Biobased adsorbents for drying of gases

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Fundamental, structural and compositional studies on the properties of corn grits and their ability to selectively adsorb water from organic vapors have resulted in new bio-based adsorbents. Structure/function relationships of these bio-based adsorbents are reviewed. © 1997 by Elsevier Science Inc.

Keywords: Cellulose; starch; drying; ethanol; pressure swing; sorbents; biosorbents; desiccant

Drying of organic vapors by starch and cellulose

Cellulose and starch-containing materials have been shown to remove water from a wide range of organics since 1979, when Ladisch and Dyck first demonstrated the separation of ethanol-water vapor mixtures over cracked corn, starch, and carboxymethyl cellulose. Other biomass materials, including corn grits, corn meal, corn cobs, xylan, crystalline cellulose (Avicel®), and wood chips, have been shown to separate water from ethanol. Water was also removed from the alcohols: methanol, isopropyl alcohol, and tert-butyl alcohol.

The sorption of water from alcohol by corn grits was established using a fixed bed nonisothermal adsorption column, with nitrogen or air at 100–110°C as the regeneration gas. The corn grit system for drying ethanol was first scaled up for industrial use in 1984 as part of a team effort that brought together researchers from Purdue and Archer Daniels Midland (ADM). Today, the system is used to annually dry about 750 million gallons of ethanol processed from 285 million bushels of corn. Methanol, ethanol, isopropanol, and t-butanol vapors at 85°C containing 17.5 mol% water gave 105, 151, 284, and 358 g anhydrous product/kg adsorbent, respectively, per adsorption cycle. The increase in alcohol vapor heat capacity (methanol < ethanol < isopropanol < t-butanol) correlated with increased water loading and the transition from combined wavefront behavior (for methanol and ethanol) to thermal wave behavior (for isopropanol and t-butanol). More recently, the potential of starch-based adsorbents for the gas-phase drying of propionaldehyde, MEK, acetonitrile, organic acids (acetic, propionic, butyric), and ethers (ethyl ether, MTBE, ETBE) has been indicated by gas chromatograph runs.

Starch-based adsorbents in pressure swing drying systems

Most processes for drying industrial gases (air, natural gas, synthesis gas, olefins, etc.) use pressure swing adsorption cycles. Gas purification processes utilize a significant fraction of the 30,000 metric tons/yr of synthetic zeolites and 25,000 tons/yr of alumina, as well as a smaller fraction of the 150,000 tons/yr silicas produced annually. Consequently, the compatibility of a starch-containing adsorbent (i.e., corn grits in this case) in a pressure swing adsorber is of considerable practical significance. Biodegradability of starch-containing materials also may prove beneficial, given the impending landfill and disposal restrictions for spent catalysts and sorbents.

Pressure swing air dryers which utilize molecular sieves as the desiccant are common in many industrial applications such as ozone generation, paint spraying, microwave antenna and telephone cable pressurization, environmental chamber testing, and continuous emissions monitoring. Intrinsically, the pressure swing adsorption cycle avoids the need for an inert gas, such as CO₂ or N₂, for the regeneration of the sorbent and instead uses a portion of the dried product gas. When molecular sieves were initially replaced with corn grits in a pressure swing adsorber, it was found that the grits were physically stable but that their operational drying capacity was less than that of molecular sieves. Corn grits with 2.3 mm average particle size were demonstrated to dry moist air at a dew point of −42°C in a pressure...
Swing adsorber operated between 300 and 101 kPa pressure. Hence, there was incentive to improve the performance of the grists or to synthesize an adsorbent from natural materials that would be as effective as the sieves. Given the potential economic significance of new bioadsorbents, the synthesis and characterization of a starch-based biomaterial superior to either ground corn or corn grits was initiated.

Surface effects and the performance of starch based desiccants

Corn grits have both the advantages and disadvantages of natural material. Grits are easily available, an order of magnitude less expensive than the molecular sieves, mechanically stable, biodegradable, and easily disposable. Grits exposed to repeated adsorption/desorption cycles have no discernible change in appearance when examined by scanning electron microscopy. Stability of the sorbent with respect to gelatinization is excellent, if only because the operational sorption capacity does not exceed 15% water, and averages about 1.5–2% during the ethanol drying process. The greatest disadvantage is that the specific surface area for adsorption is limited. While the surface area can be increased by reducing particle size, i.e., by more finely grinding the corn a limit is quickly reached below which the pressure drop for flow through a packed bed of fine particles is excessive. Therefore, a mechanically stable, robust material having a higher surface area than corn grits is needed.

Starch particles (average size of 10 micron) have an equilibrium capacity of 196 mg water/g with respect to saturated air, measured at 25°C and 300 kPa. The operational capacity of corn grits, for a pressure swing air dryer is only 0.45 mg/g, which is less than 1% of the equilibrium loading. This indicates that only a small fraction of the available sorption sites of corn grits are being accessed or utilized.

