

Adsorption and Desorption Characteristics of Grain Sorghum

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CRAIN sorghum, like other grains, is hygroscopic. Thus it will gain or lose moisture, depending on the surrounding air. Because the sorption relation between grains and water vapor is important in grain conditioning, storing, and drying, numerous attempts have been made to understand adsorption and desorption processes of water vapor on grains and to develop equations relating the equilibrium state of the grain to environmental conditions (Henderson 1952; Chung and Pfof 1967; and Chen 1969). Although many theories and isotherm equations for homogeneous materials have been developed (Bradley 1936; and Brunauer et al 1938), sorption phenomena on such heterogeneous materials as grains still are not completely understood.

Many have studied sorption isotherms for corn and wheat, but few have studied grain sorghum sorption isotherms. We found studies only by Coleman et al (1928), Fenton (1941), and Haynes (1961). Isotherm equations on grain sorghum have not been well tested. Only Henderson (1952) and Chen (1969) tested their equations with data from Fenton (1941).

We (a) investigated adsorption and desorption isotherms for grain sorghum at various temperatures; (b) tested the applicability of a few known isotherm equations to grain sorghum; (c) refined Chung and Pfof's isotherm equation (1967); (d) evaluated heats of desorption for grain sorghum; and (e) examined the difference between equilibrium moisture contents of grain sorghum by dynamic and static methods.

MATERIALS AND METHODS

Field-harvested grain sorghum (Julting Hybrid 556) obtained at 30.55 percent moisture content, dry basis, the

fall of 1971 was used for the desorption tests after the dockage was removed. The samples used for the adsorption study were dockage-free grain sorghum dried to 3 percent moisture content, dry basis, by an oven dryer with 120 F air.

A static method, with a sulfuric acid solution to maintain a constant relative humidity, was used to obtain equilibrium moisture content at a constant temperature. Wide-mouth, 500-ml flasks were filled with about 200 ml of various concentrations of sulfuric acid solutions. Samples (2.0 to 4.0 g) of grain placed in fine-wire screen baskets were suspended above the solutions in the sealed flasks. Then the sealed flasks, containing the samples, were placed in a temperature-controlled chamber.

The time required for a sample to reach equilibrium with its environment was 3 weeks. The moisture content at equilibrium was determined by the standard oven method. Propionic acid (0.4 percent by weight) was used to prevent possible mold growth on a sample placed in high relative humidity (above 88 percent). Preliminary tests indicated no difference in equilibrium moisture contents between treated and untreated samples.

Vapor pressures of various concentrations of sulfuric acid solutions and saturation vapor pressures were obtained from Perry (1950). The range of relative humidities studied was about 2 to 90 percent. Adsorption and desorption isotherms were obtained at 60, 75, 80, 90, 105, 100, and 120 F.

Equilibrium moisture content by the dynamic method was obtained by forcing air through a grain sample placed in a chamber with temperature and relative humidity controlled. Sample weight changes were determined periodically until the weight remained constant. Temperatures studied in the dynamic method were 90 and 105 F, both with relative humidities of 10 and 90 percent.

RESULTS AND DISCUSSIONS

Experimental Isotherms

The adsorption and desorption isotherms at 90 F are shown in Fig. 1,

along with data from Fenton (1941) and Haynes (1961). The isotherms are sigmoid (Type II isotherm), consistent with isotherms for other cereal grains by earlier researchers. Our data indicate that hysteresis between adsorption and desorption prevails over almost the entire range of relative humidities.

As shown in Fig. 1, our adsorption data agree well with the data from Fenton (1941) and Haynes (1961). The isotherm data at various temperatures showed that equilibrium moisture contents decreased as temperature increased. Temperature effects on adsorption were much less than on desorption. Hysteresis decreased as temperature increased. Chung and Pfof (1967) reported similar phenomena for corn.

