.e., hydrophobic interac-

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tions). Thus, the chemical structure of lignin is consistent with alcohol sorption properties observed in this work.

Lignin is also a relatively inexpensive material that occurs as a significant by-product from biomass processing. Its fuel value (based on Btu content) is about 2.5–4 cents/lb. If only 10% of the available cellulosic biomass is converted to oxygenated chemicals through bioconversion processes, an estimated additional 10 billion lbs/yr of by-product lignin could be produced.\(^6\) Lignin would be readily available in large quantities at the point of use as a by-product of a biomass conversion process for producing butanol. This work shows that lignin will adsorb butanol and ethanol from dilute aqueous solution. This is important since a typical ABE fermentation with \textit{C. acetobutylicum} yields butanol–acetone–ethanol at a molar ratio of ca. 8:3.7:1 and butanol strongly inhibits the formation of concentrations of 1–1.5\%.\(^6\)

**EXPERIMENTAL**

**Sorbents**

Four different sorbents, three with increasing levels of lignin content, were used for this research. These were gin motes, wood shavings, acid-hydrolyzed shavings, and acid/enzyme-hydrolyzed shavings.

**Gin Motes**

A gin mote is a type of cotton fiber, which was supplied by Cotton Incorporated (Raleigh, NC). It was used as a representative sorbent which contained no lignin.

**Wood Shavings**

Shavings of a softwood mixture of yellow poplar, tulip poplar, and tulip tree were supplied by the Forestry Department of Purdue University (West Lafayette, IN). The wood mixture contained 28.9% (w/w) of lignin and was tested as a sorbent as well as being processed further to obtain sorbents containing a higher lignin content.

**20% H\textsubscript{2}SO\textsubscript{4} (w/v) Treated Wood Shavings**

This lignocellulose material, containing 25.9% lignin, was obtained by hydrolyzing the wood shavings in 500 mL 20% H\textsubscript{2}SO\textsubscript{4} under reflux for 4 h with a liquid-to-wood ratio of 40:1 in a 1-L, round-bottomed flask. After hydrolysis, the remaining solid was filtered and washed with deionized water until neutral. The hydrolysis under reflux resulted in a 40% weight loss and gave a lignocellulose containing 25.9% lignin. This procedure was similar to the one developed previously for corn residue.\(^7\)

**Acid/Enzyme-Treated Wood**

Acid hydrolysis followed by enzyme hydrolysis gave a lignocellulose containing 72% lignin. After hydrolysis in 20% H\textsubscript{2}SO\textsubscript{4}, the lignocellulose was washed with 2 L distilled water until neutral. The material was resuspended in 2 L of 40 mM acetate buffer at pH 4.8 containing cellulase (Cellulase 150L, a gift from Genencor, San Francisco, CA). The initial liquid-to-solid ratio was 10:1 with hydrolysis carried out for 4 days in an agitated 2-L beaker. The remaining solids were then boiled in water for an hour and washed with 2 M NaCl and then water to wash away the glucose and other hydrolyzed substances as well as the enzymes. The material was then resuspended in 2 L of fresh buffer solution containing cellulase, and hydrolysis was again carried out for 4 days. Four such enzyme treatments were performed in 16 days until the cellulose hydrolysis ceased. The cellulose hydrolysis process was monitored by periodically sampling the hydrolysis mixture, centrifuging down the solids, and measuring the glucose content in the liquid phase with a Beckman Glucose Analyzer 2 (Creve Coeur, MO). The final solid product contained 72.0% lignin. A summary of the hydrolysis time course is shown in Figure 1.

All four sorbents were ground to pass a 40-mesh screen and washed with water in Soxhlet extraction apparatus until water-soluble color was no longer evident. The remaining solids were then air dried at 105°C overnight. The lignin content of the sorbents was determined by the permanganate method.\(^8\) The densities of these materials were measured gravimetrically based on dry weight packed into a 24.5-mL volume corrected for extraparticle void volume. The densities were 0.80 and 0.85 g/mL for 26 and 72% lignin, respectively.

