

ADSORPTION-DESORPTION CHARACTERISTICS OF GRAIN SORGHUM

by

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Adsorption-Desorption Characteristics
of Grain Sorghum
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INTRODUCTION

Ten percent of the grain grown on the farm never reaches market. This loss occurs in the field and during storage. Hall (1957) classified the field losses into five areas and the storage losses into three areas. The field losses are as follows: 1) shattering of grain to the ground, 2) breakage of straw when harvested too dry, 3) wind and insect damage, 4) improper operation of harvesting machinery, and 5) poor growing conditions. The storage losses are due to mold, insect damage, and heating due to excessive moisture. Both of these losses could be reduced by timely harvest, drying, and proper storage conditions.

During drying and storage, hygroscopic materials, such as grain sorghum, gain or lose moisture when the vapor pressure in the space surrounding the grain is greater or less than the vapor pressure exerted by the moisture in the grain. The gain of vapor moisture is called adsorption and the loss is called desorption.

Adsorption is of two types: physical and chemical. Physical adsorption, or van der Waal's adsorption, is the result of intermolecular forces of attraction between molecules. A gas may condense onto the surface of a material even though the relative pressure of the gas is lower than the saturation pressure. This condensation will be accompanied by an evolution of heat which is usually larger than the heat of vaporization of the condensing vapor. The intermolecular forces can be described as the effects of dipole moments. These moments set up an electrostatic field. The positive end of one molecule attracts the negative end of another. These molecules are known as polar molecules. Chemical adsorption, or

chemisorption, is the result of reactions between the solid and the adsorbed vapor. This chemical reaction binds the adsorbed substance with a force greater than that of physical adsorption and is usually irreversible.

Predictions of adsorption and desorption equilibrium moisture contents are very important to the Agricultural Engineer in controlling grain storage environments. If the grain has an excessive gain in moisture, spoilage will occur. Predicting the grain's reaction to its environment will enable the engineer to minimize storage problems.

Another area where desorption is of great importance to the engineer is in grain drying. An understanding of desorption would allow the engineer to design grain dryers which would dry grain more economically and to easily predict input conditions (relative humidity, temperature, and rate of air flow) needed to dry the grain to the desired moisture content.

Hygroscopic properties of grain during drying and storage are a function of relative humidity and temperature of the air in contact with the grain. Cereal grains when placed in an environment of constant relative humidity and constant temperature for a long time will reach a specific moisture content. This moisture content is known as the equilibrium moisture content.

A typical isotherm of grain equilibrium moisture content is shown in Figure 1. This curve is called an isotherm. The curve represents one temperature over the entire range of relative humidities; for each relative humidity there is a corresponding equilibrium moisture content.

The representation in Figure 1 also displays another hygroscopic characteristic of grain. The equilibrium moisture content is higher for

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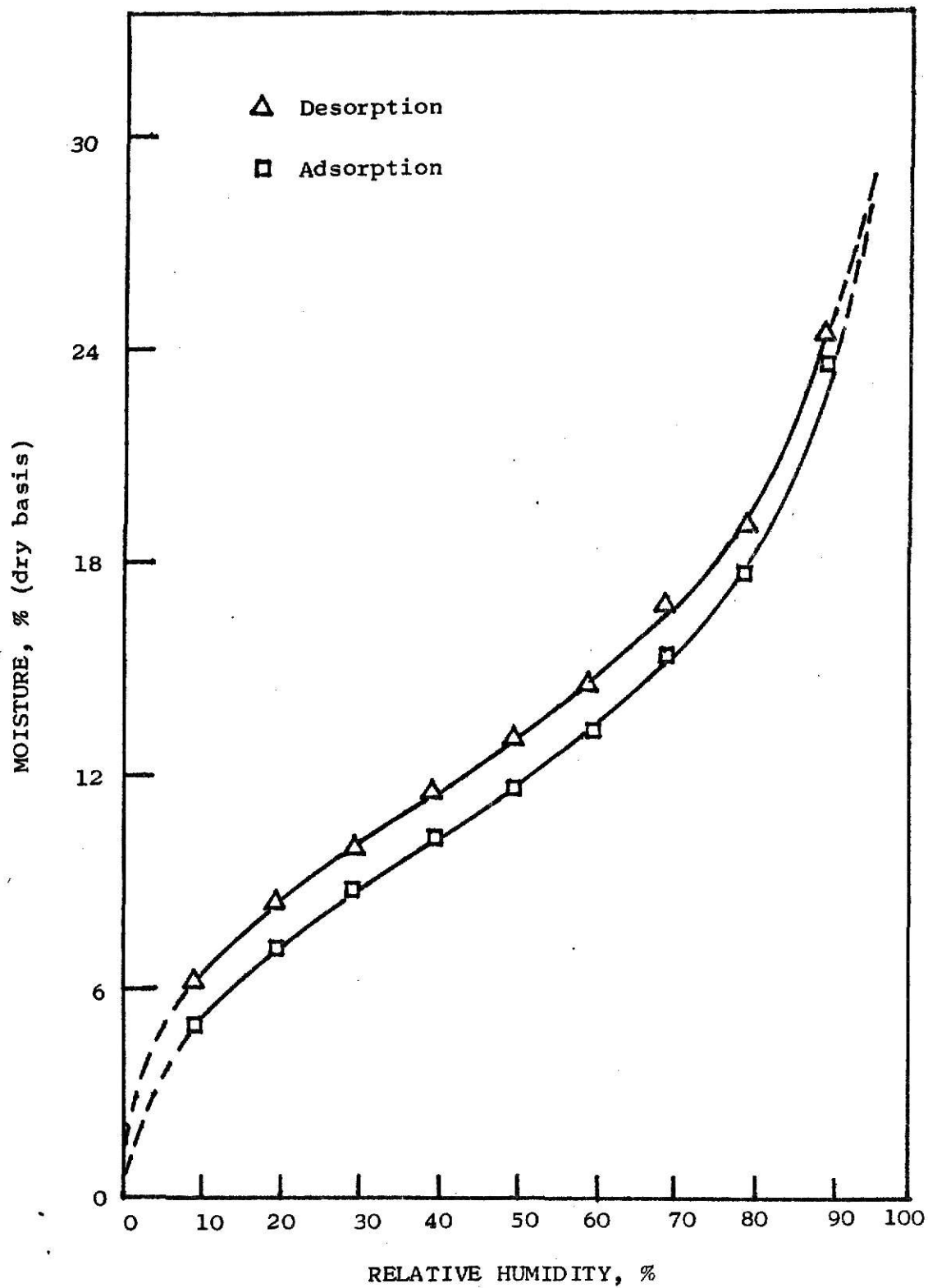


Figure 1. Adsorption-desorption isotherms of corn at 22 C showing hysteresis effect, Chung (1966).

desorption than it is for adsorption. This difference in moisture content is known as hysteresis.

Adsorption-desorption curves are commonly produced from data obtained by storing grain samples in environments with fixed relative humidities and temperatures until grain equilibrium moisture contents are reached. Relative humidities are controlled by either sulfuric acid and distilled water solutions or various salt solutions. Test sample temperatures are controlled by storing the samples in a controlled temperature chamber. The moisture content found by this method is known as a static equilibrium moisture content.

Another approach leads to a dynamic equilibrium moisture content. When air at a constant temperature and constant relative humidity is forced through a grain sample, grain moisture equilibrium is usually reached in much less time than with the static method. The dynamic equilibrium moisture content relates to the actual process during grain drying.

Adsorption and desorption for corn or wheat have been studied extensively. Many researchers have determined static equilibrium moisture contents and have studied hysteresis. Grain sorghum, which is a very important Kansas crop, has been almost neglected. To update knowledge about grain sorghum three major areas of study were made: 1) static equilibrium moisture content, 2) dynamic equilibrium moisture content, and 3) hysteresis. The most important result of this study is an equation developed to predict the equilibrium moisture content for grain sorghum for various environmental conditions.

REVIEW OF LITERATURE

Isotherm Theory and Equations

Brunauer (1943) classified adsorption isotherms into five types. These isotherms are shown in Figure 2. The type I curve is van der Waal's adsorption or Langmuir's (1918) adsorption. Type II is called the S-shaped or sigmoid curve. This curve describes the adsorption of water vapor by cereal grains such as grain sorghum. The rest of the curves have no names. Type III is closely related to type II. Types IV and V result in the adsorption onto highly porous adsorbents. ✓

Many theories and equations have been developed to describe the adsorption isotherm. The sigmoid curve, because of its great importance, has been the main curve studied. Although many equations and theories have been developed, adsorption is still not completely understood.

The first theoretical treatment of the adsorption isotherm was made by Langmuir (1918). Langmuir used three assumptions to arrive at an equation that represents the type I Brunauer curve. The following assumptions were made: 1) the surface of the adsorbent has the same energy of adsorption at every point, 2) when a gas comes in contact with a surface it behaves as an ideal gas and condenses onto the surface in one molecular layer, and 3) the rate of adsorption is related to the number of molecules hitting the surface, the surface area already occupied, and the number of molecules that remained in contact long enough for an energy change.

Langmuir¹ developed the equation

¹All of the equations in this thesis are valid in any consistent system of units unless specified otherwise.

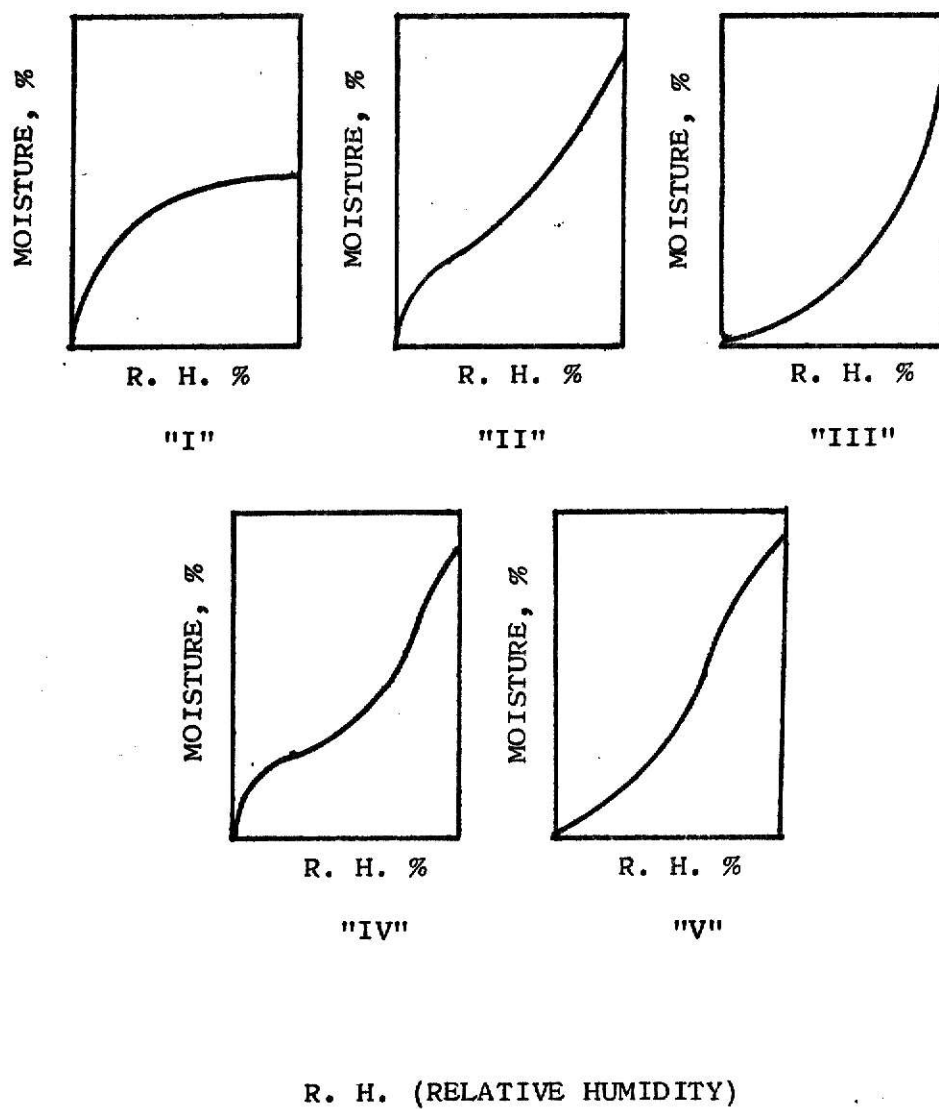


Figure 2. Types of adsorption isotherms according to the classification of Brunauer (1943).

$$m = bP / (1 + bP), \quad (1)$$

where m is the ratio of the amount of gas adsorbed to the amount adsorbed at surface saturation, b is a constant, and P is the equilibrium pressure.

The sigmoid curve, type II, is better described by a multimolecular layer theory. Polanyi (1916) was the first to consider multimolecular adsorption. His potential theory states that the surface potential for adsorption extends up through the first layer to bind another, forming multimolecular layers. The density of the bottom layer would be the greatest, compressed by the layers above it. The top layer would have the density of the gas. The forces attracting the molecules to the surface decrease with distance. The force can be defined as an adsorption potential E_i . Polanyi represented this potential by the following integral with respect to pressure dP :

$$E_i = \int_{d_x}^{d_i} V \, dP, \quad (2)$$

where d_i is the density of the adsorbed substance, d_x is the density of the gas phase, and V is the adsorbed volume. The potential theory also assumes that the adsorption potential does not change with temperature, which is denoted as

$$dE_i/dT = 0. \quad (3)$$

The potential theory can only be used by experimentally finding one isotherm and predicting others. Many studies of this theory have been made and it has been used to develop other isotherm equations.

The polarization theory by DeBoer and Zwicker (1929) was the first to account for the sigmoid isotherm. DeBoer and Zwicker explained the adsorption by assuming that the surface induces dipoles in the first layer and the first layer in turn induces dipoles in the second etc. until many layers are formed. DeBoer and Zwicker developed the equation

$$\ln(P_n / K_3 P_o) = K_2 K_1^n, \quad (4)$$

where P_n is the equilibrium pressure of the n 'th layer, P_o is the saturation vapor pressure, all the K terms are constants, and n is the ratio of the volume of gas adsorbed at P_n to the volume of gas adsorbed to cover one unimolecular layer. Bradley (1936) later developed the same equation except that the constant K_3 was equal to unity.

