MODELING OF EQUILIBRIUM SORPTION OF WATER VAPOR ON STARCH MATERIALS

P. Westgate, J. Y. Lee, M. R. Ladisch
MEMBER
ASAE

ABSTRACT
The equilibrium behavior of corn grits and corn starch at temperatures above 70°C, a region for which limited data and theory are available, are compared and found to be similar. Sircar’s model and potential theory accurately represent isotherm data for both adsorption systems as well as data for desorption from corn. Values of the model parameters indicate that physical properties of these starch-based sorption materials exhibit a temperature dependence that is likely related to the breaking of hydrogen bonds as water interacts with the sorbent. Modification of the two models with an exponential temperature relation is proposed to account for the experimentally measured temperature dependence of model parameters. The resulting modified Sircar’s model and potential theory equations are shown to fit the data for both starch and corn grits in the high temperature range. KEYWORDS. Sorption, Corn, Ethanol.

INTRODUCTION
Materials derived from corn can remove water from alcohol vapors and are used to dry fuel grade ethanol (Ladisch and Dyck, 1979; Ladisch and Tsao, 1982; Robertson et al., 1983; Ladisch et al., 1984; Bienkowski et al., 1986; Lee and Ladisch, 1987; Hassaballah and Hills, 1990). These materials contain large quantities of starch which adsorb water due to the attraction between water molecules and the hydroxyl groups that are part of the anhydrous glucose units. The adsorption and desorption of water on whole corn has been extensively studied primarily for grain drying applications. Experiments have been most frequently carried out below 60°C, with a few studies considering temperatures up to 80°C as reviewed by Chen and Morey (1989). Adsorption at higher temperatures, important for ethanol drying, has been studied less frequently. Exceptions include the investigations of Neuman et al. (1986), which considered water adsorption on corn grits between 50 and 100°C, work by Crawshaw and Hills (1990) on the adsorption of ethanol and water on grits, cooked corn, and starch at 90°C, and our studies which evaluated the adsorption of water and ethanol on starch between 70 and 115°C (Lee et al., 1991).

More than 70 equations have been used to predict the water-sorption isotherms on starch materials (van den Berg and Bruin, 1978). In the high temperature range, we found that Sircar's model (1985) and the potential theory (Polanyi, 1914) represented adsorption data on starch over a wide range of temperature reasonably well (Lee et al., 1991). In addition, these two models require a minimal number of adjustable parameters which are physically significant in describing the adsorption process. Water sorption on corn grits at high temperatures has been predicted using a modified Henderson’s model (Neuman et al., 1986). However, it is difficult to determine the physical significance of two parameters in this model.

Since the adsorption of water on corn primarily occurs as the result of interaction with starch, it would be expected that the isotherms should be similar to those for starch alone. The objectives of this work were: 1) to determine if models which were previously shown to be suitable for predicting adsorption on starch can also represent high temperature water adsorption for grits and available desorption data for corn; and 2) to evaluate the temperature dependence of parameters in the models. Particular emphasis was placed on the interpretation of the model parameters in light of the properties of corn and starch.

SORPTION MODELS
Review of the literature suggested five models which might be consistent with the phenomena associated with the adsorption of water on starchy materials. Two of these models, the BET equation and a modified version of Henderson’s equation, were used by Neuman et al. (1986), to predict the adsorption of water on corn grits at high temperatures. The BET equation was useful in the low relative humidity range for estimating the surface area for adsorption, but could not be used at high relative humidities since it over-predicts sorption in that range. The modified Henderson model was successful in predicting water adsorption between 70 and 100°C. However, this model is somewhat empirical and it is difficult to interpret the physical significance of the parameters. A third model, the GAB equation, (Guggenheim, 1966; Anderson, 1946; deBoer, 1953) has physically significant constants and was found to give a better fit than the BET equation for the water-starch system (van den Berg, 1981). However, unless heats of adsorption for the first and subsequent layers are known, the five adjustable parameters of this model must be fit to data using nonlinear parameter.
estimation methods. The two models which were applied to the adsorption and desorption data in this article were Sircar’s equation (Sircar, 1985) and the potential theory (Polanyi, 1914).

