Air Drying Using Corn Grits as the Sorbent in a Pressure Swing Adsorber

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Vapor streams containing organics and water can be dried in an energy-efficient manner by being passed over a cellulose or starch adsorbent such as corn grits (Ladisch and Dyck, 1979; Ladisch et al., 1984; Bienkowski et al., 1986; Hassaballah and Hills, 1990). The success of this dehydration method appears to be related to differences in the rates of adsorption (Lee et al., 1991), as well as differences in the strength of interaction between each species and the adsorbent. Hence, compounds which exhibit either weak interactions or slow rates of adsorption are expected to be readily separated from those that exhibit strong, relatively fast interactions with the adsorbent.

Humid air, a mixture of nitrogen, oxygen, and water, would appear to be an excellent candidate for dehydration on this basis. Water, a highly polar molecule, is rapidly adsorbed by starch (Lee et al., 1991). Nitrogen and oxygen, on the other hand, do not interact with starch to any substantial degree. The starch matrix apparently allows the larger, more polar water molecules to penetrate, while nonpolar molecules such as nitrogen are excluded (Hellman and Melvin, 1950).

Air drying is of practical industrial importance having utility in areas such as telephone cable and microwave antenna pressurization, continuous emissions monitoring, ozone generation, and environmental chamber testing. Dehydration can be carried out by adsorbing the water on molecular sieves at a relatively high pressure and then regenerating the sieves using a fraction of the dry air at atmospheric pressure, that is, by the Skarstrom cycle (Skarstrom, 1960, 1972). This method of pressure-swing adsorption is commonly used in industry and has recently been reviewed by Tondeur and Wankat (1985) and Yang (1990). This and other gas purification processes use a significant fraction of the 30,000 metric ton/yr of synthetic zeolites and 25,000 metric ton/yr alumina produced annually (Yang, 1990).

The goal of this work was to evaluate the operation of a pressure-swing air dryer utilizing corn grits as the adsorbent. Compressed air of known moisture content was dried using this starch-containing sorbent over an 88-day period. Performance was evaluated based on both drying characteristics and structural integrity of the grits. The experimental results suggest that corn grits are inexpensive, biodegradable adsorbents which may provide a useful alternative to molecular sieves. Estimates of equilibrium loading, evaluated using a modified potential theory (Westgate et al., 1992), show that operation is far from equilibrium, and rate considerations limit the degree of drying.

Materials and Methods

The system utilized in this study is depicted in Figure 1a. The internal workings of the dryer are shown in Figure 1b. Air at approximately 320 kPa and 25°C was humidified by bubbling through distilled water in a 1-L bulb. Traces of oil which were carried over from the compressor were removed in two oil traps. The gas was then metered at 300 kPa to a Puregas dryer (Model HF 2000A106-A130, General Cable Co., Westminster, CO) with 6-in. (152-mm) desiccant chambers containing 4A molecular sieves [1/16-in. (1.6-mm) pellets]. The dryer cycles between loading and regeneration at 30-s intervals. Outlet flow of air was maintained at 1.8 L/min (STP, 273 K, 101.3 kPa) using a Matheson model 8240 flow controller. The dry air flow used for regeneration, measured at the purge outlet, was 11.5 L/min (STP).

Moisture content was determined using a Shimadzu GC14A gas chromatograph with a 100/120 Haysep D column [6 ft × 1/8 in. (1.8 m × 3.2 mm)] (Supelco, Inc., Bellefonte, PA). Operation was at 145°C at a flow rate of 20 mL/min. A thermal conductivity detector at 145°C (150 mA current) and a Hewlett-Packard Model 3390A integrator were used to quantify water content in 100- and 500-μL air samples. Moisture content was calculated based on a standard curve that was generated by measuring the moisture content of air saturated over water in the temperature range of 0 to 25°C. Unless otherwise noted, concentrations and relative humidities were calculated on the basis of 25°C and atmospheric pressure.