The theory that is the most widely tested and used is the theory of multimolecular adsorption developed by Brunauer, Emmett, and Teller (1938), which will be referred to as the BET theory in this thesis. The equation they developed is a generalization of the work by Langmuir (1918). They assumed that the heat of liquefaction is equal to the heat of adsorption of a bulk liquid. The evaporation-condensation cycle at equilibrium explains the adsorption for each layer. The rate of condensation onto the surface is equal to the rate of evaporation from the first layer. This is extended to say that at equilibrium the rate of condensation onto the i 'th layer is equal to the evaporation from the $(i+1)$ 'th layer. They developed the equation

$$V = V_m C P / (P_o - P) \left[1 + (C-1) (P/P_o) \right], \quad (5)$$

where V is the volume adsorbed, V_m is the volume adsorbed when the entire surface of the adsorbent is covered with one layer, C is a constant, P is the partial pressure of the vapor, and P_0 is the saturation vapor pressure. The constant C is usually much greater than unity; therefore, the isotherm will consist of two regions. A smaller C causes a reduction in the sigmoid shape which can be seen in the lower pressure region. At P much less than P_0 , the equation reduces to

$$V = (V_m CP/P_0)/(1+CP/P_0), \quad (6)$$

which is concave to the pressure axis and is a special case of Langmuir's equation. At higher pressures, at which P approaches P_0 , the volume becomes large. At this point the curve becomes convex to the pressure axis. Thus, the equation also accounts for the sigmoid curve. The equation can be put in the form

$$P/V(P_0-P) = 1/V_m C + (C-1)(P/P_0)/V_m C \quad (7)$$

for testing. Plotting $P/V(P_0-P)$ against P/P_0 should yield a straight line. From the slope $(C-1)/V_m C$ and the intercept $1/V_m C$ the unknowns V_m and C can be evaluated. The constant C can be defined approximately as follows:

$$C = (E_1 - E_L)/RT, \quad (8)$$

where E_1 is the heat of adsorption of the adsorbate in the first adsorbed

layer, E_L is the heat of condensation of the adsorbate, R is the universal gas constant, and T is the absolute temperature.

A solution of the condensing vapor and the adsorbent results in some systems at high relative humidities. The Flory-Huggins theory considers the interaction of solid and vapor to be a solution phenomenon in which polymer segments are equivalent and interchange with vapor molecules. This theory, developed by Flory (1942) and Huggins (1943), has been applied with partial success to higher vapor pressures but does not describe the lower region at all.

Hoover and Mellon (1950) proposed that many isotherms between 30 and 90 percent relative humidities could be described by the simple equation

$$\log V = KP/P_0 + b, \quad (9)$$

where V is the volume adsorbed, P/P_0 is the relative vapor pressure and K and b are empirical constants. Hoover and Mellon tested adsorption onto proteins and compared their results with the polarization theory by Bradley. They stated that the equation by Bradley (1936) was good for relative humidities of 6 to 93 percent.

Studies based on statistical thermodynamics have been done. Hill (1950) derived the equivalent of the BET equation using the methods of Fowler and Guggenheim (1939). He also corrected and extended the attempt of Cassie (1945) to account for sorption by wool.

Huttig (1948) developed an isotherm equation by a slight modification of the BET equation. Huttig developed the equation

$$V/V_m = C(P/P_0)(1 + P/P_0)/(1 - CP/P_0). \quad (10)$$

The notation is the same as for the BET equation. The BET equation and theory assumes that an overlying layer completely stops evaporation from a lower layer. The Huttig Equation (10) is not based on this assumption.

Smith (1947) divided sorbed water into two parts: 1) the amount of water that is bound to the inner or outer surface of an adsorbent by forces greater than those responsible for condensation of water, and 2) that which is normally condensed. Therefore

$$W = W_b + W_c, \quad (11)$$

where W is the total amount of water condensed onto the surface, W_b is the bound water at greater than condensation force, and W_c is that which is normal condensation. Smith defined W_c as follows:

$$W_c = -W' \ln(1 - P/P_o), \quad (12)$$

where W' is the weight of normally condensed vapor (per gram of sorbent) required to saturate the first layer of the W_c portion. Thus,

$$W = W_b - W' \ln(1 - P/P_o). \quad (13)$$

In a non-swelling substance a plot of W versus the dimensionless pressure function, $-\ln(1 - P/P_o)$, should be linear.

Becker and Sallans (1956), working with wheat, found that the BET equation holds up to 35 percent relative humidity. They also found that the Smith equation holds for the relative humidity range of 50 to 95 percent. They proposed that drawing a tangent to the Smith curve to

intersect the BET curve at its point of inflection, as shown in Figure 3, results in a good isotherm curve for wheat.

Cook (1948) criticized the BET equation and explained that the error above 35 percent relative humidity is due to one of the BET's basic assumptions, namely that the evaporation-condensation properties of the second layer and higher are not the same as the liquid state.

Henderson (1952) developed the equation

$$1 - RH = \exp(-KTM^n), \quad (14)$$

where RH is the relative humidity in decimals, K is a factor varying with the material, T is the absolute temperature in degrees Rankine, M is the equilibrium moisture content (percent dry basis), and n is an exponent varying with the material.

Hall and Rodriguez-Arais (1958) used shelled corn for experimentation. They concluded that the BET equation yielded satisfactory plots in the 5 to 35 percent relative humidity range. The Smith equation was good in the 45 to 90 percent range. The equation by Henderson was good in the 10 to 60 percent range. They stated that the method of Becker and Sallans was an excellent approach to find the intermediate range.

Although he didn't produce an isotherm equation in comparison to the ones already discussed, Othmer (1940) developed the following equation:

$$\log P = L_v \log P_r / L_{vr} + C, \quad (15)$$

where P is the vapor pressure of the grain moisture at equilibrium, P_r is

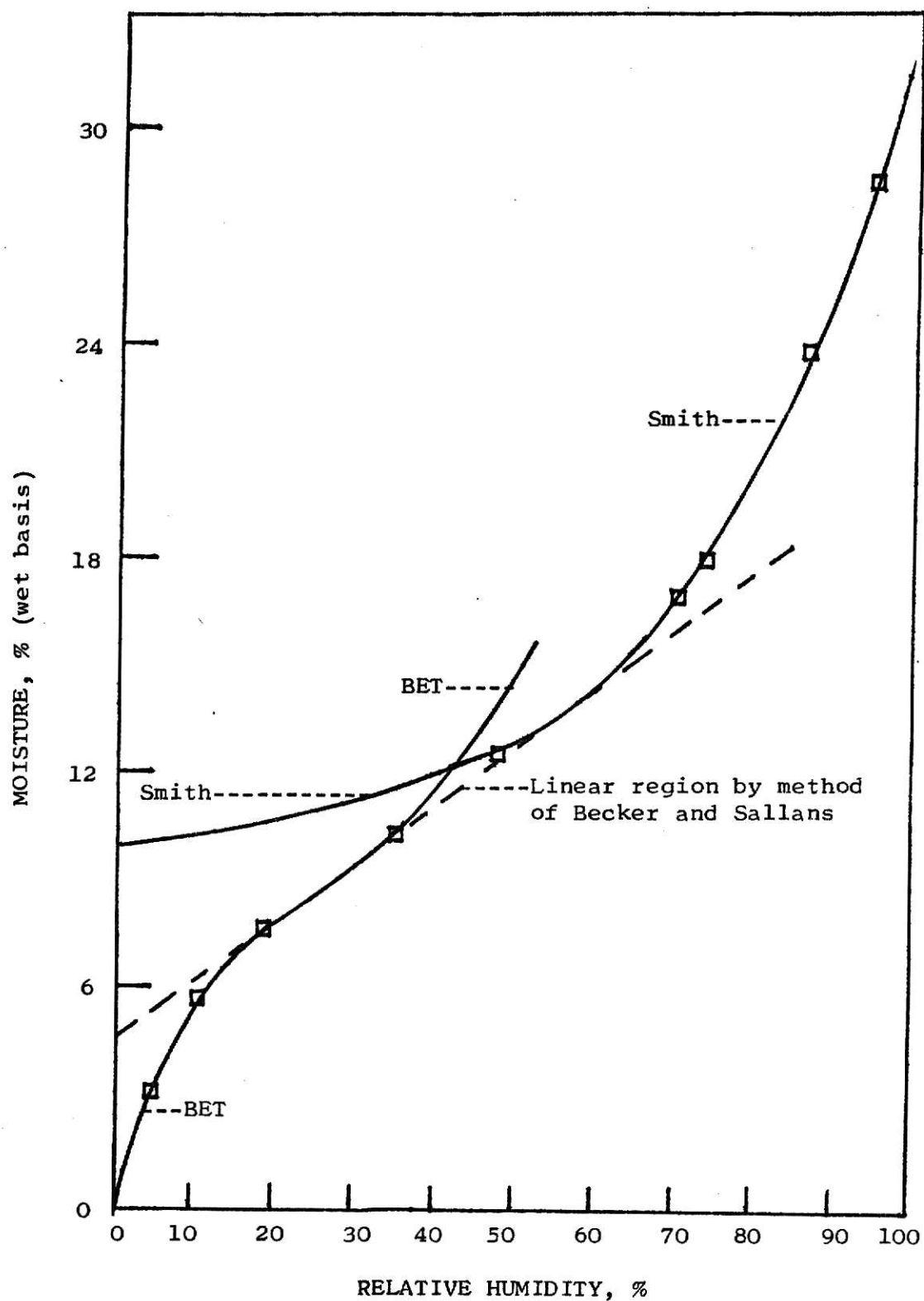


Figure 3. Desorption isotherm of wheat at 25 C showing the method of Becker and Sallans (1950) for the linear region from the curves of the BET and Smith equations.

the vapor pressure of water at the same conditions, L_v is the heat of vaporization of the grain moisture, L_{vr} is the heat of vaporization of water, and C is a constant. All the defined parameters are taken at the same temperature. A plot of $\log P$ versus $\log P_r$ produces a straight line which has the slope L_v/L_{vr} . This slope defines the constant grain moisture content line. Thompson and Shedd (1954) showed that for wheat and corn the Othmer lines give good results in the intermediate range of relative humidities.

Haynes (1961) tested seven grains and found that he could represent six of them (blue lupine, crimson clover, rescue, wheat, corn, and sorghum) by the following equation:

$$Y = C + C_1 X_1 + C_2 X_2 + C_3 X_2^2 + C_4 X_1 X_2, \quad (16)$$

where Y is the logarithm of the seed moisture vapor pressure; X_1 is the logarithm of the pure water vapor pressure at the test temperature; X_2 is the seed moisture content, dry basis; and all the C terms are constants. Haynes credited the isotherm equation to Dr. W. D. Hanson, formerly with Biometrical Services, Plant Industry Station, Beltsville, Maryland.

Day and Nelson (1965) modified the equation by Henderson. The modification was made to account for the temperature dependence of Henderson's constants. The modified equation is

$$1 - P/P_0 = \exp(-aM^b), \quad (17)$$

where $a = a'T^{a''}$, $b = b'T^{b''}$, and the rest of the terms are defined the

same as used earlier in Henderson's equation. The a and b terms are empirical constants. Day and Nelson found that the modified equation for wheat was good for relative humidities up to 70 percent.

Chung and Pfoest (1967) developed the isotherm equation

$$\ln(P/P_0) = -(A/RT)\exp(-BM), \quad (18)$$

where P/P_0 is the equilibrium relative humidity, R is the universal gas constant, T is the absolute temperature, M is the equilibrium moisture content, and A and B are constants. Chung and Pfoest assumed that the free energy function decreases exponentially with the increasing thickness of the adsorbed layer or moisture content. This assumption is stated mathematically as

$$DF = -A\exp(-Bm), \quad (19)$$

where DF is the free energy change. Setting the above assumption equal to the equation for free energy change,

$$DF = RT\ln(P/P_0), \quad (20)$$

leads to the isotherm Equation (18). Chung and Pfoest found that for corn the equation covers a wide range of relative humidities and they stated the basic assumption should hold for other cereal grains and their products.

Strohman and Yoerger (1967) developed the equation

$$\ln(P/P_s) = -\ln(P_s/P_0) f_3(M), \quad (21)$$

where P_s is the saturation vapor pressure of water, P is the equilibrium vapor pressure of the grain moisture, P_0 is the characteristic pressure, and $f_3(M)$ has many values. One value given for $f_3(M)$ was $\exp(-Bm)$, which makes this equation very similar to the equation developed by Chung and Pfost. Strohman and Yoerger developed their equation from Othmer lines in comparison to the free energy approach used by Chung and Pfost. Strohman and Yoerger put the equation in final form as follows:

$$P/P_0 = \exp[a \exp(bm) \ln P_0 + c \exp(dm)], \quad (22)$$

where a , b , c , and d are constants depending on the grain used, and m is the equilibrium moisture content as used previously. They found, for corn, that $a = -0.8953$, $b = -0.1232$, $c = -5.482$, and $d = -0.1917$.

Chen (1969) developed the isotherm equation

$$Y = \exp(K + me^{nx}), \quad (23)$$

where Y is the relative humidity; m is the equilibrium moisture content, wet basis; and k , n , and x are constants. The governing theory involves the assumption that diffusion is the rate controlling mechanism.

Nelson, Clary, and Agrawal (1969) developed the equation

$$w = f_1(w) + f_2(w)T, \quad (24)$$

where $f_1(w)$ and $f_2(w)$ are functions of relative humidity, w is the average weight fraction of water in seeds, and T is the absolute temperature. The

equation was developed by referring to the curves relating relative humidity, moisture content, and temperature as shown in Figure 4. Empirically it was shown for rough rice that the moisture content decreases with increasing temperature and that the constant relative humidity lines are straight and nearly parallel. These two facts suggest the equation as stated. The functions $f_1(w)$ and $f_2(w)$ were defined empirically for peanut hulls so that the above equation became

$$M^S = C_1 Rh + C_2 Rh^2 + C_3 T + C_4 RhT, \quad (25)$$

where M^S is the moisture content of the swollen hull in percent, Rh is the relative humidity in percent, and T is the test temperature in degrees centigrade. Nelson, Clary, and Agrawal also investigated several sorption equations which include BET, Chung and Pfoest, Smith, Strohman and Yoerger, and others.

Ngoddy and Bakker-Arkema (1970) developed an isotherm equation with the assumption that the basic concepts of the theory of Polanyi, the kinetic concept as exemplified by the BET theory, and Zsigmondy's (as used in this reference) "capillary condensation" theory, may be coordinated into a self contained model of sorption. The equation developed is not in a form that can be used easily so it will be neglected for the present. The basics of the equation are very good and the resulting equation may have a lot of merit.