**Sircar’s Model**

Sircar (1985) developed a model for nonporous adsorbents which compensates for the over prediction of the BET equation at high relative humidities. The three parameter equation assumes that a multilayer is formed at any relative humidity and that the surface area of each layer increases as the relative humidity increases. With these assumptions the equation is:

\[ \frac{v}{v_m} = \frac{C_1 (P/P_0)[(1 + (C_m - 1)(P/P_0))]}{(1 - P/P_0)[1 + (C_1 - 1)(P/P_0)]}, \]

(1)

\( P/P_0 \) is the relative humidity and \( v \) is the amount adsorbed. The parameter \( v_m \) is the quantity adsorbed in a monolayer while \( C_1 \) and \( C_m \) are temperature dependent constants describing the adsorbate-surface interactions for the first and subsequent layers, respectively. For an adsorbent that does not undergo significant change during adsorption, \( v_m \) should be constant. A functional relationship between temperature and the parameters \( C_1 \) and \( C_m \) was not suggested by Sircar. Since higher values reflect stronger binding, these values are expected to decrease as temperature increases. Values of \( C_m \) can range from zero, for which the model reduces to a monolayer, Langmuir-type equation, to one, when the model is equivalent to the BET equation.

Sircar showed that the parameters in the model can be evaluated by first considering that at low relative humidities essentially only a monolayer is formed and the effect of \( C_m \) is negligible. For these conditions the equation can be approximated by the Langmuirian form:

\[ \frac{v}{v_m} = \frac{C_1 (P/P_0)}{1 + (C_1 - 1)(P/P_0)}. \]

(2)

This can be written in linear form:

\[ \left[ \begin{array}{c} \frac{P}{P_0} - 1 \\ 1 - \frac{P}{P_0} \end{array} \right] = \frac{1}{v_m} \left[ \begin{array}{c} \frac{P/P_0}{(1 - P/P_0)} \\ C_1 \end{array} \right]. \]

(3)

\( C_1 \) and \( v_m \) are estimated from the slope and intercept of equation 3 fit to data obtained at low relative humidities. The third parameter, \( C_m \) in equation 1, is estimated based on the best fit of all of the data. Since the temperature dependence is not defined, these parameters must be determined separately for each isotherm.

**Potential Theory**

Unlike the other models considered, the potential theory (Polanyi, 1914) represents equilibrium adsorption at different temperatures based on a single correlation. The basis of this model is that the adsorption potential, the work done to transfer molecules from the gas to the adsorbent phase, is related to temperature independent forces. Hence, the adsorption potential is a function of the volume of the adsorbed phase and, for an ideal gas, can be written as:

\[ \varepsilon = RT \ln \left( \frac{P_o}{P} \right) = f(N, V_m) \]

(4)

where

\[ \varepsilon = \text{the adsorption potential,} \]
\[ R = \text{the gas constant,} \]
\[ T = \text{temperature,} \]
\[ N = \text{moles of adsorbate,} \]
\[ V_m = \text{liquid molar volume of adsorbate.} \]

Dubinin (1960) proposed relationships between the adsorption potential and volume of the adsorbed phase for two types of adsorbents, microporous materials (in which adsorbate interacts with opposite walls in the pore) and materials with large or no pores (in which the adsorbate interacts with a single surface). The linear form of the relationship for microporous materials is:

\[ \ln W = \ln W_o - \frac{K_1}{\beta} \left[ RT \ln \left( \frac{P_o}{P} \right) \right]^2 \]

(5)

where

\[ W = N \cdot V_m, \text{ the volume of the adsorbed phase,} \]
\[ W_o = \text{limiting volume for adsorption,} \]
\[ \beta = \text{affinity coefficient,} \]
\[ K_1 = \text{small pore constant.} \]

For large pore and nonporous materials, the relationship is:

\[ \ln W = \ln W_o - \frac{K_2}{\beta} \left[ RT \ln \left( \frac{P_o}{P} \right) \right] \]

(6)

where \( K_2 = \text{large pore constant.} \)

The constants \( K_1 \) and \( K_2 \) are related to the distribution of pore volume and, like \( W_o \), are expected to be constant for an adsorbent. The affinity coefficient characterizes the polarizability of the adsorbate and is also constant for a given system. A plot of \( \ln W \) versus \([RT \ln (P_o/P)]^2 \) or \([RT \ln (P_o/P)]\) should give a linear relationship for small and large pore adsorbents, respectively, from which the limiting volume for adsorption and the ratio of pore constant/affinity coefficient is determined. Since only the abscissa variable has any temperature dependence, all of the data would be expected to fall on one characteristic line. This is the primary advantage of the potential theory.

