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Separation of Alcohols from Solution by Lignin Gels

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Abstract: Partition relationships of radioisotope labeled ethanol and 1-butanol between aqueous solutions and a hydrated commercial Kraft softwood lignin gel are presented. These initial evaluations indicate that lignin hydrogels preferentially concentrate 1-butanol and, to a lesser extent, ethanol. The process implications and potential use of lignin as an inexpensive extractant are discussed.

Keywords: alcohol, extraction, lignin

INTRODUCTION

The U.S. federal government and private industry are committing substantial, increasing resources to production of C_1-C_4 alcohols, most notably ethanol and 1-butanol, from biomass. In a typical process, the carbohydrate portions of woody biomass are hydrolyzed to fermentable sugars using a combination of inorganic chemicals and enzymes. Lignin, a random, netted polymer comprised of three aromatic subunits, coniferyl, sinapyl, and *p*-coumaryl alcohols, typically constitutes 20–30% of wood and woody biomass and 15% to 25% of grasses (1). In most processes, lignin hydrolysis is minimized because lignin is usually perceived as a non-fermentable process residue. As such, lignin dissolved in waste liquors or separated as a solid residue is normally burned for process energy. Interaction between lignin and alcohols has been ignored by most process developers.

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A scoping study indicated that lignin might have a significant impact on the concentration and yield of fermentation-produced alcohols. In the scoping study, lignin hydrogel particles were added to cultures of *Clostridia* bacteria which produce low concentration mixtures of solvents that included 1-butanol, 2-propanol, ethanol, and acetone in a 3 to 5 day cycle. During fermentation, the lignin hydrogel particles became swollen and the duration of the fermentation cycle increased by weeks. The cultures were able to ferment additional amounts of carbohydrate. It appeared that the lignin gels might be sorbing the solvents produced by the bacteria.

Interactions between lignin and alcohols could impact the yield of fermentation processes in many different ways. Sorption of alcohols by lignin could increase process efficiency by increasing the overall concentration of alcohols in a process liquor. However, the sorption of alcohols by the lignin in process liquors or residues being burned for power could significantly lower yield.

A basic understanding of the interactions between lignin and alcohols appears to be critical to the development of efficient, cost-effective processes for conversion of cellulosic biomass to alcohols. This paper reports a series of preliminary experiments performed to evaluate partition of the two major fermentation-produced alcohols, ethanol and 1-butanol, from aqueous solution into lignin.

EXPERIMENTAL

Chemicals

All of the chemicals, with the exception of the commercial Kraft softwood lignin, Indulin AT,^{TM} were reagent grade materials used as obtained.

Lignin

Indulin AT,^{TM} a commercial Kraft lignin, was the kind gift of Mike Lake of Westvaco. It is produced by precipitation from Kraft pulping liquors and further purified to limit salt content. Prior to use, the Indulin AT^{TM} was repurified by several extractions with 10 volumes of dilute hydrochloric acid to remove residual salts. The solution was then neutralized to pH 5–6 with ammonia and washed several times to remove fines. It was then air-dried and sieved. After this purification, the Indulin contained 0.06% ash.

Radiolabeled Alcohols

^{14}C (1-butanol) and ^{3}H (ethanol) labeled alcohols were obtained from Amersham.

Extractions

Extraction samples typically consisted of 2 ml liquid. Although the procedure was varied if needed, generally 200 mg of dry lignin was weighed into test tubes and 1 ml. of water was added. The tubes were vortexed briefly, heated to 70°C for 30 minutes to hydrate the lignin, and cooled. The remaining 1 ml of solution, together with a spike of the radiolabeled alcohol (~10,000 cpm, ~10 microliters per sample, prepared as a stock solution), was added. The tubes were capped, vortexed, and placed on a "tilt-table" mixer at 25°C for at least 12 hours. An aliquot of the aqueous phase was removed, passed through a syringe filter to remove lignin particles, mixed with scintillation fluid, and counted.

Calculation of Distribution Coefficients

Lignin unfortunately has very high light absorption in the range of the scintillants used liquid counters and the volatility of ethanol and 1-butanol precluded use of dry counting methods.

The distribution coefficients were calculated by difference as follows. The partition of alcohols from solution into lignin was estimated as the difference in dpm between the stock solution and the lignin-extracted solution divided by the weight of dry lignin used in a sample (dpm per gm dry lignin). The dpm per cc aqueous was as determined by scintillation counting of the filtered solution after extraction.