Hysteresis

Many investigators have observed that when agricultural products are allowed to reach equilibrium by adsorption and by desorption the

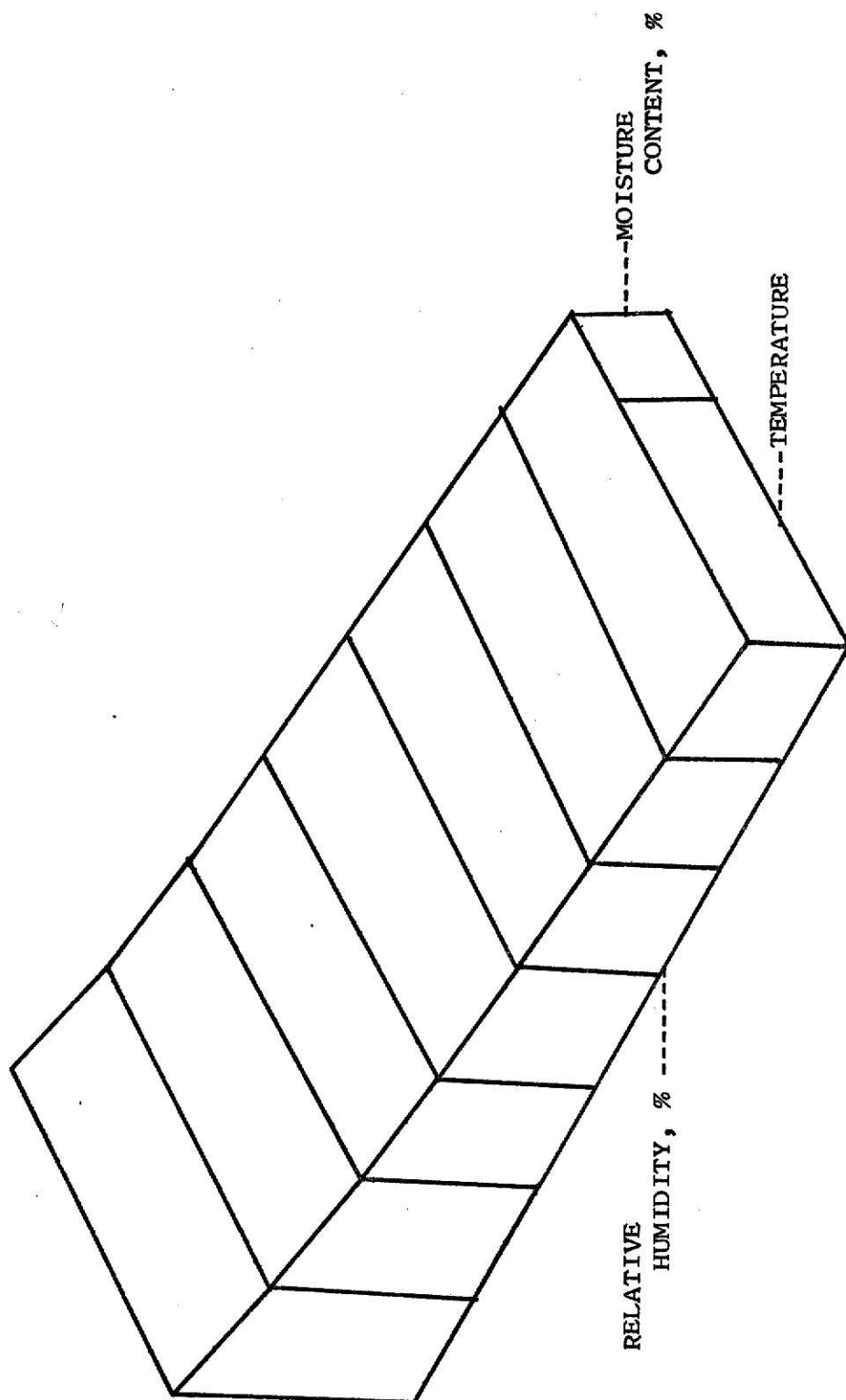


Figure 4. Relative humidity, equilibrium moisture content, and temperature diagram as discussed for the Nelson, Clary, and Agrawal (1969) equation.

equilibrium moisture contents are different. The equilibrium moisture content for desorption is higher than that of adsorption. This phenomenon is known as hysteresis. Many theories have been developed to explain hysteresis. Most of the theories are based on the capillary structure of the adsorbent.

Zsigmondy (1911) made the first explanation of hysteresis. He stated that during adsorption incomplete wetting takes place in the capillaries because of impurities, mostly permanent gases adsorbed on the walls of the capillary. This causes the adsorption moisture content to be lower than the desorption moisture content.

Smith (1947) suggested that hysteresis is due to swelling which increases the surface area and due to the presence of rigid structural elements of much greater dimensions than those of the sorbate molecules. This is very similar to the view supported by Cassie (1945). Cassie stated that the difference shown by vapor pressure isotherms is largely a reflection of mechanical hysteresis. At a given region, or at a given swelling, the hydrostatic pressure on the adsorbed water will be greater during adsorption than during desorption.

Young and Nelson (1967) stated that hysteresis is subject to a wetting environment. The water that is first adsorbed on the surface forms into a unimolecular layer. The surface molecules of the cell exert binding forces on the molecules preventing them from moving inward. As the amount of water builds up, the diffusional forces exceed the binding forces and allow some molecules to move into the cell. During desorption there is no force to pull the moisture out of the cell until all of the moisture has been removed from the surface.

Chung and Pfof (1967) postulated the cause of hysteresis by introducing the hypothesis that more sorption sites are available to water vapor during the desorption process than during the adsorption process. They justified their hypothesis by investigating the difference between the heat of adsorption and the heat of desorption. Chung and Pfof explained the causes of difference in the availability of sorptive sites in the sorption process by crack formation due to wetting (increase in sites) and by molecular shrinkage (decrease in sites). Strohma and Yoerger described this explanation as excellent. Chung and Pfof also investigated the hysteresis effect as it cycles around the hysteresis loop. They found that hysteresis tends to disappear. Henderson (1969) found the same effect.

Henderson (1969) also investigated the effect of respiration on hysteresis. Respiration was found not to effect the hysteresis of rice for the regions tested. Henderson suggested that the respiration effect should be investigated for high moisture contents during the long periods of time required for equilibrium conditions.

Hart (1964) found that as temperature increases, the hysteresis effect decreases. He also found that the initial rate at which high moisture wheat loses moisture is greater than the rate at which low moisture wheat regains moisture.

Dynamic Versus Static Equilibrium

During storage the equilibrium moisture content of a grain is reached by static conditions. The moisture content reached in an aerated storage or during drying is reached by dynamic conditions.

The solution of a differential equation describing the drying process needs an equilibrium moisture content as a boundary condition. In many cases theoretical equations have not satisfied experimental values when static equilibrium moisture content was used. Jones (1951) originated the idea of using a dynamic equilibrium moisture content instead of static equilibrium moisture content in describing the drying process with Fick's diffusion equation. Jones stated that during the falling rate period of grain drying, as shown in Figure 5, the surface moisture content of a grain remains above the static equilibrium moisture content.

McEwen, Simmonds, and Ward (1954) defined static and dynamic equilibrium moisture contents based on the way they are measured. In the static method a sample is stored in a constant relative humidity and temperature environment until equilibrium is reached. The dynamic equilibrium moisture content was defined as the asymptotic value of the drying curve, as shown in Figure 6.

Bakker-Arkema and Hall (1965) reviewed the literature on dynamic equilibrium content and tested alfalfa which could be cut into thin slices to determine the surface moisture content. The surface moisture was found by using thin slices of the surface. They found that the principle of dynamic equilibrium moisture content is questionable, at least for forage wafers. They stated that the wafer surfaces reached static rather than dynamic equilibrium moisture content.

The problem of dynamic equilibrium moisture content versus static equilibrium moisture content is still to be resolved. Are they the same, is static moisture content a good boundary condition, or is there a dynamic moisture equilibrium that is as yet not defined for the drying process?

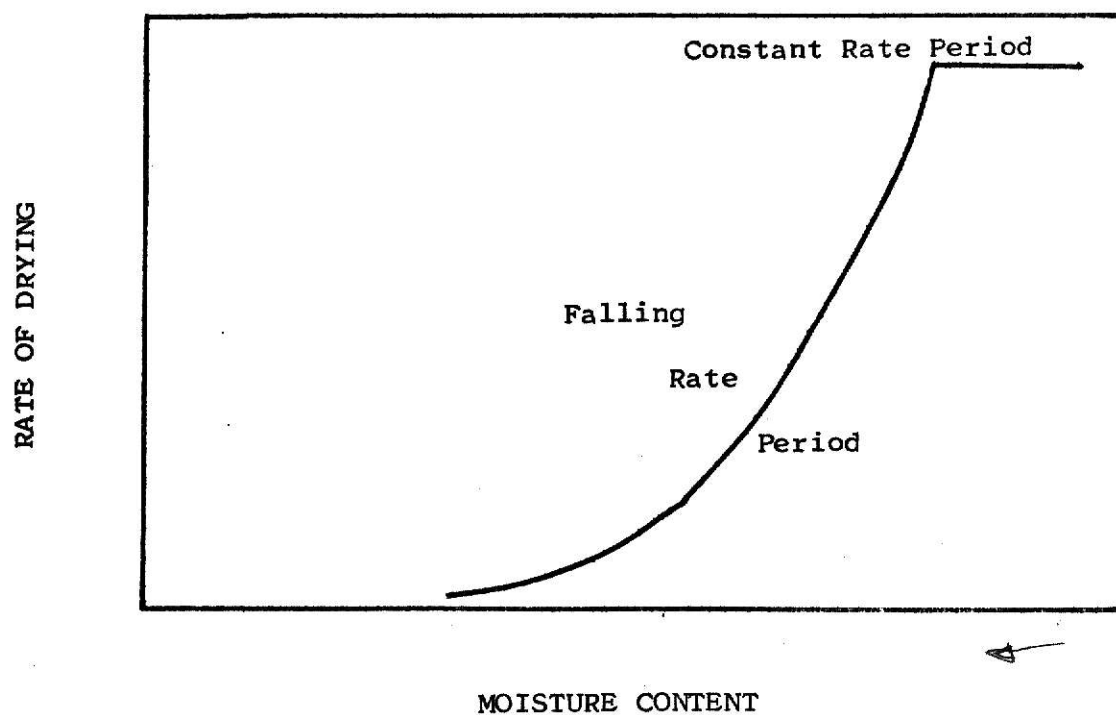


Figure 5. An example curve demonstrating the falling rate period.

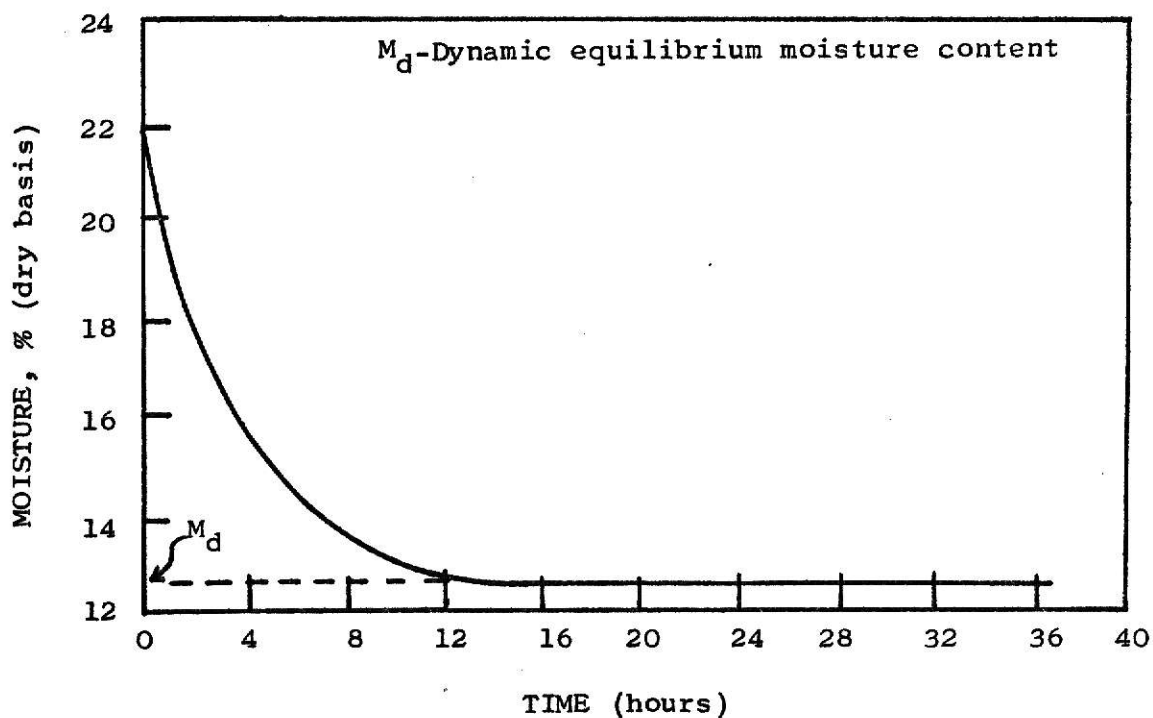


Figure 6. Moisture content of grain sorghum during drying as demonstrated by Hukill (1947).

Grain Sorghum Research

A lot of work has been done on equilibrium moisture contents for corn, wheat, and other agricultural grains, but very little has been done on grain sorghum. The Agricultural Engineering Yearbook (1970) makes reference to grain sorghum work by Coleman, Rothgeb, and Fellows (1928), Fenton (1941), and Haynes (1961). The tabulated data by Fenton, and Coleman, et al. is given in Table 8 in the Appendix. Figures 7 and 8 show the curves published in the yearbook and in the original publications by Fenton and Haynes.

Henderson (1952) tested his equation to the data by Fenton, and found that his equation fails below 35 percent relative humidity. The upper region of Fenton's curve is unreliable because of mold growth associated with the long exposure time required for static equilibrium. The curve by Henderson did hold up to 85 percent relative humidity for the one temperature isotherm tested.

Hukill (1947) made drying tests on corn and grain sorghum. He found that the heat required to remove moisture from both corn and grain sorghum is substantially greater than the heat of vaporization of pure water. This is very similar to the statement made by Cook (1948) when he criticized the BET equation.