**RESULTS AND DISCUSSION**

**Sircar’s Model**

Data for equilibrium adsorption of water on corn grits at 70, 80, and 100°C (Neuman et al., 1986) and on starch at 70, 85, and 100°C (Lee et al., 1991) are depicted in figures
1 and 2, respectively. The quantities of water adsorbed and the shape of the isotherms for corn grits and starch are similar except at 70°C and relative humidities greater than 0.5. At 70°C and P/Pg > 0.5, the loading of water is expected to be at the highest levels, and water adsorbs to a greater extent on starch than on corn grits. Sirca's model gives a reasonable fit of the data for adsorption on both materials (solid lines in figures 1 and 2). As shown in figure 3, the model also fits data for equilibrium desorption isotherms of water on corn at 4.4 to 60°C (Rodríguez-Arias, 1956). In light of the similarities in the shapes of the isotherms, this result is not unexpected. The trends in the model parameters are summarized in Table 1.

The values of v_m, C_1, and C_m were determined using Sirca's method where the values of v_m and C_1 were estimated from data below a relative humidity of 0.32 assuming 1 g/mL is the density of the adsorbed phase. The value of v_m, the amount adsorbed in the monolayer, decreases substantially with increasing temperature for starch. We postulate this is related to the breaking of hydrogen bonds as water is absorbed. In the case of the adsorption isotherms for corn grits, v_m has a similar value to that of starch at 100°C, and also decreases with increases in temperature but the changes are much less dramatic. A similar trend was exhibited for the y_m evaluated for the water desorption isotherms. These results are consistent with those of Hellman and Melvin (1950) who concluded that the surface area available to water as determined by the BET equation was far greater than the surface area available to nitrogen or that estimated by photomicrographic methods.

### Table 1. Values of parameters in Sirca's model

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>v_m</th>
<th>C_1</th>
<th>C_m</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.089</td>
<td>6.852</td>
<td>0.188</td>
</tr>
<tr>
<td>80</td>
<td>0.087</td>
<td>6.678</td>
<td>0.131</td>
</tr>
<tr>
<td>100</td>
<td>0.072</td>
<td>7.883</td>
<td>0.190</td>
</tr>
</tbody>
</table>

### Water Adsorption on Starch

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>v_m</th>
<th>C_1</th>
<th>C_m</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>0.138</td>
<td>8.487</td>
<td>0.133</td>
</tr>
<tr>
<td>15.6</td>
<td>0.131</td>
<td>7.223</td>
<td>0.111</td>
</tr>
<tr>
<td>30</td>
<td>0.132</td>
<td>5.243</td>
<td>0.057</td>
</tr>
<tr>
<td>37.7</td>
<td>0.114</td>
<td>4.129</td>
<td>0.109</td>
</tr>
<tr>
<td>50</td>
<td>0.106</td>
<td>4.865</td>
<td>0.127</td>
</tr>
<tr>
<td>60</td>
<td>0.101</td>
<td>4.087</td>
<td>0.083</td>
</tr>
</tbody>
</table>

* Data from Neumann et al., 1986.
† Data from Rodríguez-Arias, 1956.
‡ Data from Lee et al., 1991.
The values of $C_1$ and $C_m$ reflect the strength of interaction between the adsorbent and adsorbate in the first and subsequent layers, respectively. It would be expected that these parameters would decrease with increasing temperature and that values would be similar for the sorbents studied. The values of $C_1$ evaluated for the water desorption from corn do clearly show the expected decreasing trend. The values of $C_1$ for water adsorption on grits, on the other hand, exhibit no clear trend and are much larger than the $C_1$ estimated for starch. For both adsorption and desorption, the $C_m$ values were on the order of those estimated for starch.

The results from applying Sircar’s model to the data suggest that the physical structure of starch changes as water adsorbs. The smaller temperature dependence of $v_m$ for water adsorption on grits indicates that breaking of hydrogen bonds to expose more sorption sites, is not as prevalent in corn as in starch alone. The lower levels of adsorption for corn grits compared to starch under conditions of high loading is also consistent with this interpretation and reflects fewer available adsorption sites as well as a smaller extent of change under these conditions. The relatively large values of $C_1$ for corn grits indicate a stronger interaction between the first layer of water and the adsorption sites in the corn grits than is the case for the water-starch system and is consistent with changes which occur in the physiochemical properties of starch during its processing (Takeda et al., 1988).

**Potential Theory**

The potential-theory was also applied to the adsorption isotherms for starch and corn grits, and desorption isotherms for com, respectively. As was previously found for starch, the small pore theory substantially underpredicts the data for corn at intermediate and high water loading (results not shown). The large pore theory, however, agrees reasonably well with the adsorption data for corn grits as shown in figure 4. (Note that use of the mass of the adsorbed water in the potential theory is possible if the assumption is made that the adsorbed phase has a constant density.) Unlike the previously reported results for starch, the isotherms for the grits appear to fall on a single characteristic line. The desorption isotherms, on the other hand, do not fall on a single characteristic line, although a linear relationship is still observed for each of the temperatures at loadings of less than 0.14 g/g (corresponding to $\ln (\text{water adsorbed g/g}) = -2.0$) as shown in figure 5. The large pore theory underpredicts the highest levels of loading (above about 0.14 g/g). Once again swelling at high loadings is believed to provide an explanation.