**Determination of Alcohol Concentration**

Characteristics of the alcohols and organic components examined in this work are summarized in Table 1. The methanol, \(n\)-propanol, \(n\)-butanol, \(n\)-pentanol, \(iso\)-butanol, sec-butanol, and tert-butanol were certified grade from Fisher Scientific, the ethanol used was 100 proof from Midwest Grain, the \(n\)-hexanol was 99+ % from Aldrich Chemical, and the acetone was Chrom AR grade from Mallinckrodt. The concentrations of alcohol solutions in

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**Figure 1.** Fractional conversion of cellulose (20% H\textsubscript{2}SO\textsubscript{4}-treated softwood) to glucose by enzyme hydrolysis (I, II, III, IV represent four enzyme treatments).
the adsorption studies were determined quantitatively by a differential refractometer (Refractometer Model 1037, Milton Roy, Riviera, FL). The detection system, shown in Figure 2(a), consisted of a liquid chromatograph in which the column was replaced with a zero dead-volume fitting. Since the dead volume between the injector and the refractive index detector was very small, the peak was very sharp, and alcohol concentration was proportional to the height of the peak. The linear relation between peak height and alcohol concentration gave a correlation coefficient of 0.999.

**Packing of Sorbents into Liquid Chromatography Columns**

The sorbent was packed into the column as a dry powder using a standard tap/fill procedure for chromatography. The sorbent was dried at 105°C to a constant weight and weighed. After packing, the remaining sorbent was weighed again. The weight of the sorbent packed was calculated from that weight change. The properties of the columns used are summarized in Table I. The columns were evaluated in a typical liquid chromatography (LC) apparatus [illustrated in Fig. 2(b)].

**Liquid Chromatography: Relation of Peak Retention to Equilibrium**

The void volume external to the sorbent, $V_e$, was determined from the retention volume of the large molecules of dextran (molecular weight of $5\times10^4$). The internal void volume, $V_i$, of the sorbents was based on the difference between the elution volume of NaCl (a small, included solute) and external void volume, $V_e$.

$$V_i = V_{NaCl} - V_e \quad (1)$$

![Image](image_url)  
Figure 2. Schematic diagram of liquid chromatography system (a) alcohol detection system and (b) adsorption measurement system.
The relation between the retention volume, \( V_r \), of a solute which penetrates the sorbent and effective mobile phase solute concentration, \( C^* \), is

\[
Q = \frac{V_r - V_0}{W} C^* \tag{2}
\]

where

\( Q = \text{mmoles (or mg) of alcohol which penetrates and/or adsorbs on 1 g sorbent} \)

\( W = \text{the weight of the total sorbent in the column (g)} \)

\( C^* = \text{effective solute concentration of the adsorbate in the mobile phase (mols/L or g/L) = } \frac{C_v V_{eq}}{V_{eq}} \)

with

\( V_{eq} = \text{sample volume injected (mL)} \)

\( V_0 = \text{peak volume eluted (mL)} \)

\( C_v = \text{initial concentration of injected sample (mM/L)} \)

Peak broadening (i.e., dispersion) occurs throughout the length of the column, and consequently the use of the outlet concentration to represent \( C^* \) could be an approximation. However, given the dilution which occurs, the adsorbate–sorbent equilibrium concentration curve was assumed to fall within a linear range. This was later proven to be true using batch equilibrium experiments. Therefore, eq. (2) can also be written as

\[
K = \frac{Q}{C^*} \tag{3}
\]

where \( K = (V_r - V_0)/W \text{ (mL/g).} \) A pulse injection of alcohol solution (20 \( \mu \text{L} \)) was found to be diluted in the column by up to 100 times. The value of \( K \) was a constant, as would be expected at low solute concentration. Batch equilibrium studies showed the equilibrium to be linear up to the highest concentration examined in this work, which was 20 \( \text{g/L} \).

### Determination of Void Fractions and Porosity

Void fraction, external to the stationary phase, was determined using dextran having a molecular weight range of 5–40 million daltons. Internal void fraction was based on retention volumes of NaCl [see eq. (1)]. Void fraction \( \varepsilon \) is defined as the ratio of \( V_i \) to \( V_0 \) to the total column volume. Table II gives values of \( \varepsilon \) for the various materials used in this study.

