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Cellulose Based Adsorbent Materials for the Dehydration of Ethanol Using Thermal Swing Adsorption

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Abstract. In this study, a thermal swing adsorption (TSA) column was used to evaluate the effectiveness of three ligno-cellulose based adsorbents on the removal of water from ethanol/water mixtures of 90, 95, and 97 wt% ethanol. The three adsorbents studied were bleached wood pulp, oak sawdust, and kenaf core. A glass adsorption column with an inside diameter of 2.54 cm was used to generate breakthrough curves to determine the effectiveness of the adsorbents and to allow comparability with starch based adsorbents that are currently used within the ethanol industry. Experimental results indicate that water is preferentially adsorbed allowing for complete dehydration of ethanol. Also, an evaluation has been made of the mass transport properties for the diffusion of water molecules into the porous matrices of the adsorbents as well as the length and velocity of the mass transfer zone.

Keywords: adsorption, ethanol, water, ligno-cellulosics, dehydration

1. Introduction

During the production of ethanol, large quantities of water are produced with the ethanol. The fermenter effluent typically has an ethanol concentration of approximately 10 percent, by weight. This ethanol/water mixture must be separated to produce ethanol with an ethanol concentration of 99.5 wt% or higher. Alcohol for automobile usage is refined through distilling processes to a maximum ethanol concentration of approximately 95.6 wt% and then another separation method is required. This second step is typically referred to as the dehydration step and is usually an adsorption process.

An industrial column is packed with an adsorbent that will preferentially adsorb water, leaving pure ethanol as the effluent product. Using this method of separation requires identifying adsorbents that will not only readily adsorb water during the adsorption phase of operation but also will easily desorb the water during the regeneration phase (Crittenden and Thomas, 1998; Crittenden and Sowerby, 1990).

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Adsorbents that readily adsorb water have already been examined and are in commercial use (Davis and Kristen, 1974; Grethlein and Thomas, 1992). Molecular sieves were the first adsorbent to be used. The biggest drawback with molecular sieves is the high cost of regeneration because of the high temperatures required to desorb the water that collects within the pores (Al-Rub et al., 1999; Banat et al., 2000; Davis et al., 1974).

This has driven the search for new and more efficient adsorbents. Dr. Michael Ladisch at Purdue University has investigated the use of natural materials as adsorbents (Ladisch, 1979). In the early 1980's, he proposed and patented the use of corn grits as a water adsorbent. With this discovery, a new approach to the ethanol dehydration problem emerged. It was found that biomass materials were generally less expensive to regenerate when compared to the molecular sieves (Ladisch, 1982). Also, if regeneration was not feasible, the biomass adsorbent could be used as a feedstock to the fermenter at the forefront of the chemical process.

Biomass materials that have been investigated and found to be viable adsorbents include corn grits, potato starch, amylose, and maize starch (Lee and

Ladisch, 1987; Lee et al., 1991; Neuman, et al., 1986; Bienkowski, 1986). These materials are starch-based adsorbents with high levels of amylopectin. Another class of adsorbents, such as wheat straw and woodchips, are derived from cellulosic-based materials. These materials use xylans and hemicelluloses as the major adsorbing mechanism instead of amylopectin. Little research, however, has been performed on cellulosic materials. It is currently unclear which materials will provide the highest degree of adsorption at the lowest cost.

The cost factor is assessed, not only in terms of water uptake efficiency, but also on regeneration or adsorbent replacement costs. If the material is to be replaced after each adsorption run, then the adsorbent must be cheap, readily available, and easily and safely disposed. TSA is more appealing than membrane separation, which uses costly vacuum and refrigeration equipment. Industrially, an array of columns is necessary. Some of which are in the adsorption phase, and others that are in the desorption phase.

2. Methods and Materials

A thermal swing desorption system was employed to remove the water from the adsorbent. A glass column apparatus with a 1.0 L flask was employed to determine the adsorption of water in gas-phase conditions. A mixture of ethanol and water was heated to produce a vapor stream that traveled upwards through the vacuum jacketed column packed with adsorbent. A column with an inside diameter of 1.0 inch (25 mm) and a length of 35 inches (89 cm) was used to provide sufficient column length and an adequate amount of adsorbent material to make dynamic column calculations possible. An inch of inactive packing made of 316 SS was placed at the bottom of the column to ensure an even radial distribution of the vapor stream.