Results and Discussion

Initial runs were made with the molecular sieves supplied with the dryer. After saturation the inlet air contained 0.35-mM water, which corresponds to a relative humidity of 0.85 at 300 kPa and 25°C. After about 1 hour of operation, the

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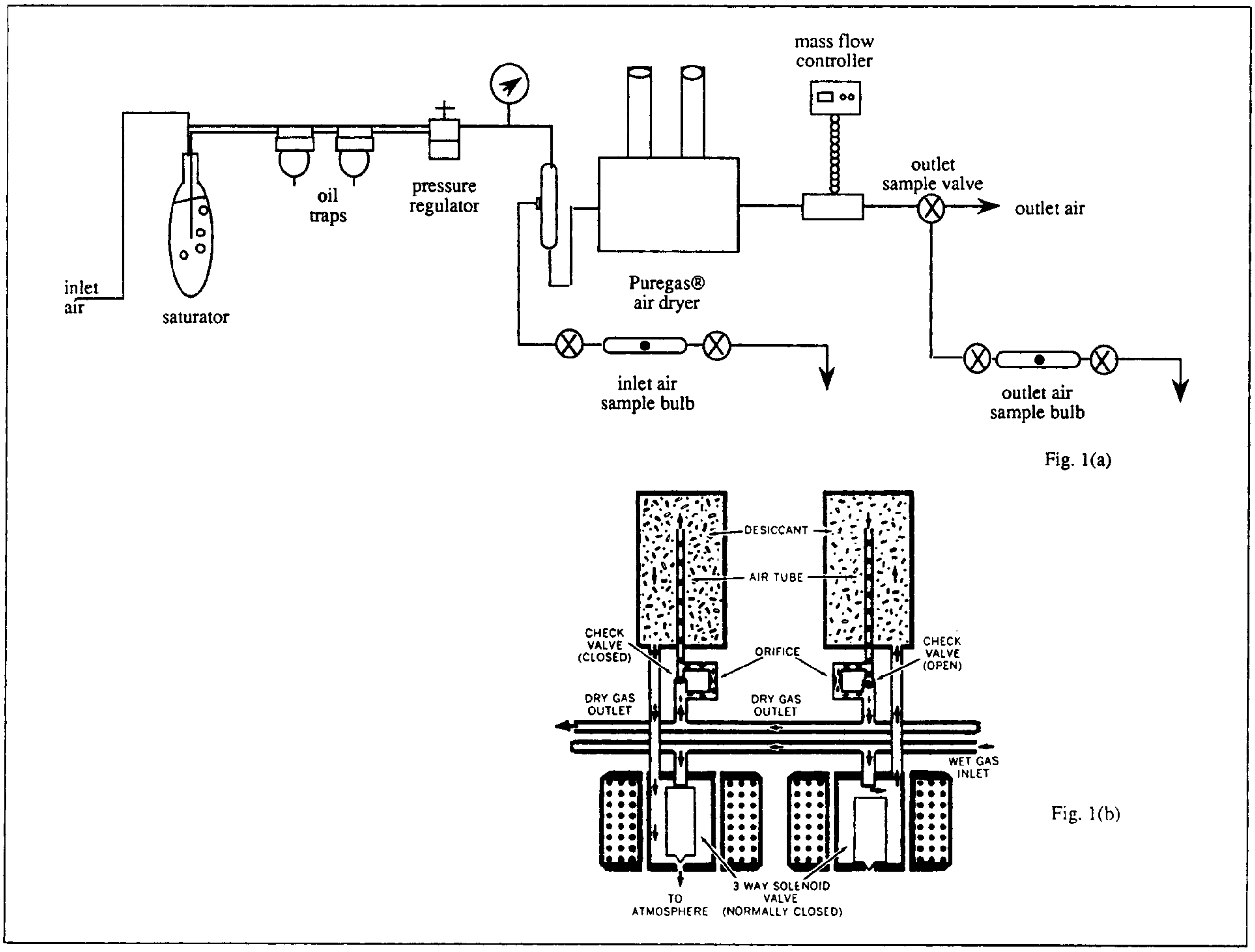

Figure 1. (a) System for studying air drying and (b) internal workings of the air dryer.

Internal workings courtesy of Puregas General Cable Co.
The direction of air flow is altered during each cycle by changing the positions of the solenoid valves.