Distribution coefficients were calculated based on decreases as the follows.

$$K_d = (\text{dpm per gm dry lignin})/(\text{dpm per cc aqueous})$$

RESULTS AND DISCUSSION

Ethanol and 1-butanol have been produced industrially at large scale for more than half a century (2). Low alcohol concentrations produced by fermentation, as well as the low concentrations of carbohydrates in biomass hydrolysis streams (3), have encouraged the development of a number of methods for decreasing the energy associated with alcohols separation. However, biotoxicity and cost have limited the use of many separations materials.

Several factors could have an impact on partition of alcohols into lignin. First, cellulosic biomass is typically hydrolyzed in acidic or basic solutions. The biomass itself may also contain significant amounts of salts. The concentrations of salts, as well as the solution pH, would be expected to have a measurable impact on partition of alcohols into a solvent and could have an impact on the partition of alcohols into a lignin gel. The concentrations of the materials being separated, ethanol and butanol, as well as the concentration of the material into which they are being separated, lignin gels, are expected to impact alcohol partition.

These factors will also provide a basis for estimating the beneficial and detrimental impacts of lignin gels on processes for production of alcohols from biomass.

Partition of Samples Spiked with 1-Butanol

As shown in Fig. 1, increasing the concentration of NaCl between 0 and 10% w/v in the aqueous increases the partition of 1-butanol into the lignin phase by roughly a factor of 3. In salinity ranges more characteristic of fermentations, 0–5%, the variation is within a factor of 2.

Figure 2 indicates that there is a mild increase in partition of 1-butanol into lignin between pH 6 and pH 7. These values are near the pK_as for the acids that are polymerized to form lignin. The effect is similar to the pH effects typically found in micelle and microemulsion systems.

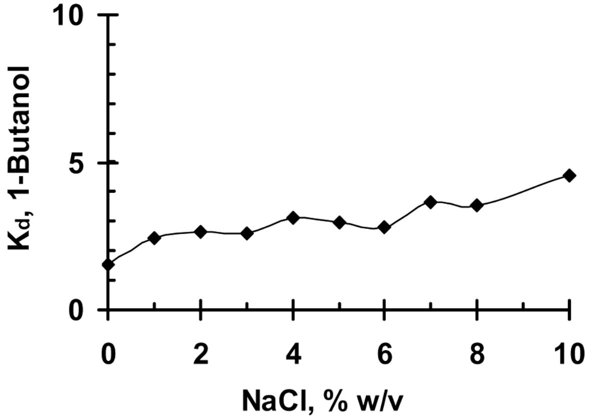

Figure 1. Effect of NaCl concentration on distribution of 1-butanol between lignin and aqueous.

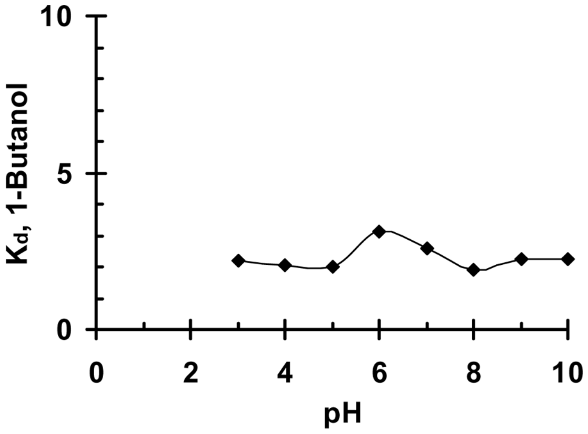

Figure 2. Effect of pH on distribution of 1-butanol between lignin and aqueous.

As shown in Fig. 3, the partition of 1-butanol into lignin rises as the ratio of lignin to aqueous, w/v, decreases. Partition of 1-butanol into lignin increases with increasing concentration of 1-butanol relative to lignin.

Figure 4 shows that the partition of 1-butanol into lignin increases with increasing 1-butanol concentration.

Distribution coefficients for 1-butanol found with hydrated commercial Kraft lignin are higher than those reported for long chain

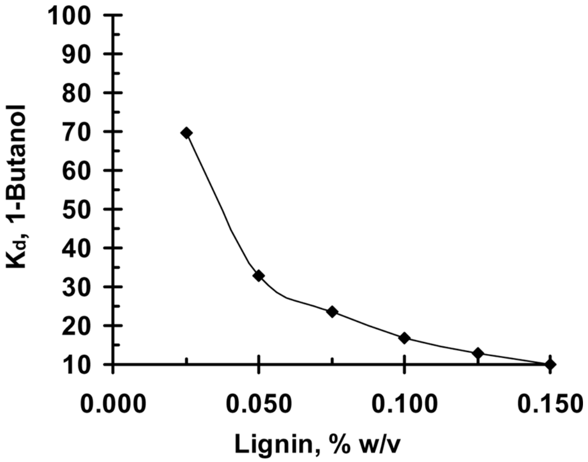

Figure 3. Effect of ratio of lignin to aqueous, w/v, on distribution of 1-butanol between lignin and aqueous.