Evidence shows that equilibrium moisture characteristics for grain sorghum are very much like wheat and corn in drying and storage. The only equations found in the literature that define parameters for grain sorghum equilibrium moisture content are the equations by Haynes, Henderson, and Chen.

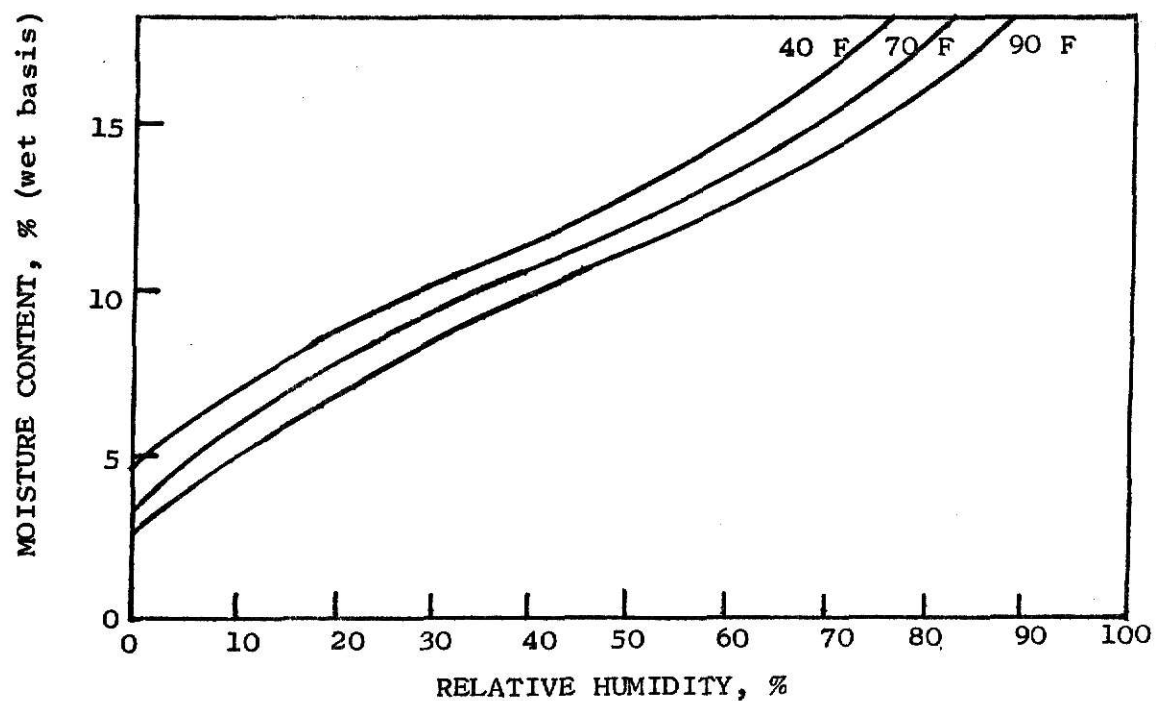


Figure 7. Grain sorghum isotherms by Fenton (1941)

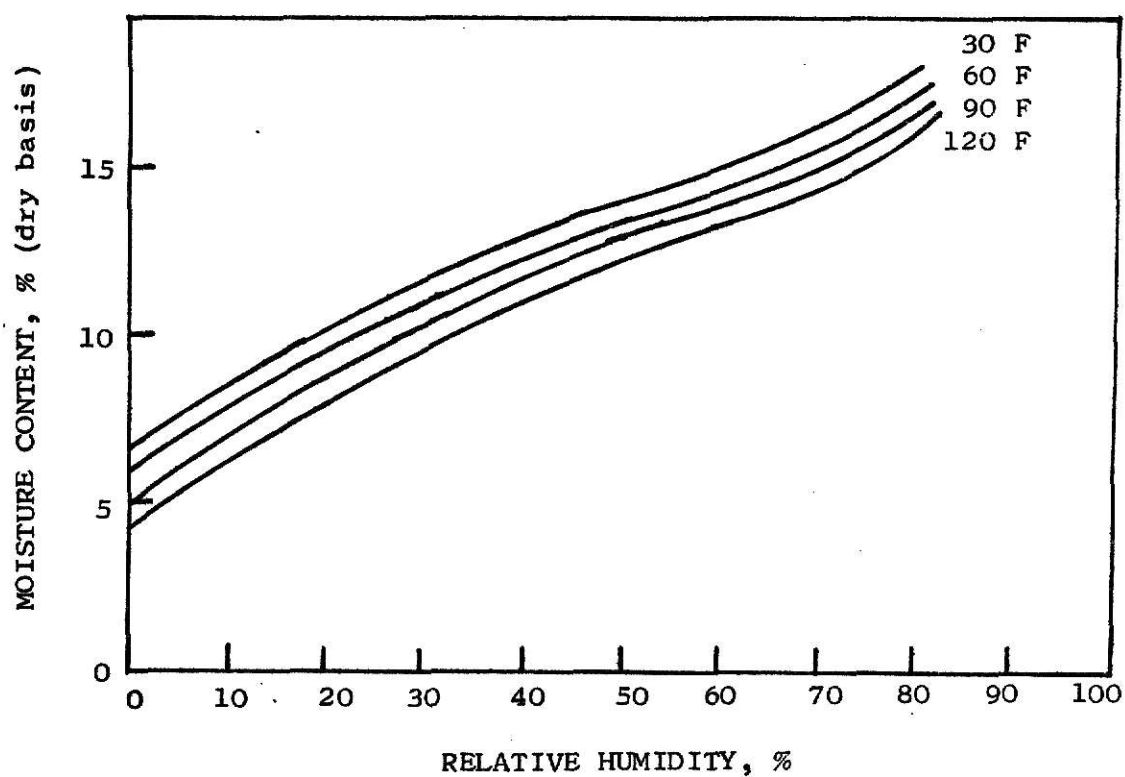


Figure 8. Grain sorghum isotherms by Haynes (1961)

INVESTIGATION

Objectives

The objectives of this investigation were:

- 1) To find the static equilibrium moisture contents for grain sorghum during adsorption and desorption for 60, 75, 90, 105, and 120 F for the entire range of relative humidities.
- 2) To test the fit of the results in equations by Brunauer, Emmett, and Teller (1938), Smith (1947), Henderson (1952), Bradley (1936), and Chung and Pfost (1967).
- 3) To develop an equation that will predict any equilibrium moisture content for grain sorghum between temperatures of 60 and 120 F, and over the entire range of relative humidities.
- 4) To determine at least one dynamic equilibrium moisture content and to compare it with static equilibrium moisture.
- 5) To study hysteresis volume change of the grain during adsorption and desorption.

Procedure, Materials, and Equipment

Field-harvested grain sorghum was obtained at 30.55 percent moisture content, dry basis. Some physical properties of the grain sorghum used are listed in Table 1. The samples used for desorption were taken directly from the field-harvested grain. The adsorption samples were oven dried at 120 F to 3 percent moisture content, dry basis. The sample sizes were 2.5 to 4.0 grams.

Table 1. Some physical properties of the grain sorghum used.

Grain Sorghum	Hulting Hybrid 556
Test Weight	52.5 lb./bu.
<i>Moisture</i> Initial Moisture Content	30.55% dry basis
USDA Sieve Test	
Broken, Passing $5/64$ triangular sieve	3.86%
Dockage, Passing $2\frac{1}{2}/64$ round sieve	0.25%
Particle size analysis by Tyler Standard Sieves	
<i>Remainder</i> Remaining on #4	0.21% stem and leaves
Remaining on #6	32.40% whole large kernels
Remaining on #8	59.14% smaller kernels and large cracked pieces
Remaining on #10	4.52% cracked kernels and foreign materials such as leaves and dirt
Remaining on #20	2.82% cracked kernels and foreign materials, mostly leaves
Through onto the Pan	0.89% dirt and grain flour

99,98 - 1

The temperature control system is shown in Figure 9. Cold air at 50 F was supplied to the inlet B. The air pump F was used to force the air through the system. The 1000-volt resistance heater G, controlled by a #R7187D1019 Honeywell Controller J and a L7038A Honeywell Thermister I, heated the air to the desired temperature. For the higher temperatures some of the exhaust air was returned by the use of the valve E.

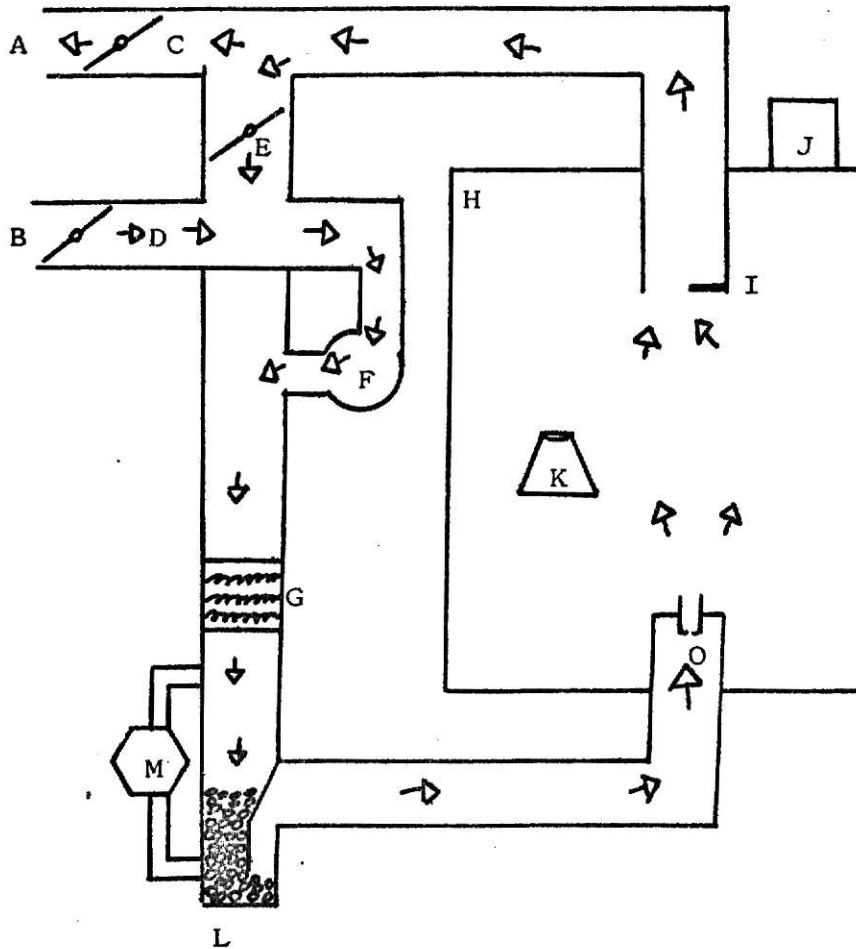
The temperature distribution in the control chamber H was checked initially and found to be uniform. Copper-constantan thermocouples connected to a 16-point recording potentiometer were used to sense and record the temperatures.

The relative humidity was controlled by solutions of sulfuric acid and distilled water. The concentration of the sulfuric acid, depending on the temperature, controlled the relative humidity. Data by Greenwalt (1925) was used to determine the solution concentration for each relative humidity. The initial concentrations by volume ranged from 11 to 60 percent sulfuric acid and established relative humidities of 2 to 90 percent.

The container used for relative humidity control was a 500 ml flask. This flask was filled with about 200 ml of sulfuric acid solution, and sealed with a No. 7 rubber stopper. The grain sample was placed in a screen basket and suspended above the solution in the sealed container. The flask containing the sample was placed in the temperature control chamber as shown in Figure 9.

The time required to insure that a sample reached equilibrium with its surroundings was found to be three weeks. This was determined by weighing the sample each day until the weight remained constant.

Fenton (1941) found unreliable results at high temperatures and high relative humidities because of mold growth. In this study mold growth



- | | |
|---|--|
| A. ^{found} Outlet | H. Controlled Chamber |
| B. Inlet | I. L7038A Honeywell Thermister |
| C. Outlet Control Valve ^{KNOWAN} | J. #R7187D1019 Honeywell Controller |
| D. Inlet Control Valve ^{beetle} | K. Grain Sample with Relative Humidity Control |
| E. Return Control Valve | L. Rocks for Dynamic Relative Humidity Control ^{water pump} |
| F. Air Pump | M. Water Pump |
| G. 1000 Volt Resistance Heater | O. Grain Placement for the Dynamic Trial |

Figure 9. The system used for temperature control and dynamic relative humidity control.

was inhibited by treating the samples with propionic acid for the tests at high temperatures and relative humidities. The concentration used was 0.4 percent by weight.

The moisture content at equilibrium was determined by the standard USDA two stage oven test (1959). The scales used weighed the samples to ± 0.001 grams.

The grain for the dynamic study was placed in the bottom of the control chamber in the duct as shown in Figure 9. For the dynamic desorption test the 50 F air supplied at B was heated to the desired temperature which lowered the relative humidity to about 10 percent. Experiments were conducted at 90 and 105 F. The relative humidity was measured by a dry bulb-wet bulb method. As the grain dried the weight change was recorded and the volume was measured by an air pycnometer. For the adsorption test the rocks L in Figure 9 were sprayed with water which increased the air relative humidity to about 90 percent.

RESULTS AND DISCUSSION

Experimental Isotherms

The equilibrium moisture contents for grain sorghum are given in Table 2, and plotted in isotherm curves in Figures 10 through 14. Figure 12 also shows a comparison of the results of this study to earlier work by Haynes and Fenton. The comparison is discussed on page 38. It can be seen that for both desorption and adsorption the equilibrium moisture content increases with an increase in relative humidity. This can be explained very simply. At equilibrium the vapor pressure of the water in the grain is the same as the pressure of water in its environment. As the environmental pressure increases, or relative humidity increases, the pressure of the water in the grain must increase to reach equilibrium. This results in an increase in moisture content.

Figures 10 through 14 also show that the equilibrium moisture content decreases with an increase in temperature. This can be explained by the "Principle of LeChatlier", Sienko and Plane (1957). The principle states that if a stress is applied to a system at equilibrium, the system will readjust to decrease the stress. The stress in this case is a function of temperature. As the temperature increases the kinetic energy increases, causing an increase in stress. To reduce this stress some of the molecules escape to the environment, thus decreasing the moisture content. The temperature dependence can be seen for desorption isotherms as shown in Figures 10 through 14. The adsorption isotherms show no significant temperature dependence.