Porosity \( \kappa \) is based on the dry weight of sorbent packed into the column (Table II) and is the ratio of \( V_i \) to the dry weight packed. Since the porosity gives an indication of the inherent pore volume on a weight basis, it also reflects accessibility of the lignin to the adsorbate.

### Batch Adsorption Experiments

Batch equilibria were initially carried out using 0.5 g of 105°C air-dried sorbent. The sorbent was mixed with 10 mL water in a 25-mL Erlenmeyer flask (sealed with a rubber stopper) and allowed to equilibrate for 1 h at the temperature of the run. Then 10 mL of the alcohol solution was added and mixed with the aqueous lignin slurry to give concentrations ranging from 0.3 up to 20 g/L of butanol. The adsorption temperature was maintained for 20 h in a water bath with the sample subjected to intermittent shaking. After incubation the sample was centrifuged to obtain a clarified supernatant which was analyzed for alcohol concentration as described above.

Each adsorption equilibrium curve was plotted from measurements for 15–18 concentrations with three replicate runs made at each concentration. The calculation of the alcohol adsorbed based on \( C^* \), the equilibrium concentration, requires that a correction be made for the concentration change caused by water uptake by the initially dry sorbent. When a liquid–sorbent ratio of 40 mL/g was used in the batch adsorption studies, the change in the free liquid volume is small. Therefore, the measured alcohol con-
concentration is within 2% of the "true" alcohol concentration at equilibrium, corrected for water uptake in the pores of the lignin. The value of Q is

\[ Q = (C_0 - C^*)/C_* \]  

where \( C_* \) represents the sorbent concentration in terms of grams per milliliter.

Figure 3 compares a typical butanol batch adsorption isotherm obtained at a liquid–sorbent ratio of 40 mL/g (\( C_* = 0.025 \)) with that obtained at a liquid–sorbent ratio of 5 (\( C_* = 0.2 \)). Statistical analysis of the data showed experimental error could be as high as ±40% for an individual measurement at \( C_* = 0.025 \). Consequently, if analyses are carried out at this dilution, approximately 50 data points are needed for each curve. Statistical error was decreased to ±5.5% by increasing \( C_* \) and using the internal void volume obtained from column chromatography [eq. (1)] to correct for water uptake. When the liquid volume is at 5 mL/g, the concentration change due to the water adsorption must be corrected for when an initially dry sorbent is used. For example, the internal void volume of the acid-hydrolyzed shavings (25.9% lignin) is 2.76 mL by eq. (1) (12.03 – 9.27). The dry weight of the sorbent packed was 11.99 g and gave a porosity of 2.76 mL/11.99 g = 0.23 mL/g. Correction of the calculated final solute concentration for a water uptake equivalent to 0.23 mL/g gave data which coincided with the data obtained with the liquid–sorbent ratio of 40 mL/g [Fig. 3(a)]. Statistical analysis of the two sets of data also showed that the two groups of data were the same (case a in Table III).

The adjustment of water adsorption is very important at values of \( C_* > 0.10 \). If the observed concentrations were used directly without adjustment, the apparent extent of adsorption will be lower than the alcohol actually taken up by a wet lignin containing sorbent. Comparison of the adjusted and the observed data (without adjustment) is given in Figure 3(b) and Table III (case b). Statistically significant differences existed between them, which meant that consideration of water batch adsorption was necessary for the adsorption studies using low liquid–sorbent ratio.

**Breakthrough Studies**

Breakthrough profiles were generated for 25.9% lignin sorbent using the same LC apparatus. In this case, however, the alcohol–water solution was used as the eluent. Fractions of the eluent were collected and the alcohol concentration was determined by the method described above.

Alcohol concentration as a function of elution volume gave a symmetrical elution profile (Fig. 4). Given concentration \( C \) as a function of volume \( V \),

\[ C = f(V) \]  

the adsorption relation is given by

\[ Q = \left( \frac{V_e - V_i}{V_e} \right) \times C_0 - \int_{V_i}^{V_e} f(v) dv \]  

\[ W \]  

where

\[ Q = \text{solute adsorbed per unit weight of sorbent} \]

\[ V_e = \text{elution volume at the point where the alcohol concentration in the effluent equals the inlet concentration } C_0 \]

Figure 4 indicates that \( C_{1/2} = C_0/2 \). For a symmetrical curve, the areas \( A_{1/2} \) and \( A_1 \) will be equal, and eq. (6) is

\[ Q = \left( V_{e_1/2} - V_i \right) \times C_0/W \]

where \( V_{e_1/2} \) is the retention volume which coincides with \( C_{1/2} \). The breakthrough curves were all approximately symmetrical, and therefore, eq. (7) was used for different initial alcohol concentrations to obtain corresponding values of \( Q_e \), and which were then used to generate the adsorption isotherms.