The value of the intercept, representing the mass of adsorbate which would fill the limiting volume available for adsorption, decreases with increasing temperature in all three cases (Table 2). The ratio of $k_2/\beta$ is related to the pore volume distribution and polarizability of the adsorbate.

**Table 2. Values of parameters for large pore potential theory (determined from data below 0.135 g/g loading)**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k_2/\beta$</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.000217</td>
<td>-1.96</td>
</tr>
<tr>
<td>80</td>
<td>0.000202</td>
<td>-2.00</td>
</tr>
<tr>
<td>100</td>
<td>0.000193</td>
<td>-2.12</td>
</tr>
</tbody>
</table>

**Water Adsorption on Starch:**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k_2/\beta$</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.000242</td>
<td>-1.66</td>
</tr>
<tr>
<td>85</td>
<td>0.000239</td>
<td>-1.82</td>
</tr>
<tr>
<td>100</td>
<td>0.000254</td>
<td>-2.04</td>
</tr>
</tbody>
</table>

**Water Desorption from Corn:**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k_2/\beta$</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>0.000190</td>
<td>-1.69</td>
</tr>
<tr>
<td>15.6</td>
<td>0.000201</td>
<td>-1.72</td>
</tr>
<tr>
<td>30</td>
<td>0.000213</td>
<td>-1.78</td>
</tr>
<tr>
<td>37.7</td>
<td>0.000224</td>
<td>-1.84</td>
</tr>
<tr>
<td>50</td>
<td>0.000232</td>
<td>-1.85</td>
</tr>
<tr>
<td>60</td>
<td>0.000230</td>
<td>-1.98</td>
</tr>
</tbody>
</table>

* Data from Neumann et al., 1986.
† Data from Rodriguez-Arias, 1956.
‡ Data from Lee et al., 1991.
and will change in value if these properties are affected by adsorption, although in this work the variability with respect to an average value is less than ±12%. Consequently over the range of 4.4 to 60°C, the indicated values were used directly with Equation 6 to give the result (solid lines in figure 5). Otherwise a simple average value was utilized with Equation 6 to give the results in figure 4.

As was the case for Sircar's model, the results from the potential theory indicate that changes occur in the sorbent structure, particularly for starch, during adsorption. The similarity between starch and corn as adsorbent materials is reflected by characteristic curves with similar slopes and intercepts. The higher capacity for adsorption on starch is likewise indicated by the larger values of the intercept.

**TEMPERATURE DEPENDENCE IN SIRCAR’S MODEL AND POTENTIAL THEORY**

The temperature dependence exhibited by \( \nu_m \) in Sircar's model and the limiting volume for adsorption in the potential theory is not typical of many sorbents used in the chemical industry since physical properties generally do not change substantially with adsorption. An exponential type temperature dependence was found for the adsorption and desorption isotherms under consideration:

\[
\nu_m = \nu'_m \exp \left( \frac{A_1}{T} \right) \tag{7}
\]

\[
W_o = W'_o \exp \left( \frac{A_2}{T} \right) \tag{8}
\]

Equations 7 and 8 gave a satisfactory fit of the data in figures 6 and 7 providing a correlation with temperature (Table 3). The constants \( \nu'_m \) and \( W'_o \) represent the values the parameters appear to approach at low loadings and high temperatures where the sorbents would not experience hydrogen bond breakage. Values of the constants \( A_1 \) and \( A_2 \) give the temperature dependence.

An analogous form of temperature dependence for \( C_1 \) and \( C_m \) gives a modified Sircar’s model:

\[
\frac{\nu}{\nu'_m \exp \left( \frac{A_1}{T} \right)} = C_1 \exp \left( \frac{A_2}{T} \right) \left[ \frac{P}{P_o} \right] \left[ 1 + \left( \frac{C_1}{C_m} - 1 \right) \left( \frac{P}{P_o} \right) \right] \left( 1 - \frac{P}{P_o} \right) \left[ 1 + \left( C_1 \exp \left( \frac{A_2}{T} \right) - 1 \right) \left( \frac{P}{P_o} \right) \right] \tag{9}
\]

Values of the constants in Table 3 were used with equation 9 to generate the fit shown in figures 1-3 (dashed lines). In all cases a reasonable fit is obtained that is similar to the fit by the unmodified model.