Table 2. Experimental isotherm data for grain sorghum during adsorption and desorption.

Temperature (deg. Fahr.)	Relative Humidity** (%)	Moisture Content, % (dry basis)	
		Desorption	Adsorption
60	2.10	7.03	----
	4.46	7.34	----
	11.59	8.85	7.32
	20.72	10.82	8.64
	30.91	12.85	9.95
	42.95	14.89	11.25
	53.99	16.58	12.89
	67.91	19.03	16.35
	78.53	21.43	17.95
	89.63	25.08*	23.09*
75	2.31	5.56	----
	4.90	6.48	----
	11.73	8.15	----
	21.11	10.31	8.38
	31.17	12.10	9.40
	42.92	13.75	11.21
	53.51	15.39	12.57
	66.86	18.02	14.97
	78.12	20.29	17.44
	88.98	24.41*	-----
90	2.37	4.72	----
	5.01	5.73	----
	11.92	7.81	----
	21.33	9.60	----
	31.42	11.54	9.58
	43.25	13.61	11.12
	54.06	14.84	12.59
	65.54	17.21	14.86
	78.94	19.55	17.61
	90.05	23.69*	23.35*
105	4.99	5.64	----
	11.79	7.77	----
	21.14	9.30	8.32
	31.19	10.78	9.70
	42.84	12.64	11.01
	53.17	14.35	12.64
	66.79	16.58	14.96
	78.08	18.64	17.66
	88.91	23.73*	22.58*

Table 2 (cont.)

120	5.31	5.41	----
	12.05	7.27	----
	21.65	9.13	7.92
	31.85	10.94	9.34
	43.52	12.75	10.78
	53.65	14.34	12.69
	67.10	16.18	14.50
	79.08	-----	17.56
	89.72	-----	21.27*

* Grain treated with proprionic acid to inhibit mold growth.

** Calculated to these values from Greenwalt (1925).

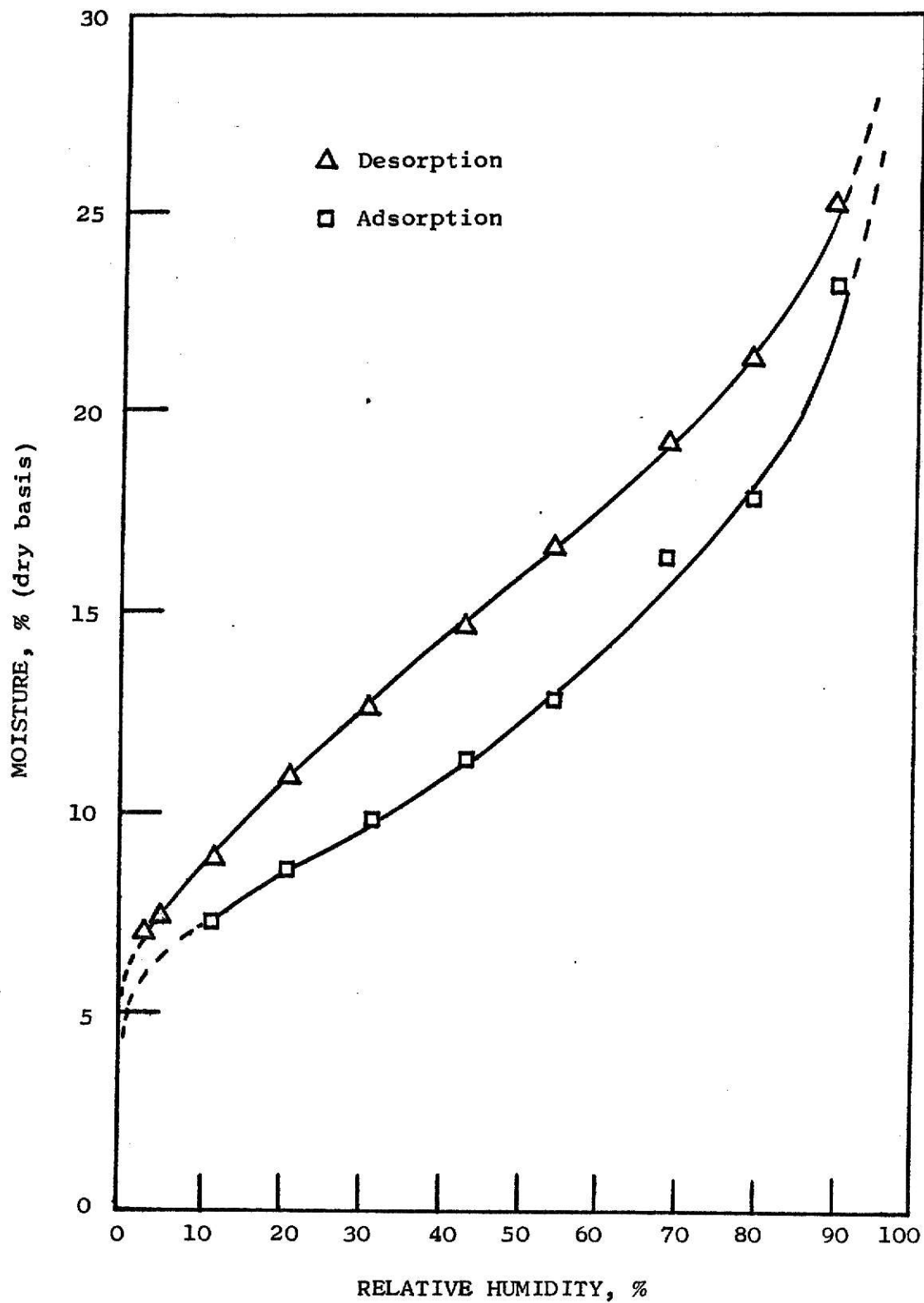


Figure 10. Adsorption-desorption isotherms of grain sorghum at 60 F showing hysteresis effect.

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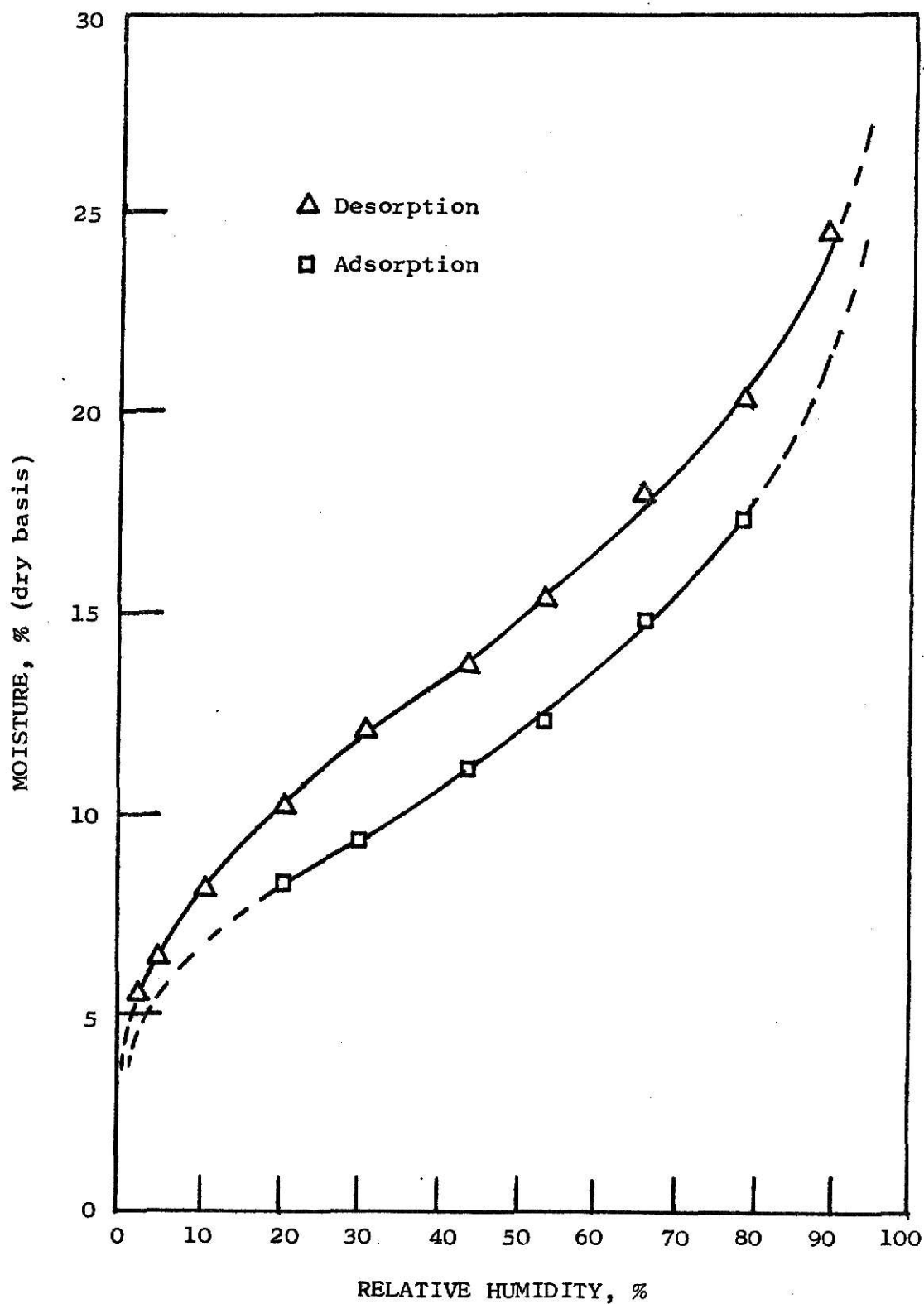


Figure 11. Adsorption-desorption isotherms of grain sorghum at 75 F showing hysteresis effect.

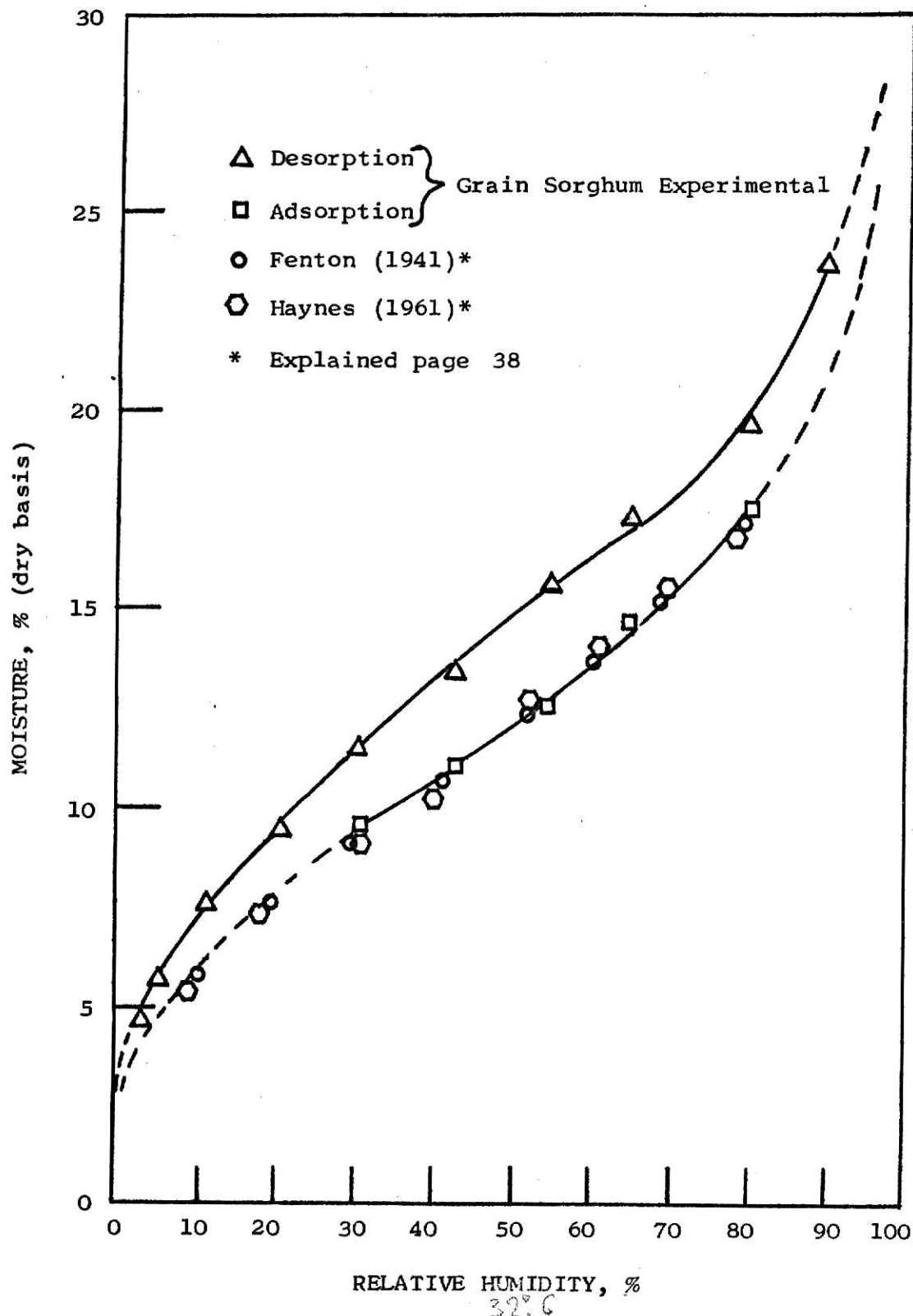


Figure 12. Adsorption-desorption isotherms of grain sorghum at 90 F and comparison to published data by Fenton and Haynes.