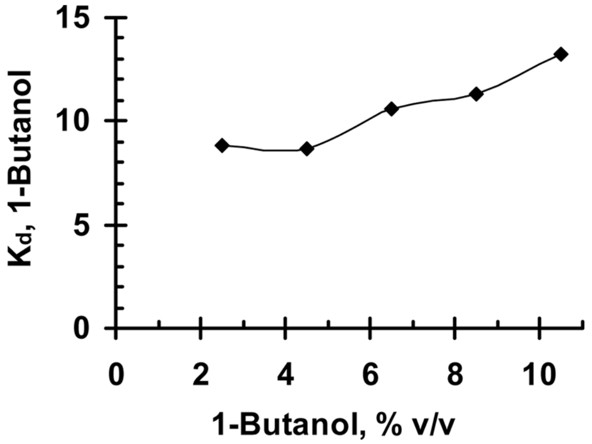

Figure 4. Effect of 1-butanol concentration on distribution of 1-butanol between lignin and aqueous.

alcohol solvent extractants such as 1-octanol or 1-dodecanol (4). Two factors are likely to contribute to this. As indicated by Yang and coworkers, lignins in the form of concentrates (residues) prepared from softwood by acid hydrolysis are capable of selectively sorbing C_1 to C_6 alkanols from dilute aqueous solutions (5). Although some variation between lignins from acid hydrolysis of cellulosic biomass and Kraft lignins would be expected, both will be short chain aromatic polymers with polar sidebranches which could sorb short chain alcohols. This behavior is similar to the partition of aliphatic alcohols into micelles and microemulsions (6,7), and with Sarkanan's observation that formation of lignin gels is favored in the presence of mixed solutions which contain water and small amounts of two or more alcohols or ketones (1).

Partition of Samples Spiked with Ethanol

As with 1-butanol, ethanol partition, shown in Fig. 5, increases slightly as NaCl concentration rises from 1% to 10% w/v. However, the partition of ethanol into lignin decreases slightly with increasing pH, as shown in Fig. 6.

As shown in Fig. 7, partition of ethanol into lignin increases as the concentration of ethanol increases.

Separation factors for ethanol are lower than are those for 1-butanol. This is consistent with the behavior of micelles and with the observations of Yang and coworkers.

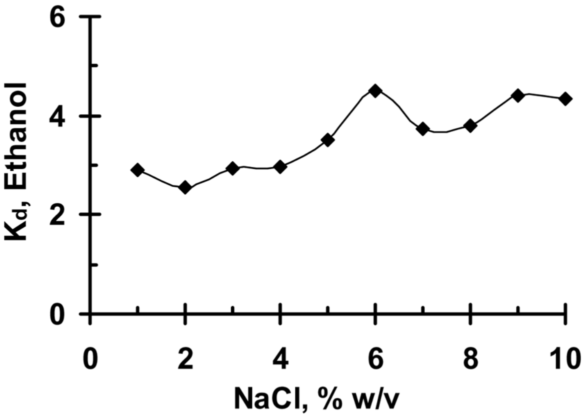

Figure 5. Effect of NaCl concentration on distribution of ethanol between lignin and aqueous.

Discussion of Process Implications

At the concentrations that might be expected in a fermentation broth (2–4%), distribution coefficients for 1-butanol found with hydrated commercial Kraft lignin are above 7. As an extractant, lignin may be competitive with long chain alcohol solvent extractants such as 1-octanol or 1-dodecanol (4). Softwood acid hydrolysis lignin residue is capable of selectively sorbing C_1 to C_6 alkanols from solutions comparable in

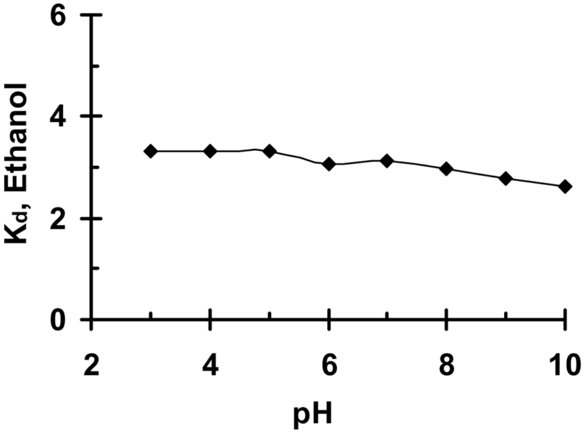

Figure 6. Effect of pH on distribution of ethanol between lignin and aqueous.