Grits contain 78% starch and have two kinds of regions, the smooth and yellow vitreous regions interspersed with opaque regions consisting of tightly packed spheroidal starch particles. The operational capacity of the corn grits was postulated to be caused primarily by the surface area of the starch particles in the opaque regions. This form of ground corn is heterogeneous in appearance and consists of yellow and white patches. The white patches correspond to areas densely populated with starch particles of 10–15 μ in size on the surface, as seen by scanning electron microscopy. In comparison, the yellow patches correspond to areas having a lower number of starch particles. Much of the starch in grits is in a less accessible form of a solid surface having a few cracks.

Corn grits at 15% moisture feel dry to the touch and form a freely flowing material. The adsorption mechanism of water on corn grits was hypothesized to include transport of water molecules into the structure of adjacent starch molecules present in the small spherical bodies immobilized on the surface of the corn grit. However, the low porosity of the starch matrix in the grits results in a low surface area per unit bed volume. This led to the hypothesis that agglomerates of starch particles with large micropores and a high internal surface area would have an improved performance over the native grits. The objective of the research was to increase the operational capacity by increasing accessible surface area while avoiding the high-pressure drop of 2–10 μ starch particles. For corn grits with an average diameter of 900 μ, the estimated external surface area is 0.0065 m²/g, which is equivalent to 0.0045 m²/m³ column volume. Starch particles, in comparison, have an average particle size of 10μ and a calculated surface area of 0.72 m²/g or 0.41 m²/ml, assuming that there would be 1.3 x 10⁹ particles/ml column volume. An ideal adsorbent was postulated to be a macroreticular material coated with starch which would have the same accessible surface area as starch particles alone.

Rate effects

A systematic study of the fundamental sorption properties of corn grits and starch showed that the selectivity of grits for adsorption of water over ethanol was a rate-dependent, rather than an equilibrium-dependent process. This explained why short sorption cycles and gas chromatographic studies gave negligible ethanol sorption, whereas ethanol was retained during longer runs under conditions that also resulted in high water loading. Ethanol can adsorb onto water which has previously absorbed onto starch, but it also adsorbs directly onto dry starch, although at a much slower rate than water. At 80–85°C, the equilibrium loading for water is achieved in 2–3 h, as compared with about 120 h for ethanol. The rate of ethanol sorption increases with increasing temperature. This supports an earlier suggestion that the slower adsorption of ethanol compared with water (on wheat starch) reflects a slower diffusion rate.

Immobilization of starch particles on a cob flour scaffold

The research evolved to examine the synthesis and evaluate several different types of adsorbents based on polysaccharides. These included: macroporous cellulose matrices (i.e., corn cob flour) coated with intact starch particles; macroporous cellulose matrices coated with a starch film; and starch particles, cross-linked to give a macroreticular, self-supporting particle. Starch films were found to have poor water adsorption properties, whereas starch aggregates tended to fall apart. The research thus focused on synthesizing agglomerates based on a cob scaffold coated with starch particles in a joint effort with collaborators in Materials Engineering.

Corn cobs consist principally of xylan (30–32%), cellulose (40–48%), lignin (7%), pectins (3%), and ash. Cobs are very tough, with one application being that of an abrasive in “sand” blasting. Xylan itself can separate water from ethanol, and cellulose also has sorptive properties. Consequently, corn cobs complement the moisture adsorbing properties of starch. Although cob particles at first glance were a potentially attractive sorbent, the particle size used here (<250 μ), is too small for operation in an industrial packed bed at a reasonable pressure drop. Similarly, pure starch has a particle size (2–10 μ) which is too small for operation in large diameter desiccant towers.

Scanning electron micrographs had indicated that the
macropores in some cob materials are larger than the starch particles, thus enabling a higher surface area, accessible to gas, because inner parts of particles could provide a scaffold on which to immobilize starch. Consequently, the strategy was to immobilize the starch onto a macroporous matrix, followed by formation of larger particles or pellets from the cob particles to which the starch had been immobilized. The adhesive property of starch plays a role in both immobilizing the starch particles, as well as pelleting the adsorbent.\textsuperscript{19-21} The performance of these materials suggests that they have potential as a biodegradable desiccant for dynamic adsorption in a market which was recently estimated to be approximately 100,000 metric tons/yr.\textsuperscript{22}

Summary

The interesting properties of corn, starch, and cellulose motivate further efforts to synthesize and characterize biomaterials for use in drying gases and organic vapors. The biomaterials are being formulated from polymers of glucose (i.e., starch and cellulose) and pentoses (i.e., xylans and hemicelluloses as found in corn cobs) in the search for sorbents which are robust, biodegradable, and compatible with existing fixed bed, industrial gas separation processes, and hardware. The starting template for sorbent characteristics is provided by corn grits.

Acknowledgments

The preparation of this literature survey was supported by the Department of Agricultural and Biological Engineering and the Purdue University Agricultural Experiment Station. Parts of the material reviewed in this paper were supported by NSF Grant BCS-9202702 and U.S. Department of Agriculture Contract 92-37500-8013. The author thanks Kyle Bercy and Dr. Ayda Sarikaya for helpful comments during the preparation of this manuscript.

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