Heats of Desorption

When adsorbed water vapor is desorbed, heat is taken up (the heat of desorption). The heat of desorption is a measure of the heat or energy that must be added to adsorbed water to break the intermolecular force. We evaluated heats of desorption (ΔH_d) at constant moisture contents by using the formula,

$$\Delta H_d = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \frac{P_2}{P_1} \dots [1]$$

where P_1 and P_2 are equilibrium vapor pressures at the absolute temperatures T_1 and T_2 , respectively. Chung and Pfof (1967) give more detailed procedures to evaluate ΔH_d .

Heats of desorption of grain sorghum are plotted as a function of moisture content in Fig. 2. Calculated values of heats of desorption ranged from 29.5 x 10³ Btu per lb-mole or 1639 Btu per lb to 19.4 x 10³ Btu per lb-mole or 1078 $\frac{\text{Btu}}{\text{lb}}$, and were comparable with those obtained by Chung and Pfof (1967) for corn. Fig. 2 shows that heats of desorption decrease continually with increasing moisture content. Also shown is that heats of desorption are consistently higher across the entire range of moisture contents than are heats of pure water vaporization.

The net heats of desorption, addition-

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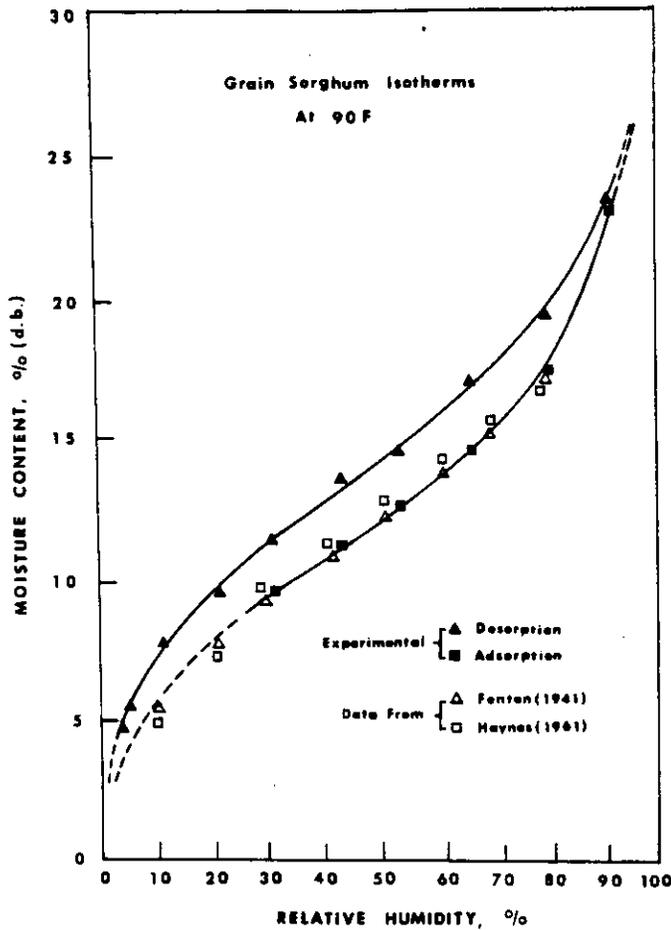


FIG. 1 Adsorption-desorption isotherms of grain sorghum at 90 F and comparison with isotherms from Fenton and Haynes data.