**Comparison of Batch Equilibria, LC Retention, and Breakthrough Data**

The equilibrium data for butanol obtained by batch experiments correlated with peak retention and breakthrough ex-
Table III. Statistical analysis of the similarity between batch adsorption data obtained from different methods.

<table>
<thead>
<tr>
<th>Statistics</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slopes ($\beta_0, \beta_n$)</td>
<td>(0.16030)</td>
<td>(0.21926)</td>
<td>(0.40798)</td>
<td>(-0.18697)</td>
</tr>
<tr>
<td>Intercept ((b_0))</td>
<td>(0.00014)</td>
<td>(0.00003)</td>
<td>(-0.02714)</td>
<td>(-0.00606)</td>
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<tr>
<td>Type III SS (F(\beta_0, b_0))</td>
<td>(0.33)</td>
<td>(0.52)</td>
<td>(0.99)</td>
<td>(-0.33)</td>
</tr>
<tr>
<td>Type III SS (F(\beta_n, b_n))</td>
<td>(0.15)</td>
<td>(0.00)</td>
<td>(-1.3)</td>
<td>(-0.24)</td>
</tr>
<tr>
<td>Type III SS (P(F &gt; F))</td>
<td>(0.7476)</td>
<td>(0.6157)</td>
<td>(0.3878)</td>
<td>(0.7485)</td>
</tr>
<tr>
<td>Type III SS (P(F &gt; F))</td>
<td>(0.8822)</td>
<td>(0.9989)</td>
<td>(0.2356)</td>
<td>(0.8842)</td>
</tr>
<tr>
<td>Interpretation</td>
<td>Insignificant, slopes are the same</td>
<td>Insignificant, slopes are the same</td>
<td>Insignificant, slopes are the same</td>
<td>Insignificant, slopes are the same</td>
</tr>
<tr>
<td>Intercepts ((b_0))</td>
<td>4.88753</td>
<td>16.09216</td>
<td>0.57532</td>
<td>3.13412</td>
</tr>
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<td>Type III SS (P(\beta_0, b_0))</td>
<td>1.39</td>
<td>8.20</td>
<td>0.26</td>
<td>1.34</td>
</tr>
<tr>
<td>Type III SS (P(\beta_n, b_n))</td>
<td>0.2478</td>
<td>0.0164</td>
<td>0.5694</td>
<td>0.2716</td>
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<td>Significant, intercepts are different</td>
<td>Insignificant, intercepts are the same</td>
<td>Insignificant, intercepts are the same</td>
</tr>
<tr>
<td>Conclusions</td>
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<td>1 and 2 are different</td>
<td>No difference between 1 and 2</td>
<td>No difference between 1 and 2</td>
</tr>
</tbody>
</table>

Columns a, comparison of batch adsorption data from \(C_i = 0.025\ (g/mL)\) (1) with that from \(C_i = 0.200\ (g/mL)\) (2) with water sorption adjustment.

Column b, comparison of batch adsorption data from \(C_i = 0.200\ (g/mL)\) with (1) and without (2) water sorption adjustment. Column c, comparison of batch adsorption data (1) with breakthrough data (2). Column d, comparison of adsorption data at \(30^\circ\)C (1) with that at \(60^\circ\)C (2).

![Figure 4. The breakthrough curve of liquid chromatography (1.00 g/L broth through 25.9% lignin sorbent column; column dimension of 1.27 cm i.d. x 44 cm long)](image)

Experiments (Fig. 5). The solid line, obtained from retention time data and equation (3) \((K = 1.26 mL/g)\), coincided with data from batch adsorption experiments (diamonds) and from breakthrough curves (squares). Table III summarizes the statistical analysis which further supports the conclusion that the breakthrough and batch adsorption results are the same.