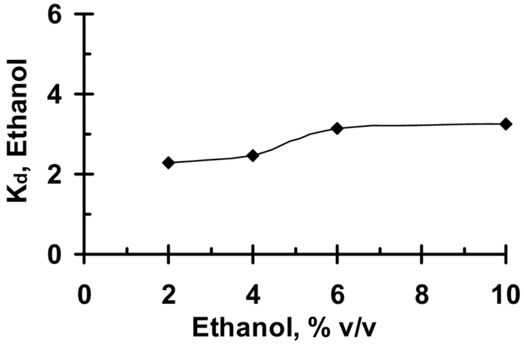

Figure 7. Effect of ethanol concentration on distribution of ethanol between lignin and aqueous.

concentration to fermentation broths (5). It has also been shown that lignin and lignin carbohydrate effectively function much as do micelles or liquid crystals, with both dissolved and solid species aggregating and interacting with small organic molecules (6). This behavior is consistent with and provides a basis for Sarkanan's observation that the formation of lignin gels occurs most readily in the presence of mixed solutions which contain water and small amounts of two or more alcohols or ketones (1).

The growing use of miceller, microemulsion, and reverse micelle systems in tailored separations indicates that these nanoscale-ordered aggregates may incorporate, sorb, or sequester materials in a form which provides stable transport through a process. These surfactant based systems are finding increasing use at industrial scale (7). Alcohols, most particularly butanols, partition readily into micelles and microemulsions (8,9) used to separate and concentrate materials ranging from metals to *p*-cresol (10,11).

Although further information would be required to support a formal process analysis, there are several parts of a normal cellulosic biomass conversion process where the sorption of alcohols by lignin are expected to have a significant impact on the process yield. First, the ability of lignin micelles and microemulsions to preferentially and stably incorporate alcohols into hydrate gels and other nanoscale solution structures will tend to carry the alcohols through unit operations and to retain it with separated lignin residues. The high amount of lignin, 15 to 30% of typical grass or wood cellulosic biomass, is sufficient to strip a significant amount of 1-butanol or ethanol from fermentation broths as a part of process residues. Whether this occurs will depend on the hydrolysis and separation system used in a particular process train and should be evaluated.

Distillation remains the major process used for recovery of ethanol and 1-butanol from fermentation broths. Many micelles and microemulsions are stable at temperatures near those used for distillation of fermentation broths. The effect of lignin on distillation operations should be evaluated.

The beneficial effects of lignin on fermentations should also be evaluated. Historically, it has been difficult to find low-toxicity, effective extractants for fermentation-produced alcohols and better materials have been expensive. Lignin is an inexpensive, relatively non-toxic byproduct of most cellulosic ethanol and butanol processes which is burned to provide process heat and minimize waste. Use of lignin as a sorbant or extractant which could permit production of higher concentrations of fermentation alcohols should be explored for these reasons.

CONCLUSIONS

The data in this paper provide information on the effects of pH, salt, and concentration of alcohols on the separation of alcohols into hydrated gels of a commercial softwood Kraft lignin recovered from pulping liquor. Partition of 1-butanol into lignin was higher than partition of ethanol. Partition of 1-butanol rose with increasing concentrations of salt and 1-butanol, and with decreasing concentrations of lignin. A slight increase in partition near neutrality was also noted.

For ethanol, the effects of increasing ethanol and salt were significant, but the effects of pH were not pronounced.

In combination with the literature, they indicate that partition of small organics into lignin could have a significant effect on the group of bacterial and yeast fermentation and separation processes being implemented for production of alcohols from cellulosic biomass. It may, for example, be possible to use lignin to strip alcohols or other small organic molecules from fermentation broths, increasing either the production rate or the highest concentration of an alcohol that can be produced. The low cost and high availability of lignin may make this approach useful in processing low-concentration biomass hydrolysis streams used as ethanol or butanol feedstocks. Lignin may also be useful, based on literature reports, as a fermentation stream pretreatment to remove toxicants prior to processing of acid or steam explosion liquors.

Alternatively, the low process yields which are observed in some fermentations of biomass-derived feedstocks may potentially be due to partition of alcohol products into lignin.

Further studies, combined with development of process models, are needed to determine how best to manage byproduct lignin to enhance the value of products, including lignins, from biomass fermentation processes.

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