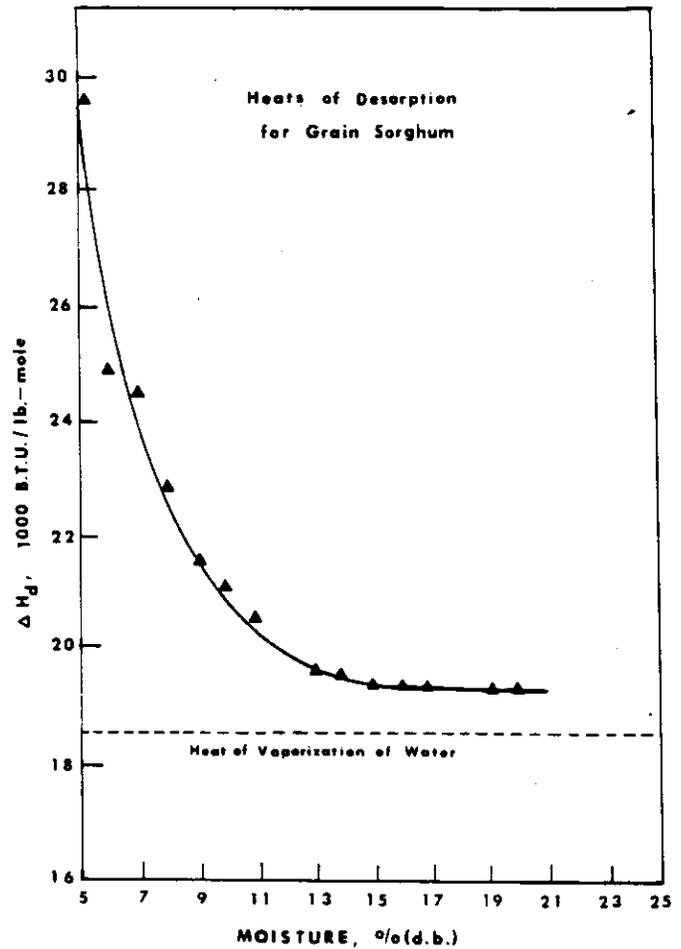


FIG. 2 The heats of desorption for grain sorghum at 112 F.

al heat required over the heat of vaporization, ranged from 10.95×10^3 Btu per lb-mole or 608 Btu per lb to 850 Btu per lb-mole or 47 Btu per lb, which indicates that additional heat over that of vaporization of pure water is needed to evaporate moisture in grain sorghum.

Applicability of Known Isotherm Equations

The five isotherm equations we tested were by Brunauer et al (1938), Smith (1947), Henderson (1952), Bradley (1936), and Chung and Pfost (1967). Each equation transformed to a linear form, and its region of applicability to grain sorghum isotherm data are given in Table 1.

The equation by Brunauer et al (1938) could be successfully applied only to relative humidities below 43 percent. The Smith equation was applicable only in the 43 to 90 percent relative humidity range. Equations by Chung and Pfost, Bradley, and Henderson were applicable to the entire range of relative humidities tested. Chung and Pfost, and the Bradley equations had the best overall correlation.

Equation Development

Constants in each isotherm equation varied with temperature. So to develop an equation for any isotherm, temperature dependence of the constants must be described. We refined the Chung and Pfost equation,

$$\ln \frac{P}{P_0} = -\frac{A}{RT} e^{-BM} \dots \dots \dots [2]$$

to describe temperature's dependence of its constants and evaluated constants, A and B (equation [2] to describe grain sorghum isotherms at various temperatures (Table 2).

Two empirical equations we proposed to describe the temperature dependence of constants in equation [2] are:

$$\frac{\ln A}{RT} = C + DT \dots \dots \dots [3]$$

TABLE 1. FIVE ISOTHERM EQUATIONS TESTED IN LINEAR FORMS AND THEIR APPLICABILITY TO GRAIN SORGHUM DATA

Equation	Equations in linear forms			X'	Relative humidity* range applicable, percent
	Y'	A'	B'		
BET (1938)	$\frac{P/P_0}{V(1-P/P_0)}$	$\frac{1}{V_m C'}$	$\frac{C'-1}{V_m C'}$	P/P_0	2-43
Smith (1947)	M	W_b	$-W'$	$\ln(1-P/P_0)$	43-90
Henderson (1952)	$\ln(-\ln(1-P/P_0))$	$\ln KT$	n	$\ln M$	2-90
Bradley (1936)	$\ln(-\ln P_0/P)$	$\ln K_2$	$\ln K_1$	a	2-90
Chung and Pfost (1967)	$\ln(-RT(\ln P/P_0))$	$\ln A$	B	M	2-90

*Range having $r = \pm$ at least 0.98

and

$$\frac{B}{RT} = E + FT \dots\dots\dots [4]$$

where A and B are constants in equation [2]; R is the universal gas constant; T is the absolute temperature; and C, D, E, and F are empirical constants.