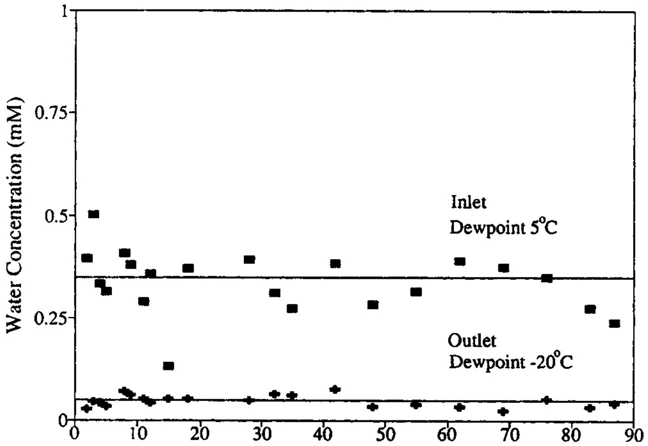

Figure 2. Water concentration before and after drying by corn grits in the Puregas dryer.

Air was introduced to the dryer at 300 kPa, 25°C at a flow rate of 13.3 L/min (STP). Outlet and purge flow rates were 1.8 and 11.5 L/min (STP), respectively.

outlet air contained 0.032 mM of water corresponding to a relative humidity of 0.025.

After the unit was tested and baseline data were obtained, operation was suspended and the molecular sieves were replaced by an equal volume (128 mL/bed) of corn grits (J. R. Short Milling Co., Kankakee, IL). The grits were packed at 15% moisture based on the assumption that standard drier operation would condition the grits to the operational moisture level. Operation was then restarted at the same conditions that were used for the molecular sieves. The grits came to a stable operating baseline within a day, and over 88 days gave an average outlet air moisture content of 0.050 mM, which corresponds to a relative humidity of 0.039 (Figure 2).

The success of this experiment led to another run using a saturated inlet air stream containing water droplets in the form of a mist (sometimes referred to as a "fog"). This represents a realistic operating condition, since misting can occur when a water-saturated gas is cooled. In this case, the inlet air stream contained 0.57-mM water, which corresponds to a relative humidity greater than 1 at the inlet conditions. This experiment was carried out for 5 days over which the outlet air moisture content was 0.03 mM.

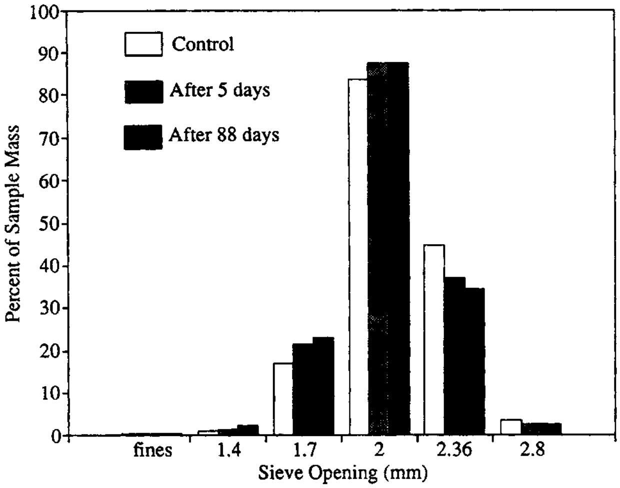

Figure 3. Particle size distribution of fresh grits and samples used in experimental runs.

Distributions are the average of two determinations in each case.

The other measure of performance during dryer operation was mechanical stability of the grits. A particle size distribution of fresh grits compared to those used in the experiment (Figure 3) shows that the average particle size changed only slightly. The quantity of dust decreased during operation and appeared to be trapped in the cloth filters at the outlets of the chambers. No dust was detected by scanning electron microscopy of a glass wool filter placed in the system outlet for 5 hours. The mass of the grits, weighed on day 10, was 86.7 and 91.8 g for each of the two adsorption beds, respectively, and 87.5 and 92.4 g after 88 days. Significant weight loss had not occurred. In fact, a slight (1%) weight gain was noted and could be due to sorption of trace quantities of oil present in the inlet compressed air. Bed volume reduction over this same period was about 5% and is typical of settling encountered with an adsorbent bed. Consequently, the grits were shown to be stable under pressure-swing conditions.