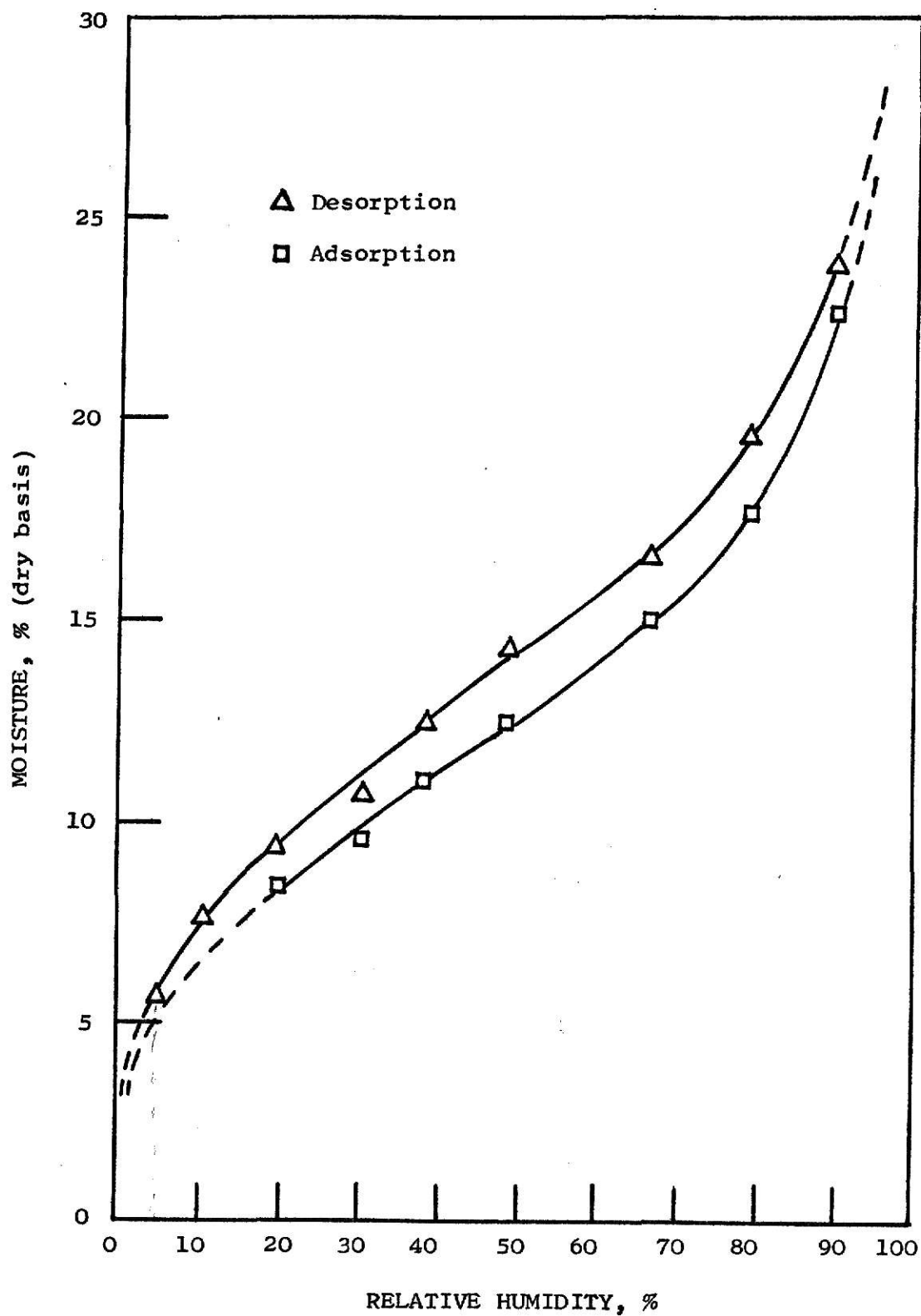


Figure 13. Adsorption-desorption isotherms of grain sorghum at 105 F showing hysteresis effect.

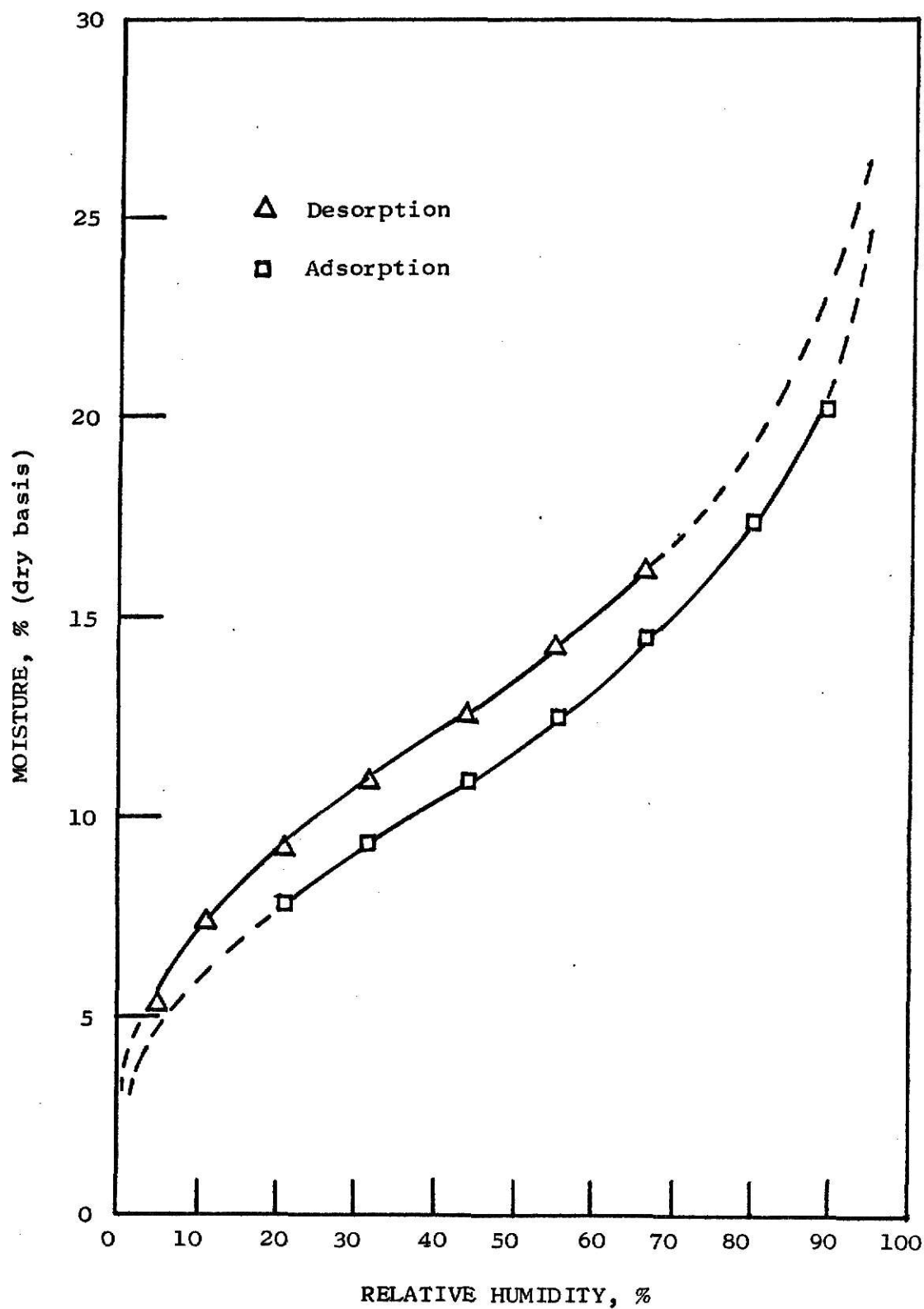


Figure 14. Adsorption-desorption isotherms of grain sorghum at 120 F showing hysteresis effect.

A comparison of results to earlier work would check the validity of the results. Figure 12 shows a comparison of results of this experiment to the results found by Haynes and Fenton. Fenton (although not stated in the publication) used an initial moisture content of about 12 percent dry basis, and found the equilibrium moisture contents for grain sorghum with the use of sulfuric acid solutions for controlling relative humidity. The 12 percent initial moisture content would mean that part of his data is desorption and part is adsorption. Assuming that the adsorption isotherm is the lowest moisture contents possible and the desorption isotherm the highest, Fenton's data should lie within the bounds of adsorption and desorption found by this investigation. This is shown in Figure 12. The data by Haynes, on the other hand, was collected by placing samples at known moisture contents in a sealed container and measuring the resulting relative humidity produced by the grain moisture. The history of the grain before it was placed in the container would determine the equilibrium point as desorption or adsorption. The history of Haynes' sample was very complex so that no decision could be made to establish his results as adsorption or desorption. The adsorption and desorption bounds should also define the results found by Haynes. The Haynes data should also lie between the adsorption and desorption bounds found by this investigator. This is shown in Figure 12.

The grain used by Fenton and Haynes also could vary because of grain variety or the condition of the sample, such as damaged kernels and foreign materials. Therefore an exact comparison of moisture contents cannot be made. The comparison discussed shows the validity of the results found by this experimenter compared to those of other researchers.

Application of the Isotherm Equations

Five different isotherm equations were tested to find their applicability to the results of this investigation. These equations are given in Table 3 with their equation number from the review of literature. Bradley's equation is the same as equation (4) in the review with K_3 equal to one. To apply these equations (see Table 3) they are put into the form

$$Y_i = A + BX_i \quad (26)$$

which is the model for simple linear regression given by Fryer (1966). Y_i is the ^{value} dependent variable, X_i is the ^{independent} independent variable, A is the intercept of the best fitting line, and B is the slope of the best fitting line. The best fitting line is found by a least squares analysis. Not all of the equations listed in Table 3 have a good correlation for the entire range of relative humidities. Therefore the portion of the range that has a correlation of at least ± 0.98 or better will be used to evaluate the constants in each equation.

Figures 15 through 19 show examples of the best fit linear plot for Y_i versus X_i for each equation tested. Similar results were found at all temperatures of desorption and adsorption. For each equation the linear portion found and shown in Figures 15 through 19 has an r of ± 0.98 or better. The entire range of data is linear only for the Bradley, Henderson, and the Chung and Pfoest equations. The equations by Smith and BET have a best fit with the required r for only a portion of the region. Table 9 lists the best fit region (relative humidity range), correlation, and constants for each equation when applied to the experimental results.

Table 3. Linear form of the five isotherm equations tested.

Equation	Equation Number in the Review	Y_i	=	A	+	B	X_i
BET							
$\frac{V}{V_m} = \frac{CP}{(P_o - P)(1 + (C-1)P/P_o)}$	5	$\frac{P/P_o}{V(1-P/P_o)}$		$\frac{1}{V_m C}$		$\frac{C-1}{V_m C}$	$\left[\frac{P/P_o}{P_o} \right]^{RT}$
Smith							
$W = W_b - W' \ln(1-P/P_o)$	13	W		W_b		$-W'$	$\ln(1-P/P_o)$
Henderson							
$1 - P/P_o = e^{-KTM^n}$	14	$\ln(-\ln(1-P/P_o))$		$\ln KT$		n	$\ln M$
Bradley *							
$\ln(P_o/P) = K_2 K_1^a$	--	$\ln(\ln P_o/P)$		$\ln K_2$		$\ln K_1$	a
Chung and Pfost							
$\ln P/P_o = -\frac{A}{RT} e^{-BM}$	18	$\ln(-RT \ln(P/P_o))$		$\ln A$		$\ominus B$	M

* Bradley's equation is the same as Equation (4) in the review with K_3 equal to 1.

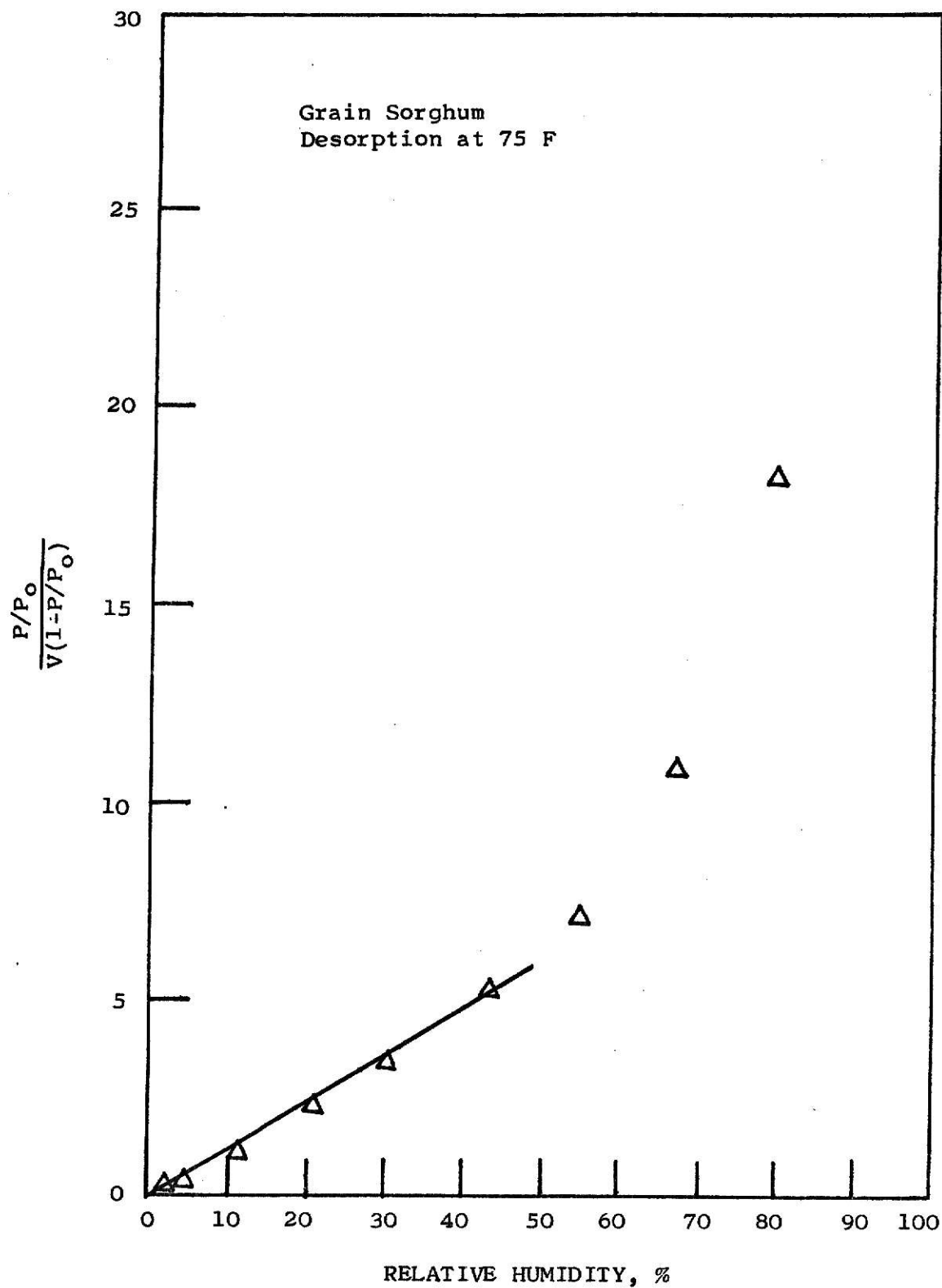


Figure 15. Plot of desorption data for grain sorghum at 75 F according to the BET equation.