Using our isotherm data and least square analysis, we obtained two linear regression lines (equations [3] and [4]). In evaluating the constants, we used only isotherm data at 60, 75, 90, 105, and 120 F and reserved 80 and 100 F to test the proposed equations later. Equations [3] and [4] gave correlations coefficients 0.922 and 0.978, respectively, for the desorption and 0.954 and 0.612 for the adsorption data.

The four constants evaluated, C, D, E, and F in equations [3] and [4], are given in Table 2, with constants evaluated from corn data by Hall and Rodriguez-Arias (1958). Correlation coefficients from using data of Hall and Rodriguez-Arias (1958) were 0.997 and 0.878, respectively, for equations [3] and [4]. The results show that the refined extended Chung and Pfof equation is applicable to corn as well as grain sorghum. Substituting equations [3] and [4] into equation [2] gives

$$\ln \left(RT \ln \frac{P_0}{P} \right) = RT (X - YM) \dots [5]$$

where X and Y are defined as $X = C + DT$ and $Y = E + FT$.

To test equation [5] we predicted two isotherms at 80 and 100 F by using

the constants given in Table 2. The predicted isotherms at 100 F, along with experimental isotherms are shown in Fig. 3. The predicted and experimental values closely agree. To further test

applicability of equation [5], we used the statistical test on the difference in two groups. It showed no significant difference ($\alpha = 0.05$). Therefore, equation [5] may be used to generate or describe grain sorghum isotherms at any temperature between 60 and 120F, and also to describe isotherms for corn.

In addition, we compared four equilibrium moistures by the dynamic method with the static method (Table 3). Differences were small, with dynamic values tending to be higher than static values. Time required to determine dynamic values was about 36 hours compared with 3 weeks for static values.

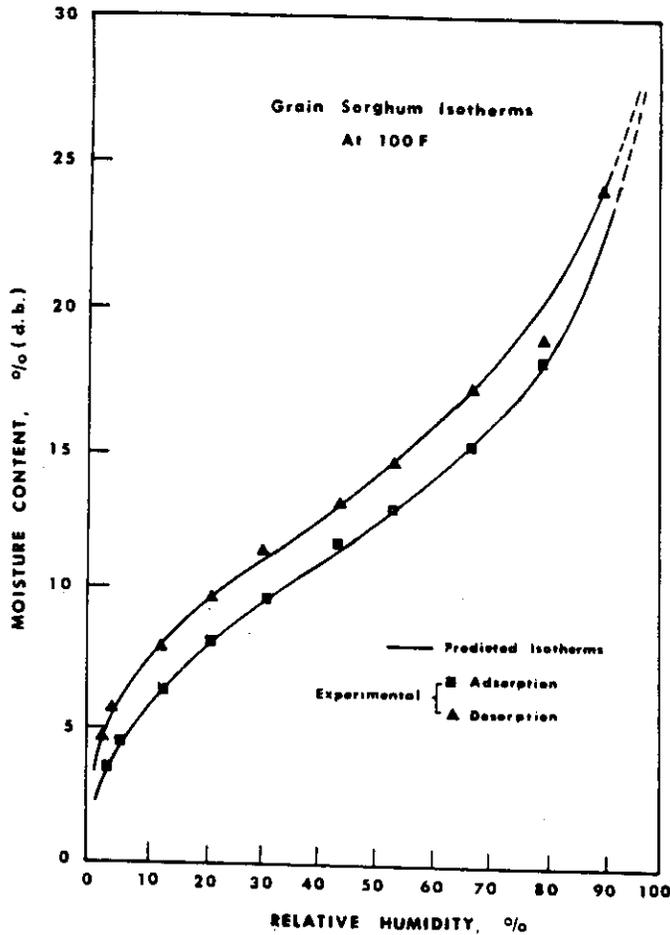


FIG. 3 Isotherms predicted by the extended Chung and Pfof equation compared with experimental isotherms at 100 F.