These initial experiments were carried out at the maximum outlet setting (1.8 L/min) for the Matheson flow controller. The purge flow of 11.5 L/min was then regulated by the orifice size, as can be seen in Figure 1b. Practical application of corn grits as a commercial drying agent would require higher dry air recovery than the 14% in these initial experiments. The feasibility of higher product/purge ratios was tested by repacking the chambers with fresh grits (99.6 and 97.2 g at ambient conditions) and running with the flow controller fully open (uncontrolled) for one week. The product and purge flow rates in this case were approximately 5.4 and 8.9 L/min (STP), respectively, which correspond to a 38% dry air recovery. Samples taken on the last 3 days of operation showed that air containing 0.04 mM of moisture was obtained from feed that had a moisture content of 0.30 mM. Further increases in the product/purge ratio may be possible, but could not be tested with the current configuration.

In some cases, a useful approach for modeling pressure-swing adsorption is to assume local equilibrium between the sorbent and bulk phase (Yang, 1990). Equilibrium loading of corn grits can be predicted by the potential theory for large-pore sorbents, modified to reflect the temperature-dependent swelling of starch due to water vapor uptake (Westgate et al., 1992):

$$q=\rho\left[W'_o \exp\frac{A_2}{T}\right]\left[\exp\left(-\frac{\kappa_2}{\beta}RT\ln\left(\frac{P_o}{P}\right)\right)\right] \tag{1}$$

where

q = quantity of water adsorbed, g/g
ρ = density of water adsorbed = 1.0 g/mL
W'_o = preexponential constant in expression for limiting volume for adsorption = 0.019 mL/g
A_2 = constant reflecting temperature dependence of limiting volume for adsorption = 695 K
T = temperature = 298 K
κ_2/β = constants in large pore theory = 0.000204 J/mol
R = gas law constant = 8.314 J/mol·K
P/P_o = relative humidity

On this basis, the calculated equilibrium loading of the particulate starch with respect to saturated air at 300 kPa and 25°C is 196 mg/g. Equilibrium loading after regeneration with atmospheric pressure air at a relative humidity of 0.04 is 38 mg/g. The difference between these values indicates that the maximum potential loading is 158 mg/g during each cycle. Actual bed loadings at the end of each cycle were calculated as 0.45 mg/g and 0.74 mg/g for the two runs.

The drastic difference between the actual loading and the maximum value indicates that only a small portion of the potential adsorption sites are being utilized. This is not surprising based on the findings of Hellman and Melvin (1950), which show the majority of water sorption sites are distributed in the interior of the starch matrix. Once the sites on the particle surface are filled, water must diffuse into the material for further loading to occur. Since the diffusion rate of water through starch materials is relatively slow (Hanson et al., 1971), the number of sites available for loading during pressure-swing operation is much less than the total equilibrium value. A similar discrepancy between actual (0.39 mg/g) and equilibrium loading (200 mg/g, Yang, 1990) exists for molecular sieves.

The molecular sieves removed from the dryer were synthesized to have large surface areas and porosities (Ruthven, 1984) as is evident from a scanning electron micrograph (Figure 4a). In comparison, corn grits (Figures 4b and 4c) have a fundamentally different appearance, consisting of smooth, light-yellow areas, referred to as vitreous regions, interspersed with areas of tightly packed spheroidal starch particles, referred to as opaque regions. We hypothesize that the opaque regions with a greater surface area are the dominant factor in determining operational capacity. Adsorption occurs via transport of the water into the starch in these regions which swells the starch matrix. This phenomenon is clearly different than diffusion in micropores in molecular sieves (Ruthven, 1984). Further studies are needed to obtain a more complete understanding of the relationships between the properties of starch and operating characteristics of the grits adsorbent.