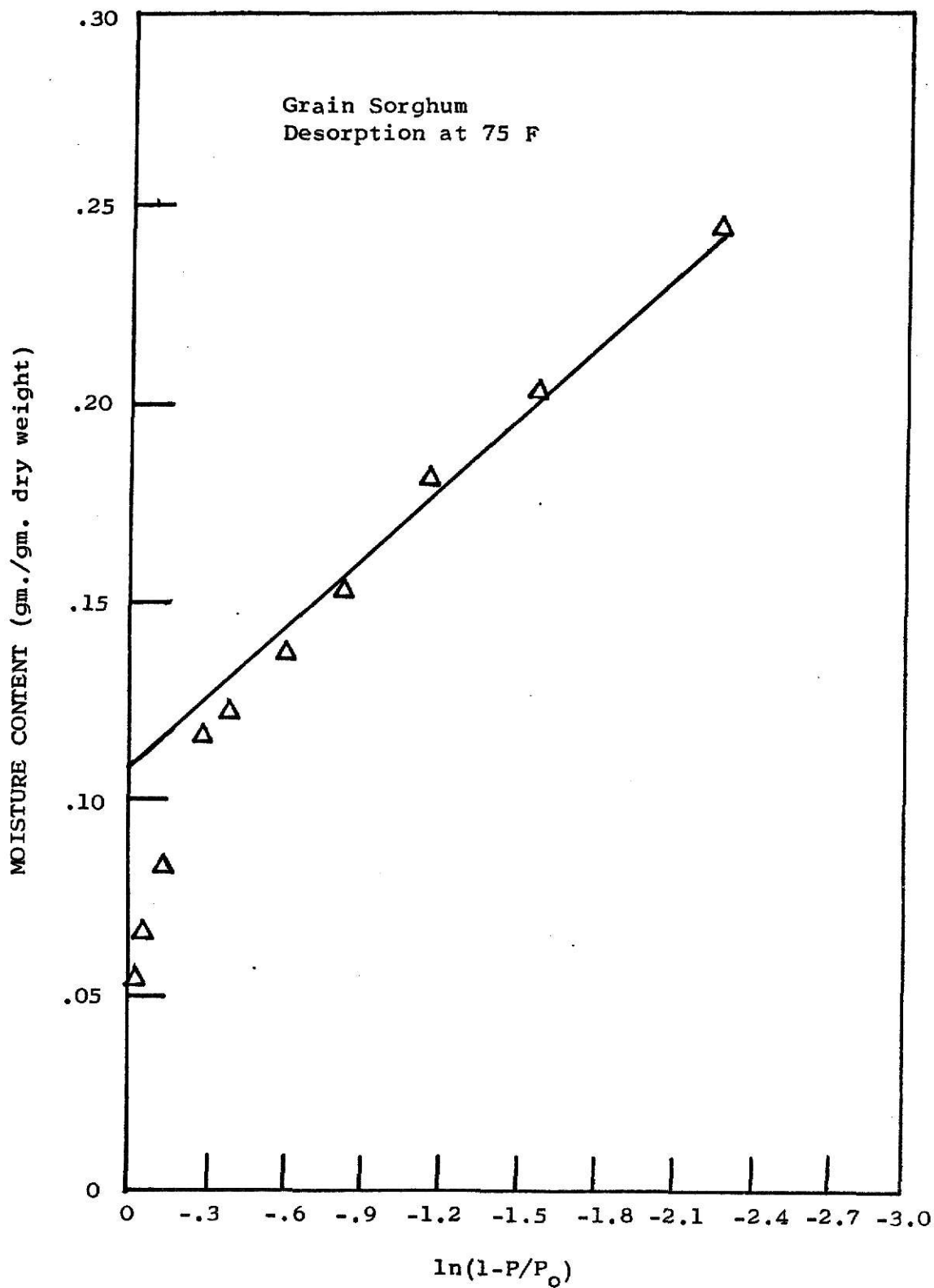


Figure 16. Plot of desorption data for grain sorghum at 75 F according to the Smith equation.

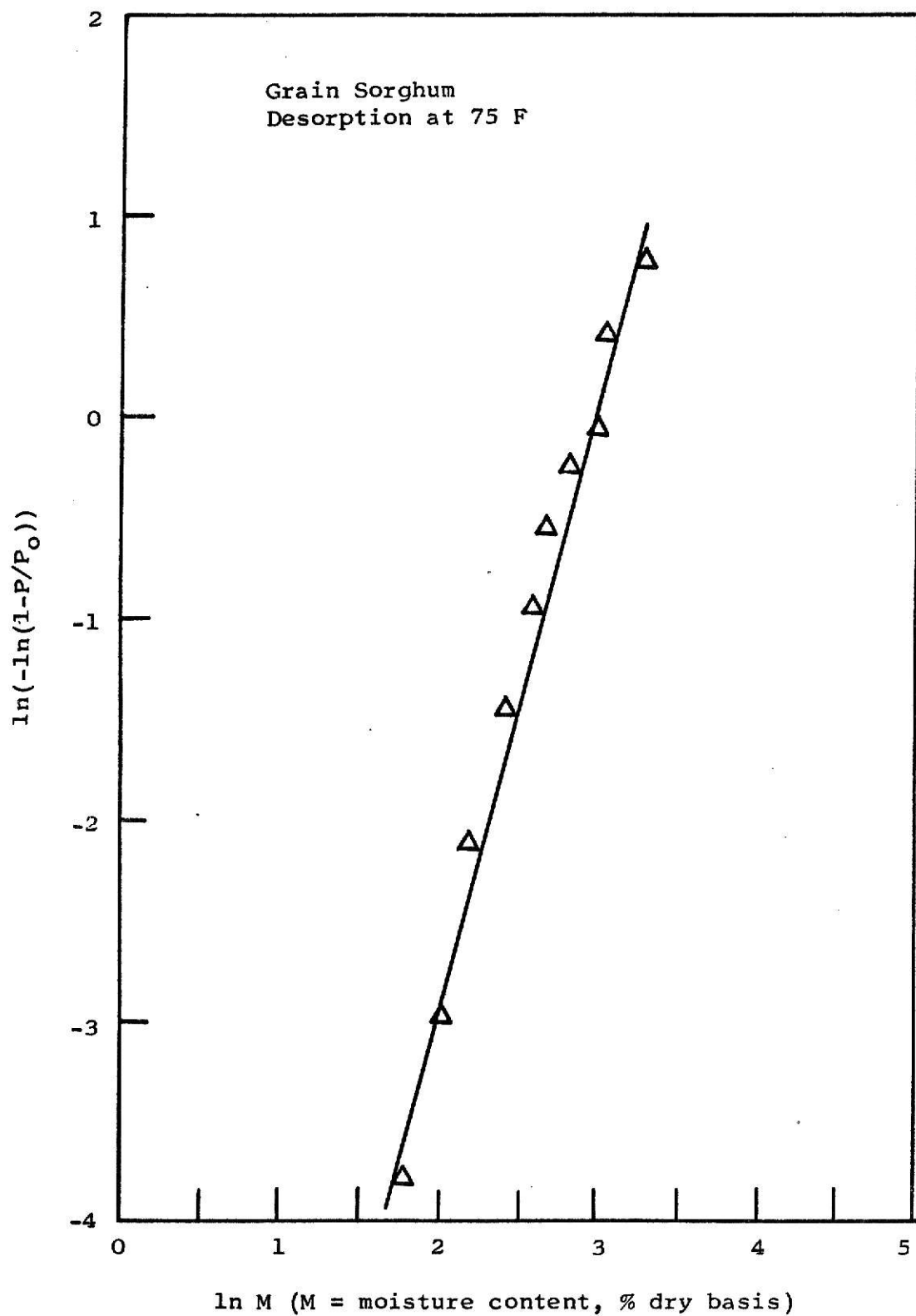


Figure 17. Plot of desorption data for grain sorghum at 75 F according to the Henderson equation.

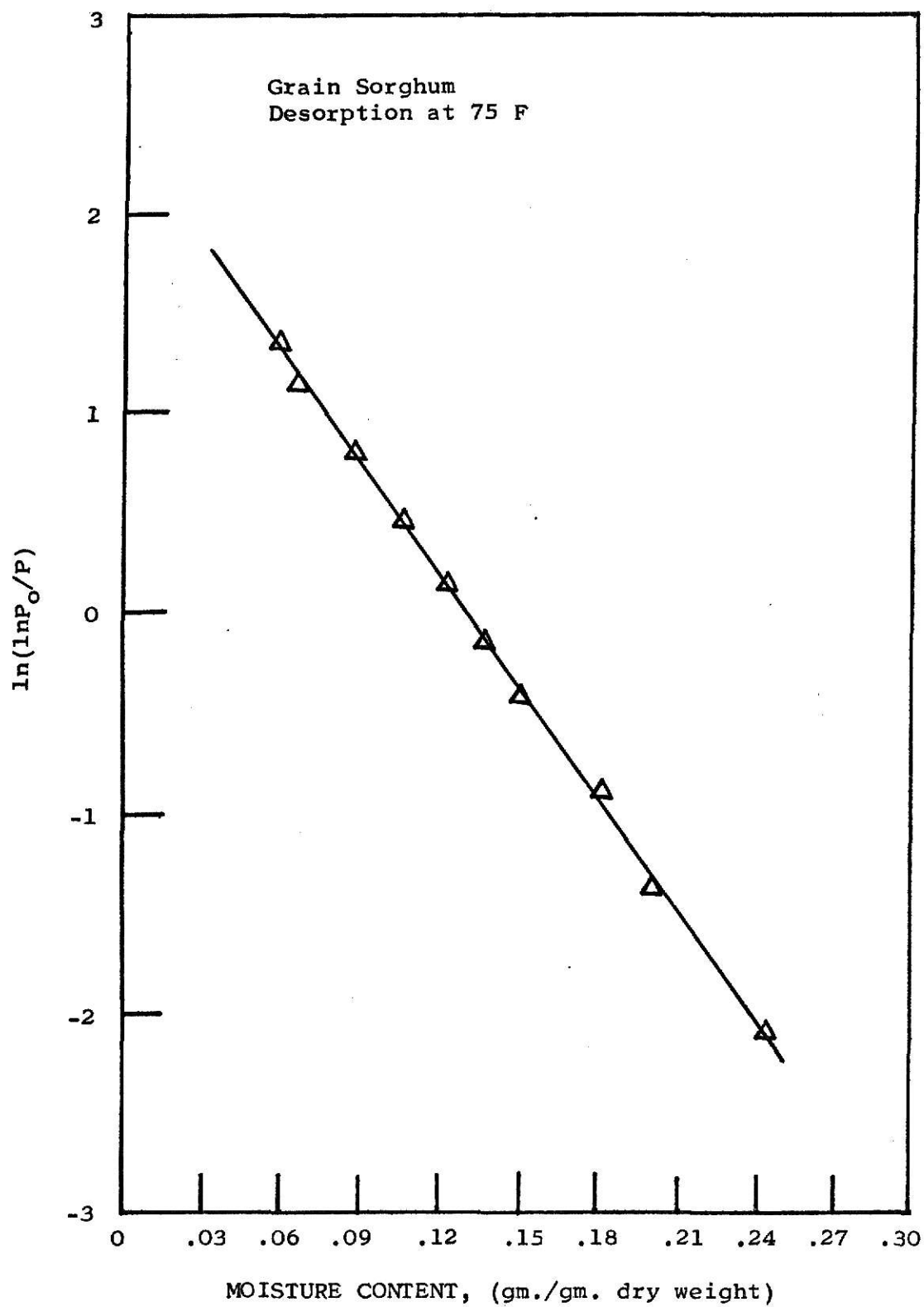


Figure 18. Plot of desorption data for grain sorghum at 75 F according to the Bradley equation.

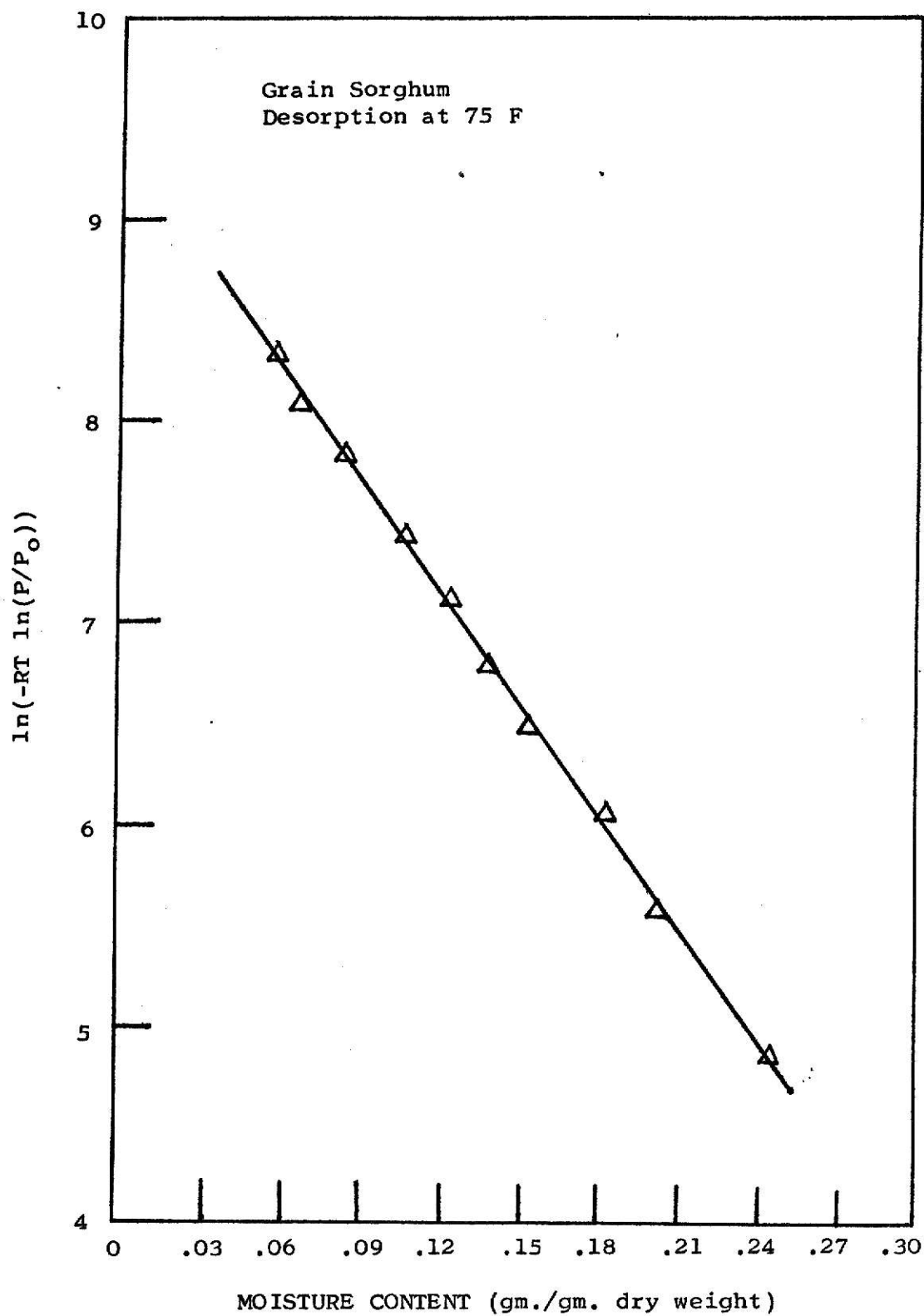


Figure 19. Plot of desorption data for grain sorghum at 75 F according to the Chung and Pfoest equation.