**Statistical Models Used for Evaluating the Similarity of Different Groups of Experimental Data**

The general equation can be used to fit experimental data\(^{15}\) for purposes of detecting differences in the data on a statistical basis:

\[
Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \cdots + \beta_n X_n
\]

(8)

For our data, \(n = 2\) was found to fit the experimental data for comparing two groups of data \((i.e., \ i = 1, 2)\).

If two groups of data were the same or followed the same distribution, then

\[
\beta_0 = \beta_0, \quad \beta_1 = \beta_1, \quad \text{and} \quad \beta_n = \beta_n
\]

(9)

First, the coefficients of all \(X^n\) terms (slope terms) were compared. If they were not all equal, the data sets were not equal. If they were all equal, there were two possibilities:

A. they followed the same distribution or

YANG, LADISCH, AND LADISCH: ALCOHOL ADSORPTION ON SOFTWOOD LIGNIN 273
B. they did not follow the same distribution, but they were parallel.

Then, $\beta_4$ were tested. If the values $\beta_4$ were also equal, these data sets were believed to follow the same distribution. Consequently, the general linear model (GLM) was chosen to fit the data and was given by the equation

$$Y_i = \beta_0 + \beta_1 X_{i1} + \beta_2 X_{i2} + \varepsilon_i$$  \hspace{1cm} (10)

where $i$ denotes the group (two groups were compared, $i = 1, 2$), and $j$ was the $j$th observation within the group. The hypothesis test for the slopes were $H_0: \beta_{11} = \beta_{12}$, $H_1: \beta_{11} \neq \beta_{12}$. Not all these equalities were true. The further hypothesis test for the intercepts were

$$H_0: \beta_{21} = \beta_{22}$$
$$H_1: \beta_{21} \neq \beta_{22}$$

The comparison of the low liquid-sorbent ratio butanol adsorption data obtained with and without water adsorption adjustment could be used as an example (case b in Table II). First, the slopes $\beta_1$ and $\beta_2$ were compared; $i = 1$ are the adjusted data, $i = 2$ are the data without adjustment. The $T$-test showed that the probability $P = 0.6157$ for $\beta_{11}$ and $\beta_{12}$; $P = 0.9889$ for $\beta_{21}$ and $\beta_{22}$. Both of them are much greater than $\alpha = 0.05$. Thus, the null hypothesis ($H_0$) should be accepted. In other words $\beta_1 = \beta_{21}, \beta_2 = \beta_{22}$. But this only proved that these two data sets were parallel. The intercept term $\beta_0$ should also be examined to certify the coincidence of these two groups of data by the $T$-test. Since $P = 0.0164 < 0.05$, the intercepts are not the same. This confirms the need to correct adsorption with respect to water uptake when $C_a > 0.10$.

RESULTS AND DISCUSSION

Butanol adsorption at 30°C on gin mottes (0% lignin), wood (28.9% lignin), acid-hydrolyzed wood (25.9% lignin), and acid/enzyme-hydrolyzed wood (72% lignin) is linear with respect to butanol concentration (Fig. 6). Furthermore, $K$ correlates with lignin content except for untreated wood [Fig. 7(a)] which had more lignin (28.9%) than the acid-treated wood (25.9% lignin) but a lower adsorption of butanol (Fig. 6). A probable explanation is based on the lower porosity of native wood ($\varepsilon_a = 0.19 \text{ mL/g}$) relative to treated wood ($\varepsilon_a = 0.23$) and, therefore, a lower fraction of exposed lignin and less adsorption. Extrapolation of the line in Figure 7(a) gave the adsorption capacity for pure lignin at $K = 3.65 \text{ mL/g}$. The equilibria of other linear alcohols were determined for gin mottes (i.e., 0% lignin), acid-hydrolyzed wood (25.9% lignin), and acid/enzyme-hydrolyzed wood (72% lignin). The resulting values of the equilibrium constant $K$ also appear to follow a linear relationship [Fig. 7(b)]. Adsorption capacity increases with increasing molecular weight of the linear alcohols and increasing lignin content.