The ethanol/water mixtures were blended using 200-proof ethanol and distilled water. Concentrations of 90, 95, and 97 wt% ethanol were used to evaluate adsorption characteristics at, above, and below the azeotropic concentration of 95.6 wt% ethanol. This study was limited to the normal boiling point of an ethanol/water mixture near the azeotrope. Distillation of ethanol/water from a fermentation broth concentration to near the azeotrope is cheaper and more attractive than using a single adsorption step. The adsorbents used in this study were oak chips, kenaf core, and bleached wood pulp.

The experimental runs were terminated when the water composition of the condensate equaled that of the feed. This usually took between 45 to 70 minutes, depending upon the adsorbent and the feed composition. After breakthrough of the water occurred, the adsorbent was regenerated using an air stream heated to 80°C and flowing at ~4.5 cfh overnight.

3. Results

Due to the ample literature on the use of molecular sieves to dehydrate ethanol, Type A molecular sieves were used to verify proper design and use of the laboratory batch column. The column, which had an inside cross sectional area of 5.07 cm^2, a vapor velocity of 3.29 mm/s was chosen to yield a volumetric flow rate of approximately 1.00 cm^3/min. The results showed similar adsorption capacities for the molecular sieves, the oak sawdust, and the kenaf core. The mass of water adsorbed per unit mass of adsorbent increases for both the molecular sieves and the cellulosic adsorbents as the water concentration in the ethanol/water mixture increases from 1 to 10 wt%.

3.1. Oak Sawdust

The sawdust was sifted in a 40-mesh screen to remove fine particles and in a 10-mesh screen to remove large particles. The vapor flow rate of the hardwood, less than 1.00 ml/min, was the smallest of all the adsorbents, which is reflected in the time of breakthrough in the adsorption curves.

For the first few experimental runs using oak sawdust, extractives leached from the wood chips and settled into the boil-up flask, giving a brown color to the ethanol/water mixture. After several repeated runs, all of the extractives appeared to have been removed. Nevertheless, the extractives did not effect the woodchips' ability to adsorb water.

3.2. Bleached Wood Pulp

The bleached wood pulp (BWP) used in this experiment was supplied in a commercially available, flat sheet form that had to be repulped using a blender and water. After drying, the adsorbent was ready for use in the adsorption column. As can be seen from the breakthrough curves, the BWP preferentially adsorbed water over ethanol in ethanol/water solutions of 3, 5, and 10 wt% water.

An important consideration with the BWP is that it has an increasing ability to swell inside the column with increasing concentrations of water. The adsorbent swelling causes a significant pressure drop across the adsorber. This, in turn, results in column flooding and poor mass transfer of water from the fluid to the adsorbent. The swelling is due to the lack of lignin within the structure of the cellulosic material. It is the lignin that gives the adsorbent rigidity. It acts as a glue to hold cellulose and hemicellulose molecules together. Without the lignin, the adsorbent, on a per weight basis, has a higher capacity to adsorb water; however, the swelling effect is counter-productive in an adsorber column.

3.3. *Kenaf Core*

The kenaf core had the shortest breakthrough time of the three cellulosic materials. There are several reasons for this. First, compared to the hardwood sawdust, a higher vapor flow rate was obtained resulting in more water per unit time that came into contact with the adsorbent. Also, its bulk density is only about one-half that of the hardwood sawdust. Therefore, fewer grams of adsorbent can be placed inside the adsorption column, leaving less surface area, per unit volume, for adsorption to occur. Secondly, compared to the bleached wood pulp, there are fewer polysaccharides, per unit mass, which provide the hydroxyl groups needed to adsorb the water molecules.

3.4. *Comparison of Adsorbents*

For all three adsorbents that were studied, as the concentration of water increases, shorter breakthrough times occur. This is because more water has been added to the system, and therefore, the adsorbent reaches its capacity quicker. The experiments conducted at the 95 wt% ethanol level prove that the ethanol can be purified past its azeotropic point. The experiments conducted at the 90 wt% ethanol level demonstrate the possibility of operating an industrial adsorption column in which the feed is somewhat below the azeotropic point.

The bleached wood pulp demonstrated the highest water loading followed by the kenaf core and then the oak sawdust. Breakthrough curves at the 90 wt% ethanol level were not obtained due to a lack of column length, and therefore, insufficient adsorbing material to remove enough water to reach the breakthrough concentration of 99.5 wt% ethanol.