TABLE 2. CONSTANTS FOR THE CHUNG AND PFOST EQUATION AND FOR THE EXTENDED CHUNG AND PFOST EQUATION

Chung and Pfof Equation			
Temperature, F deg	Constant A	Constant B	Correlation
D 60	13128	18.613	-0.998
D 75	10673	18.126	-0.999
D 90	10118	18.497	-0.998
D105	9559	18.368	-0.999
D120	9183	18.049	-0.998
A 60	7863	18.701	-0.996
A 75	8370	19.921	-0.999
A 90	6307	17.505	-0.997
A105	7309	18.163	-0.997
A120	8271	19.655	-0.999

D: Desorption A: Adsorption

Extended Chung and Pfof Equation			
Constants	Grain sorghum desorption	Grain sorghum adsorption	Corn desorption*
C	1.978×10^{-2}	1.656×10^{-2}	1.652×10^{-2}
D	-2.052×10^{-5}	-1.521×10^{-5}	-1.540×10^{-5}
E	3.660×10^{-2}	3.428×10^{-2}	0.136×10^{-2}
F	-3.599×10^{-5}	-3.101×10^{-5}	-2.873×10^{-5}

*Data from Hall and Rodriguez-Arias (1958)

TABLE 3. EQUILIBRIUM MOISTURES BY DYNAMIC METHOD COMPARED WITH STATIC METHOD FOR GRAIN SORGHUM AT INDICATED TEMPERATURES AND RELATIVE HUMIDITIES

Temperature, deg. F	RH, percent	Equilibrium moisture by dynamic method, percent d.b.	Equilibrium moisture by static method, percent d.b.
Desorption 105	8	6.59	6.50
Desorption 90	93	24.50	24.20
Desorption 90	11	7.94	7.30
Adsorption 90	93	22.76	22.40

CONCLUSIONS

Regarding grain sorghum show that:

1 The type II isotherm or sigmoid isotherm of grain sorghum was consistent with those for other cereal grains.

2 The equilibrium moisture content and hysteresis effect decreased as temperature increased.

3 Heats of desorption for grain sorghum decreased continually as moisture content increased and were consistently higher than the heat of vaporization of pure water over all moisture contents tested.

4 The Brunauer-Emmett-Teller equation was applicable only for relative humidities from 2 to 43 percent; the Smith equation, from 43 to 90 percent; and the equations by Henderson, by Bradley, and by Chung and Pfof were applicable to all relative humidities studied.

5 The extended Chung and Pfof equation developed here describes isotherms at various temperatures for grain sorghum and for corn.

6 Equilibrium moisture contents by the dynamic method tended to be

higher than those by the static method.

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NOMENCLATURE

A	= constant or referring to adsorption
A'	= intercept in a linear equation
a	= amount adsorbed at pressure P
B	= constant
B'	= slope in a linear equation
C, C'	= constants
D	= constant or referring to desorption
E	= constant
F	= constant
ΔH_d	= isosteric heat of desorption, Btu per lb-mole
K, K ₁ , K ₂	= constants
M	= moisture content (dry basis)
n	= constant
p	= vapor pressure
P _o	= saturation vapor pressure
P ₁ , P ₂	= equilibrium pressures at absolute temperatures, T ₁ and T ₂
R	= universal gas constant
r	= correlation coefficient
T	= absolute temperature, deg R
V	= volume or amount of gas adsorbed
V _m	= constant
W', W _b	= constant
X	= function defined as (C + DT)
X'	= independent variable in a linear equation
Y	= function defined as (E + FT)
Y'	= dependent variable in a linear equation
α	= confidence level