In comparison the adsorption of glucose is slight for all of the sorbents studied with an adsorption capacity constant K of 0.35 ± 0.02 mL/g. This means that the affinity of glucose for lignin is one-tenth that of butanol.

Influence of Temperature on Butanol Adsorption

The adsorption isotherm for butanol at 65°C is statistically the same as that at 30°C (Fig. 8 and Table III, case d). This suggests the following interpretation based on the change of chemical potential, $\Delta \mu$:

$$\Delta \mu = -RT \ln K_a$$  \hspace{1cm} (11)

where $K_a$ is an equilibrium constant, $R$ is the gas law constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$), and $T$ is the absolute temperature (K). In an analogy to the Gibbs-Helmholtz equation for free energy, $G$, the chemical potential, can be expressed in terms of heat of adsorption by
$$\frac{\partial (\Delta \mu / T)}{\partial T} = -\frac{\Delta H}{T^2}$$  \hspace{1cm} (12)

At constant pressure, eqs. (11) and (12) give

$$\left(\frac{\partial \ln K_s}{\partial T}\right)_P = \frac{\Delta H}{RT^2}$$  \hspace{1cm} (13)

If the adsorption is endothermic, i.e., $\Delta H > 0$, the value of $K_s$ and adsorption will increase with the increase of temperature. It is also well known that if the adsorption occurs, then

$$\Delta \mu = \Delta H - T \Delta S < 0$$  \hspace{1cm} (14)

For the adsorption in the gas phase $\Delta S < 0$, and equation (14) must have a negative value for $\Delta H$. Adsorption will be exothermic and decrease with increasing temperature.

The adsorption from a liquid solution is more complex. An entropy change of the solution is a function of both solute and solvent, which in some cases gives $\Delta S > 0$. Since the adsorption of butanol on the 25.9% lignin sorbent did not change when the temperature increased from 30 to 65°C, then $K_s$ is constant. Therefore,

$$\left(\frac{\partial \ln K_s}{\partial T}\right)_P = \frac{\Delta H}{RT^2} = 0$$  \hspace{1cm} (15)

This implies $\Delta H = 0$, and thus $\Delta \mu = -T \Delta S$ and equation (11) becomes

$$\ln K_s = \Delta S/R$$  \hspace{1cm} (16)

On this basis we conclude that adsorption of butanol on lignin reflects an entropy change. This hypothesis was further examined by determining adsorption properties of other alcohols, by measuring retention volumes of aliphatic alcohols from methanol to hexanol. This data and equation (3) gave values of $K_r$ which were plotted against the molecular weight of the alkyl parts of the alcohols [MW(R) = MW - 17]. The value 17 represents the molecular weight of an OH group. A hypothetical $K$ value at MW(R) → 0 was obtained by extrapolation and is referred to as $K(\text{OH})$, the capacity constant for a hydroxyl group (Fig. 9). For 72.0% lignin, $K(\text{OH}) = 0.45$ mL/g, and for 25.9% lignin and gin mutes, $K(\text{OH}) = 0.40$ mL/g. Since lignin is structurally very different from cellulose, some difference would be expected.

The data for cellulose (gin mutes) with respect to the alcohols methtanol through butanol show a small and consistent value of $K$ (Fig. 9). This suggests alcohol-celullosic adsorption arises from hydrogen bonding from —OH groups since there was no change in adsorption with increasing molecular weight, MW(R). In comparison, the value of MW(R) significantly affects alcohol adsorption on lignin due to hydrophobic interaction, i.e., van der Waals forces. Hence, we chose to represent the value of the adsorption capacity constant $K$ in terms of a hydrophilic and hydrophobic constant:

$$K = K(\text{OH}) + K(R)$$  \hspace{1cm} (17)