Conclusions

Corn grits and molecular sieves give similar results when used as adsorbents in a pressure-swing dryer. The ground corn has remarkable stability, and, despite the loss of dusting characteristic during the run, no weight loss was noted. Dust was

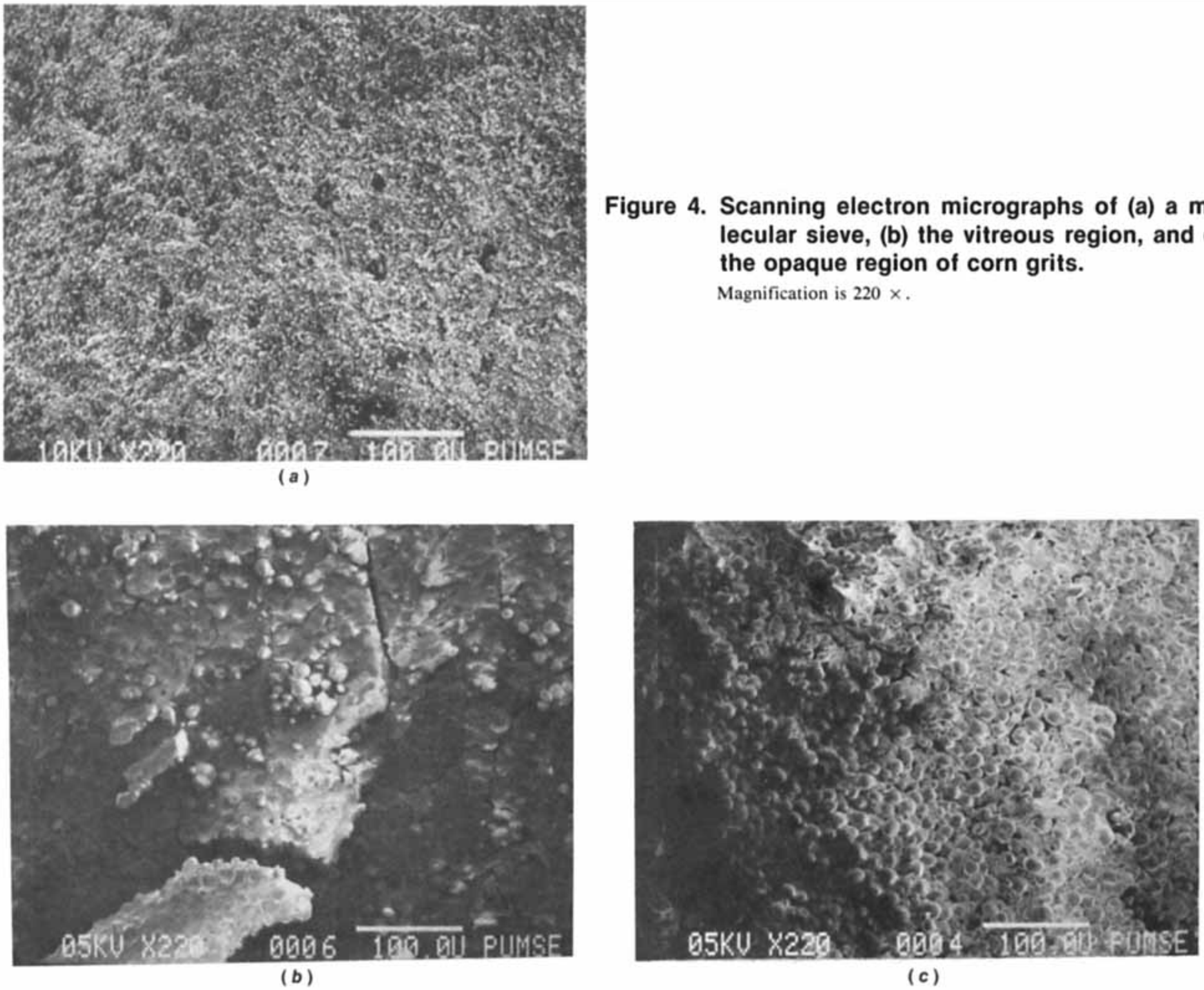

Figure 4. Scanning electron micrographs of (a) a molecular sieve, (b) the vitreous region, and (c) the opaque region of corn grits.

Magnification is 220 ×.

not observed in the outlet air suggesting that the small amount of free starch was trapped by the outlet filter of the sorption bed. The capacity and stability of this natural material are in the useful range for pressure-swing adsorption.

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