If the temperature dependent form of \( W_o \) given by equation 8 is introduced into equation 6, the large pore potential theory, the resulting equation is:

\[
\ln (W) = - \frac{\kappa_2}{\beta} \left[ RT \ln \left( \frac{P_c}{P} \right) \right] + \left[ \ln W'_o + \frac{A_2}{T} \right] \tag{10}
\]

If the temperature dependence of \( W_o \) is relatively small, as is the case for the adsorption data on corn grits, the value of the intercept, \( \ln W'_o + \frac{A_2}{T} \), is essentially constant (≈ ln \( W_o \)) and all of the data appears to fall on a single characteristic.

If the temperature dependence of \( W_o \) is substantial, as is the case for the adsorption data on starch, equation 10 predicts that the data will fall on series of parallel characteristics. Values of the constants in Table 3 were used with equation 10 to generate the lines which fit the starch adsorption data shown in figure 8. The data exhibits some variation in \( \kappa_2/\beta \) for starch (Table 2). Since the estimated \( \kappa_2/\beta \) in Table 2 deviated from an average by less than 4%, an average value (0.000245) was used in equation 10 to generate the fit (dotted lines) in figure 8. Since the potential theory is by definition temperature independent, equation 10 must be considered an empirical modification which is useful for modeling the behavior of adsorbs which exhibit a temperature dependence for \( W_o \).

**CONCLUSIONS**

The water adsorption capacity of corn is primarily related to its major component, starch. Isotherms for water adsorption at temperatures between 70 and 100°C on corn grits are similar to those on processed starch except at low temperatures.
temperatures and high humidities (conditions for high loading). Application of Sircar's model and the potential theory to the griss isotherms and water desorption isotherms indicate that, like the starch data, these results can be fit reasonably well. Variation in the monolayer and limiting adsorption parameters in these models with temperature indicates properties of the adsorbents are related to the level of water adsorption. Addition of a temperature dependent term in the model parameters result in versions of Sircar's model and the potential theory that account for the change in properties in the temperature range studied.

ACKNOWLEDGMENT. The material in this work was supported by NSF Grants CBT 8351916 and CPE8405577, the Purdue University Agricultural Experiment Station (AES), and Texas Instruments. In addition, the computer equipment was contributed by the Texas Instruments Corporation. We thank Dr. Gou-Jen Tsai, Dr. Ajoy Velayudhan, and Dr. Richard Stroshine of Purdue University, and Mr. David McCombs of Monsanto Envirochem for their helpful comments during preparation of this manuscript.

REFERENCES


SYMBOLS
\[ A_1 = \text{constant reflecting temperature dependence of } \nu_m (K) \]
\[ A_2 = \text{constant reflecting temperature dependence of } W_0 (K) \]
$A_3 =$ constant reflecting temperature dependence of $C_1$ (K)

$C_1 =$ parameter in Sircar's model (dimensionless)

$C_\infty =$ parameter in Sircar's model (dimensionless)

$C_{\infty} =$ pre-exponential constant in the expression for $C_1$
               (dimensionless)

$C_{\infty} =$ average value of $C_\infty$

$N =$ number of moles of adsorbed phase, (gmol/g)

$P =$ partial pressure of water at temperature $T$ (P_a)

$P_o =$ vapor pressure of water at temperature $T$ (P_a)

$R =$ gas constant (J/mol K)

$T =$ temperature (K)

$v =$ amount adsorbed in volume (cm$^3$/g)

$V_m =$ liquid molar volume of adsorbate (cm$^3$/gmol)

$V_m =$ parameter, monolayer amount adsorbed in volume (cm$^3$/g)

$v'_m =$ pre-exponential constant in the expression for $v_m$ (cm$^3$/g)

$W =$ $N \times V_m =$ volume of adsorbed phase (cm$^3$/g)

$W_0 =$ limiting volume of adsorbed space

$W' _0 =$ micropore volume (cm$^3$/g)

$W'_0 =$ pre-exponential constant in the expression for $W_0$ (cm$^3$/g)

Greek

$\beta =$ affinity coefficient that characterizes the polarizability of the adsorbate (dimensionless)

$\epsilon =$ adsorption potential (J/mol)

$\kappa_1 =$ constant in D-R model for large pore sorbents (J/mol)$^{-2}$

$\kappa_2 =$ constant in D-R model for small pore sorbents (J/mol)$^{-1}$