YANG, LADISCH, AND LADISCH: ALCOHOL ADSORPTION ON SOFTWOOD LIGNIN 275
were calculated from equation (20) and shown to fit experimental data obtained at 30°C [Fig. 11(a)]. For 25.9% lignin sorbent, the constants in eqs. (19) and (20) are
\[\gamma = \exp A = 0.0136 \quad B = 0.0550 \quad K(\text{OH}) = 0.40\]
and for 72.0% lignin sorbent, these are
\[\gamma = 0.0425 \quad B = 0.0508 \quad K(\text{OH}) = 0.45\]
where the values of \(A\) and \(B\) are the intercept and slope, respectively, of the lines in Figure 10. Equation (20) is convenient for calculating the alcohol adsorption \(Q\) as a function of the volume of the alkyl group, \(V_v(R)\). The adsorption of different alcohols is calculated by substituting their van der Waals volume (see Table I) into eq. (20). There is satisfactory agreement between calculated values and the experimental data [Fig. 11(b)]. The value of \(K(\text{OH})\) was from 0.40 to 0.50 in equation (20) depending on the content of lignin within the sorbents. The error of using an average
value of $K(\text{OH}) = 0.45$ is small (±5%) given the large value of the exponential term, especially when the alkyl group is large.

**Application of Polanyi Theory**

According to Polanyi adsorption potential theory, the adsorption from solution reflects condensation of adsorbate from the solution into the voids of sorbent. The volumetric concentration inside the sorbent, $Q_{\text{ads}}$, is calculated as

$$Q_{\text{ads}} = \frac{Q (\text{mmol/g})}{v (\text{mL/g})}$$  \hspace{1cm} (21)

This definition applied as long as the adsorbate is small enough to penetrate the pores, as is the case here. If the adsorbate is too large and hence excluded, this interpretation is not valid. For dilute solutions, the equilibrium constant $K_e$ is given by

$$K_e = \frac{K}{{v_e}} = \frac{[K(\text{R}) + K(\text{OH})]}{v_e}$$  \hspace{1cm} (22)

This approach is similar to one proposed by Vickenstaff, who first applied physical chemistry to dyeing, as well as Brandt et al., who used the idea to analyze hydrophobic interaction chromatography. Equations (11) and (22) link the experimental data with the thermodynamic constant. Therefore,

$$\Delta \mu = -RT \ln K_e = -RT \ln [K(\text{R}) + K(\text{OH})] - \ln v_e$$  \hspace{1cm} (23)

In our case, $\Delta \mu = 0$, and therefore, from eqs. (16) and (22),

$$\Delta S = R \ln K_e = R \ln [K(\text{R}) + K(\text{OH})] - \ln v_e$$  \hspace{1cm} (24)

Since $K(R) = y \exp[BV_e(R)]$, eqs. (23) and (24) can be rewritten as

$$\Delta \mu = -RT \ln[y \exp(BV_e(R)) + K(\text{OH})] - \ln v_e$$  \hspace{1cm} (25)

$$\Delta S = R \ln[y \exp(BV_e(R)) + K(\text{OH})] - \ln v_e$$  \hspace{1cm} (26)

Equations (25) and (26) relate the chemical potential and entropy change of the adsorption based on the volume of the alkyl group of the adsorbate. Using eqs. (22)–(24), the values of $K_e$, $\Delta S$, and $\Delta \mu$ are obtained for the various alcohols which are summarized in Table IV.

The adsorption capacity constant was divided into hydrophobic and hydrophilic parts in Eqs. (17)–(24) in an attempt to provide a correction of sorption of other organs such as acids, aldehydes, and ketones. For example, the adsorption capacity constant $K$ [from eq. (19)] for acetone was 0.70 compared to the experimentally determined value of 0.625 for 25.9% lignin. For 72.0% lignin sorbent, the experimental $K$ was 1.017 compared with a calculated value of 1.167. The experimental and calculated results may differ since the $K(\text{OH})$ for hydrophilic adsorption was now due to the hydrogen bonding of a ketone group, $C = 0$ (instead of OH). Furthermore, the $C = 0$ group is in the middle of the molecule instead of at the end, as is the case for $n$-monosaccharides. Hence, a different value of $K(\text{OH})$ should be used. This approach also requires an accurate estimate of the volume of the hydrophobic group. For example, the volumes occupied by the hydrophobic groups of $C_6H_{10}OH$ isomers are, in increasing order, CH$_3$CH$_2$CH$_2$OH > CH$_3$CH(OMe)CH$_2$OH > CH$_3$CH$_2$CH$_2$CH$_2$OH > CH$_3$OCH$_2$CH$_2$OH, but volumes calculated using van der Waals increments of atoms and groups are all the same, i.e., $V_e(R) = 73.7$ (Å$^3$). Using the equations derived from $V_e(R)$, a difference in adsorption would not be predicted. However, adsorption capacity from LC experiments show that the capacities increase with increasing hydrophobic volumes (Table V).