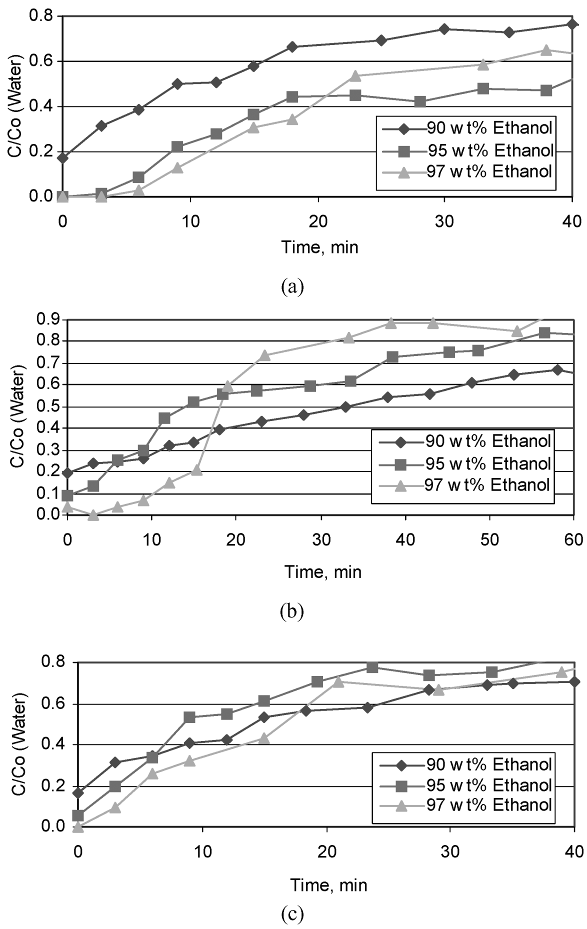

Figure 1. Breakthrough curves demonstrating adsorption characteristics (a) bleached wood Pulp, (b) oak chips, and (c) kenaf core.

4. Discussion of Results

Adsorption is a surface phenomenon, and the binding of water to an adsorbent is therefore occurring at the surface. The major constituents of cellulosic-based adsorbents are cellulose, hemicellulose, and lignin. The cellulose is composed of a moderately crystalline matrix with long microfibrils that are wound around a fiber axis. The microfibrils are joined together through hydrogen bonding and are embedded within an amorphous medium of hemicellulose. The lignin acts as a glue to hold together the other components and stiffens the cell walls.

When designing an adsorber to remove water from a mixture of ethanol and water, it is desired to find an adsorbent that is amorphous rather than crystalline. Crystalline structures have a highly ordered

Table 1. Conditions and results for vapor phase column experiments.

Adsorbent	Inlet composition (mass fraction ethanol)	Vapor flow rate (ml/min)	Breakthrough time (min)[1]	Water adsorbed (*g*)	Water loading[2]	Water adsorption rate[3]
Oak chips	0.97	0.655	14.5	0.285	0.0052	3.786
Oak chips	0.95	0.795	3	0.119	0.0022	0.7660
Oak chips	0.90	0.766	–	–	–	–
Kenaf core	0.97	0.953	7	0.200	0.0089	1.2758
Kenaf core	0.95	0.942	3	0.141	0.0063	2.1017
Kenaf core	0.90	1.010	–	–	–	–
BWP	0.97	0.989	13	0.3857	0.0125	0.9622
BWP	0.95	1.019	7	0.3567	0.0116	1.6524
BWP	0.90	0.855	–	–	–	–

Notes
[1]Breakthrough occurs at an exiting concentration of 99.5 wt% Ethanol.
[2] Water Loading is given by grams H_2O adsorbed per gram adsorbent (g H_2O/ g ads).
[3]Water Adsorption Rate is given by grams H_2O adsorbed per kilogram adsorbent per minute (g H_2O/ Kg ads/ min).

molecular arrangement and leave little room for additional molecules to be added. Cellulose has a high degree of crystallinity, up to 80%, whereas, hemicellulose is essentially amorphous. The lignin, on the other hand, adds very little to the water adsorption quality.

The interactions between molecules of water and the hydroxyl groups attached to the polysaccharides are rather involved. As the H_2O molecule is brought into contact with the OH^- group, one of the hydrogen's of the H_2O molecule becomes the proton donor, and the other hydrogen becomes the proton acceptor. Only the hydroxyls located on the adsorbent surface are available to water adsorption. That is, those that are wound within the inner microfibril matrix are not accessible to water molecules. The adsorbed molecules of water perturb the surface OH^- groups creating shifts of their vibrations to lower frequencies. The free OH^- groups have a shorter wavelength than the disrupted ones.

Therefore, a material such as bleached wood pulp is theoretically ideal because the lignin has been removed and it is an amorphous material with a high concentration of xylans. Experimentally, however, it does have its drawbacks. Without the lignin, there is no adhesion between cell walls to give the material a rigid structure. Consequently, the fibers swell with the adsorption of water providing a significant pressure drop inside the column between the boil-up flask and the condenser

The kenaf core is considered a non-wood fiber and has a lignin content of 18%. As the lignin content increases, the cellulose and hemicellulose contents decrease. As a result, fewer hydroxyl groups are available and fewer water molecules are adsorbed. It does have a

Table 2. Parameters and characteristics of the mass transfer zone.

Adsorbent	Inlet composition (wt frac etoh)	Length of Bed (cm)	Time $C_o/2$ Occurrence[1] (min)	Δt (min)	Velocity of MTZ (cm/min)	MTZ Length (cm)
Oak chips	0.97	89	18.0	23.0	3.71	85.3
Oak chips	0.95	89	14.0	47.5	6.36	302.0
Kenaf core	0.97	89	19.0	36.5	4.68	171.0
Kenaf core	0.95	89	12.0	33.0	7.42	244
BWP	0.97	89	28.5	24.0	3.12	74.9
BWP	0.95	89	37.5	41.0	2.37	97.3

Notes
[1]Time required for the water concentration in the column effluent to reach one-half of the water concentration of the influent stream. (i.e. for oak chips, the time required for composition of the column effluent to reach 0.985 wt. fraction ethanol with an inlet composition of 0.97 wt. fraction ethanol was 18 minutes.)

higher concentration of xylans, on a per weight basis, than the hardwood sawdust.

4.1. *Mass Transfer Zone Properties*

From the results of the breakthrough curves, the dynamic characteristics of the Mass Transfer Zone (MTZ) can be calculated. Table 2 summarizes the values of the parameters of the MTZ as well as the values of the length and velocity of the MTZ. The MTZ is an integral part in designing adsorption columns. Only experiments conducted at the 95 and 97 wt% ethanol were used to calculate MTZ properties. Experimental results from the 90 wt% ethanol lacked sufficient column length, and therefore, adsorbent volume to produce the necessary data for calculation of MTZ properties.

5. Conclusion

Ligno-cellulosic materials possess an affinity towards water. Their hygroscopic nature allows for the uptake of water molecules from ethanol mixtures that are at least 10 percent, by weight, water. All three materials studied demonstrated the ability to preferentially adsorb water over ethanol. These materials all contain an abundance of hydroxyl groups from their molecular makeup that are necessary to adhere water molecules to the surface of the adsorbent.

At the threshold point, called breakthrough, the bleached wood pulp performed best, followed by the kenaf core and then the hardwood sawdust. This can only be stated for concentrations of 3 and 5 wt% water. There was insufficient data at the 10 wt% water due to equipment capability. The data did show adsorption of water at this concentration; however, it was an insufficient amount to produce ethanol with at least a 99.5 wt% purity. It is believed that an increase in column length, resulting in more adsorbent, would give similar results as the 95 and 97 wt% concentrations.

The length of the Mass Transfer Zone (MTZ) and the velocity at which it travels through the adsorbent bed increases with increasing concentrations of water. This is a rather intuitive observation. As the concentration of water increases, the adsorbent will reach its threshold at a much faster rate. The bleached wood pulp has the shortest MTZ lengths and velocities, followed by the kenaf core and then the hardwood sawdust. All breakthrough curves are wide indicating long MTZ lengths. Longer adsorbent beds will make more efficient use of the bed capacity and lower regeneration costs.

Bleached wood pulp is a superior adsorbent over the kenaf core and hardwood sawdust in adsorbing water due to its large percentage of hydroxyl groups stemming from a high concentration of xylans. The bleached wood pulp was the only material that demonstrated similar water adsorbing capacities as compared to starch-based adsorbents such as corn grits.

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