### Table IV. Thermodynamic constants of alcohol adsorption on lignosulfate in water at 30°C.

<table>
<thead>
<tr>
<th>van der Waals volume of the alkyl group (Å$^3$)</th>
<th>$K_e$</th>
<th>$\Delta S$ (J/mol K)</th>
<th>$\Delta \mu$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.9% lignin, $v_e = 0.23$ mL/g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>22.7</td>
<td>1.95</td>
<td>5.55</td>
</tr>
<tr>
<td>EtOH</td>
<td>39.7</td>
<td>2.18</td>
<td>6.48</td>
</tr>
<tr>
<td>PrOH</td>
<td>56.7</td>
<td>3.26</td>
<td>9.82</td>
</tr>
<tr>
<td>ButOH</td>
<td>73.7</td>
<td>5.61</td>
<td>14.34</td>
</tr>
<tr>
<td>PeOH</td>
<td>90.7</td>
<td>9.51</td>
<td>18.72</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>167.7</td>
<td>23.30</td>
<td>26.32</td>
</tr>
<tr>
<td>72.0% lignin, $v_e = 0.42$ mL/g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>22.7</td>
<td>1.37</td>
<td>2.62</td>
</tr>
<tr>
<td>EtOH</td>
<td>39.7</td>
<td>1.74</td>
<td>4.60</td>
</tr>
<tr>
<td>PrOH</td>
<td>56.7</td>
<td>3.17</td>
<td>9.59</td>
</tr>
<tr>
<td>ButOH</td>
<td>73.7</td>
<td>6.51</td>
<td>15.57</td>
</tr>
<tr>
<td>PeOH</td>
<td>90.7</td>
<td>10.59</td>
<td>19.62</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>197.7</td>
<td>22.19</td>
<td>25.77</td>
</tr>
</tbody>
</table>

Since temperature had no influence on adsorption, $\Delta \mu = 0$.  

**YANG, LADISCH, AND LADISCH: ALCOHOL ADSORPTION ON SOFTWOOD LIGNIN** 277
Table V. Adsorption capacity constants (K) of butanol isomers at 30°C.

<table>
<thead>
<tr>
<th>Butanol Isomer</th>
<th>25% Lignin</th>
<th>72.6% Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CH₂CH₂CH₂OH</td>
<td>1.29</td>
<td>2.73</td>
</tr>
<tr>
<td>CH₃CH₂CH₃CH₂OH</td>
<td>1.21</td>
<td>2.40</td>
</tr>
<tr>
<td>CH₃CH₃CH₂CH₂OH</td>
<td>0.99</td>
<td>1.84</td>
</tr>
<tr>
<td>CH₃(CH₃)₂OH</td>
<td>0.67</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Applications

Combination of equations (3) and (17) with (24) gives the expression

\[ Q = c_0 \exp(\Delta S/R)C^* \]  

Equation (27) shows that the adsorption of alcohols on lignocellulose is due to the entropy change of the system and expresses the adsorption capacity constant \( K \) in terms of the physical interaction of adsorbate with sorbent. Equation (27) also represents a useful tool in generalizing calculation of anticipated adsorption equilibria for a number of different alcohols.

Addition of an extractant during fermentation has been reported to dramatically improve bioreactor productivity in both ethanol and acetone/butanol/ethanol fermentations. The adsorption capacity of lignin appears to be comparable to oleyl alcohol which was tested for alcohol extraction from butanol fermentation broth. The distribution coefficients calculated from the data of Roffler et al. (Figs. 3 and 5 in ref. 3) are on the order of 2-4 mL aqueous butanol/g oleyl alcohol. In comparison, lignin has a value of \( K \) between 1.3 and 3.7 mL/g lignin. Since densities of oleyl alcohol (0.85 g/mL) and lignin (0.80-0.85 g/mL) are similar, it is anticipated that similar volumes of added sorbent could give similar results. In the case of a biomass conversion process to produce solvents, lignin will be a major coproduct, and hence readily available.

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References