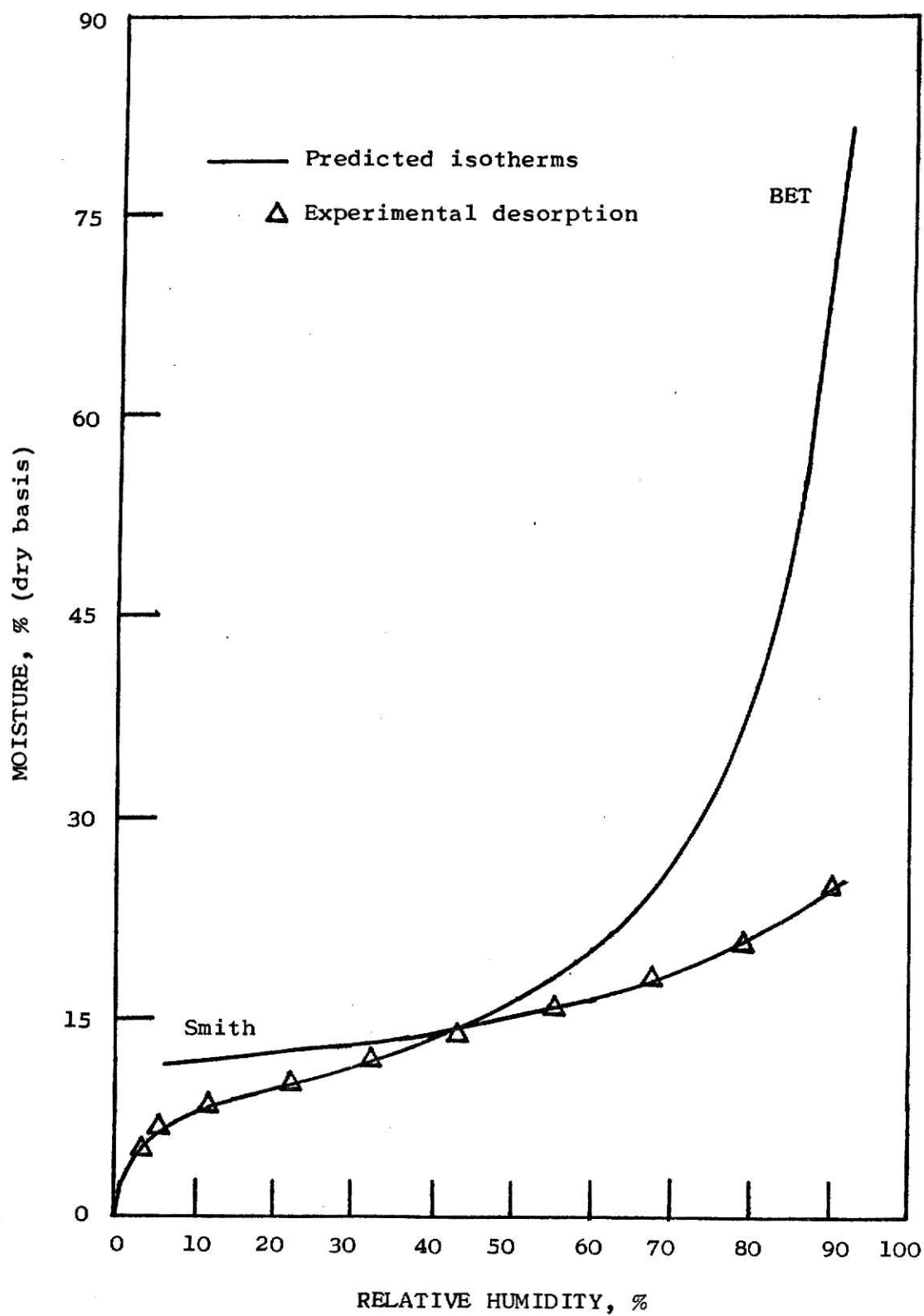


Figure 20. Comparison of the predicted isotherms by the BET, and Smith equations to the experimental desorption isotherm for grain sorghum at 75 F.

In each case the best fit region is used to find the constants for each equation. A comparison of equilibrium moisture contents predicted by the five isotherm equations with experimental data of this investigation is given in Table 10. The experimental values were taken from Figures 10 through 14.

The failure or success of the five equations to adequately predict isotherms can be used to characterize sorption phenomena. The predicted isotherms according to the Smith and BET equations for desorption at 75 F⁴²⁰ are given in Figure 20 and plotted from Table 10. The BET equation fails to predict the equilibrium moisture content above about 45 percent relative humidity. The BET equation was developed on the assumption that the evaporation-condensation characteristics of water at the second and higher layers on the adsorbent is the same as the bulk liquid. This has been proven false by Chung and Pfoest for corn by evaluating its heat of desorption. The isosteric heat of desorption is found by the use of the equation

$$DH_{st} = R \left[\frac{T_2 T_1}{T_2 - T_1} \right] \ln (P_2/P_1), \quad (27)$$

where P_1 and P_2 are the partial equilibrium pressures at the absolute temperatures T_1 and T_2 , respectively. The partial pressures were read from two isotherms at T_1 and T_2 at the same equilibrium moisture content. If T_1 and T_2 are close together, the value of DH_{st} (the heat of desorption in this case) may be taken as applying to both isotherms. However, a better approximation is to take an average isotherm whose temperature is given by

$$\frac{1}{T} = \frac{1}{2} \left[\frac{1}{T_2} + \frac{1}{T_1} \right] \quad (28)$$

and whose pressure is given by

$$P = \sqrt{P_1 P_2}. \quad (29)$$

The heats of desorption at 112 F were determined from equation (27) using data from the 105 and 120 F isotherms. The heats are given in Table 11 and in Figure 21. All of the heats of desorption evaluated are greater than the heat of vaporization of pure water. This has proven the BET assumption false. The heats of desorption for moisture contents of 15 percent and above are about 5 percent greater than the heat of vaporization of pure water.

Another factor influencing the failure of the BET equation is the shrinkage and expansion of porous grain sorghum. It will be shown later in a dynamic study that grain volume decreases and increases due to successive desorption and adsorption processes. The BET equation which was developed for a solid having a smooth surface does not explain sorption for grain sorghum.

The Smith equation explains the upper region of the curve as shown in Figure 20 but fails as it gets down into the expansion and shrinkage area of the curve. This is at a point on the linear portion of the curve where the sorptive area is significantly changed by expansion or shrinkage. The Smith equation is also dependent upon the area of sorption which explains why it fails in the expansion and shrinkage area of the curve. It also assumes that the second and higher layers act the same as a bulk liquid which is more nearly correct for only the outside layer of adsorbed molecules at high moisture contents.

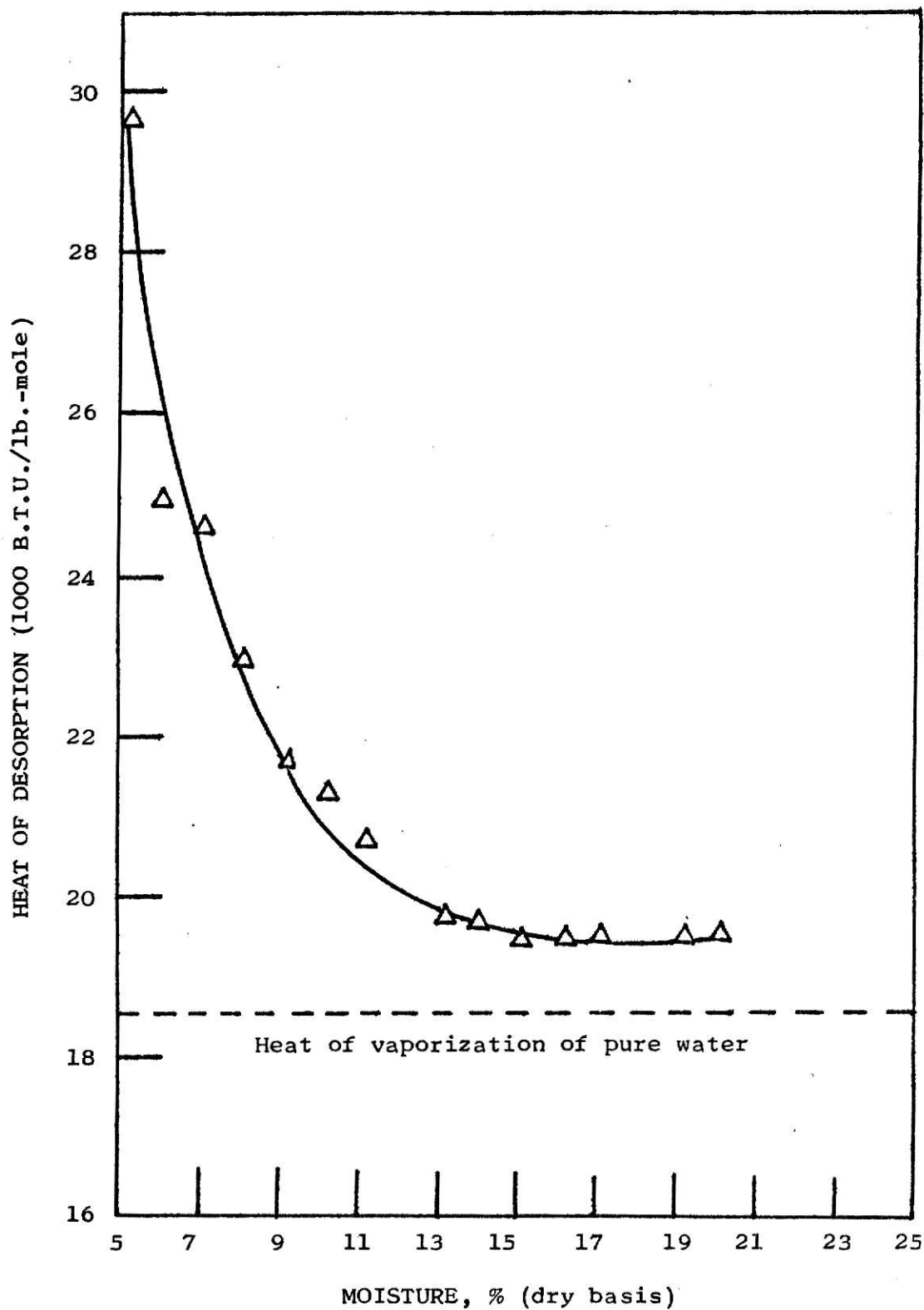


Figure 21. Heats of desorption for grain sorghum at 112 F.

The equations by Henderson, Bradley, and Chung and Pfost fit the entire range of relative humidities tested. Henderson's equation is purely empirical so no theoretical discussion can be made as to its success. Bradley's equation assumed that the sorptive energy induces dipoles in the first adsorbed layer and in turn induces dipoles in a second layer etc. until the sorptive energy is too small to induce dipoles in another layer. The amount of sorptive energy used is directly proportional to the amount of water adsorbed. The same amount of energy would be used in grain sorghum with its expansion and shrinkage as would be used if the same amount of water were adsorbed onto a similar non-expansion or non-shrinkage surface. Chung and Pfost assumed that the free energy of sorption is proportional to the amount of water adsorbed. Thus, basically the Chung and Pfost equation is the same as the Bradley equation, and when applied to the data, predicts the same moisture content. This is shown in Table 10.

Some of the other equations reviewed in the literature might explain the entire region. The main reason most of them were neglected was to limit the number of constants or parameters. Each of the equations tested at this point has only two parameters. This restriction to limit the number of constants will be important in the next section, in which an equation will be developed to describe or predict any isotherm for grain sorghum. It is desirable to keep the number of parameters at a minimum; the number of parameters required has an effect on the acceptance of the equation. Any relationship can be described if enough parameters are used. The better equation would be the one having the fewest parameters, if the predictions are as good or better than an equation with a greater number of parameters.

Equation Development

The parameters of each equation vary with temperature as shown in Table 9. To develop an equation for any isotherm the temperature dependence of these parameters must be described. The Chung and Pfoest equation will be expanded in this section to describe the temperature dependence of its parameters. The constants A and B from the Chung and Pfoest equation are plotted versus temperature in Figures 22 and 23, respectively. It can be seen that the adsorption data are very dispersed in comparison to the desorption data. This dispersion was more difficult to describe than the near linear relationship exhibited by the desorption parameters. Even with the dispersed nature of the adsorption data two empirical relationships

$$\frac{\ln A}{RT} = C + D T \quad (30)$$

and

$$\frac{B}{RT} = E + F T \quad (31)$$

can be used to explain the temperature variation of the constants A and B. By least squares analysis two linear regression lines were obtained and are shown in Figures 24 and 25. In these plots R is the universal gas constant and T is the absolute temperature. The slope and intercepts of the lines are the constants C, D, E, and F. The correlation coefficients, r, for desorption are .992 and .978 for A and B, respectively, and .954 and .612 for adsorption. As anticipated, the adsorption data, because of

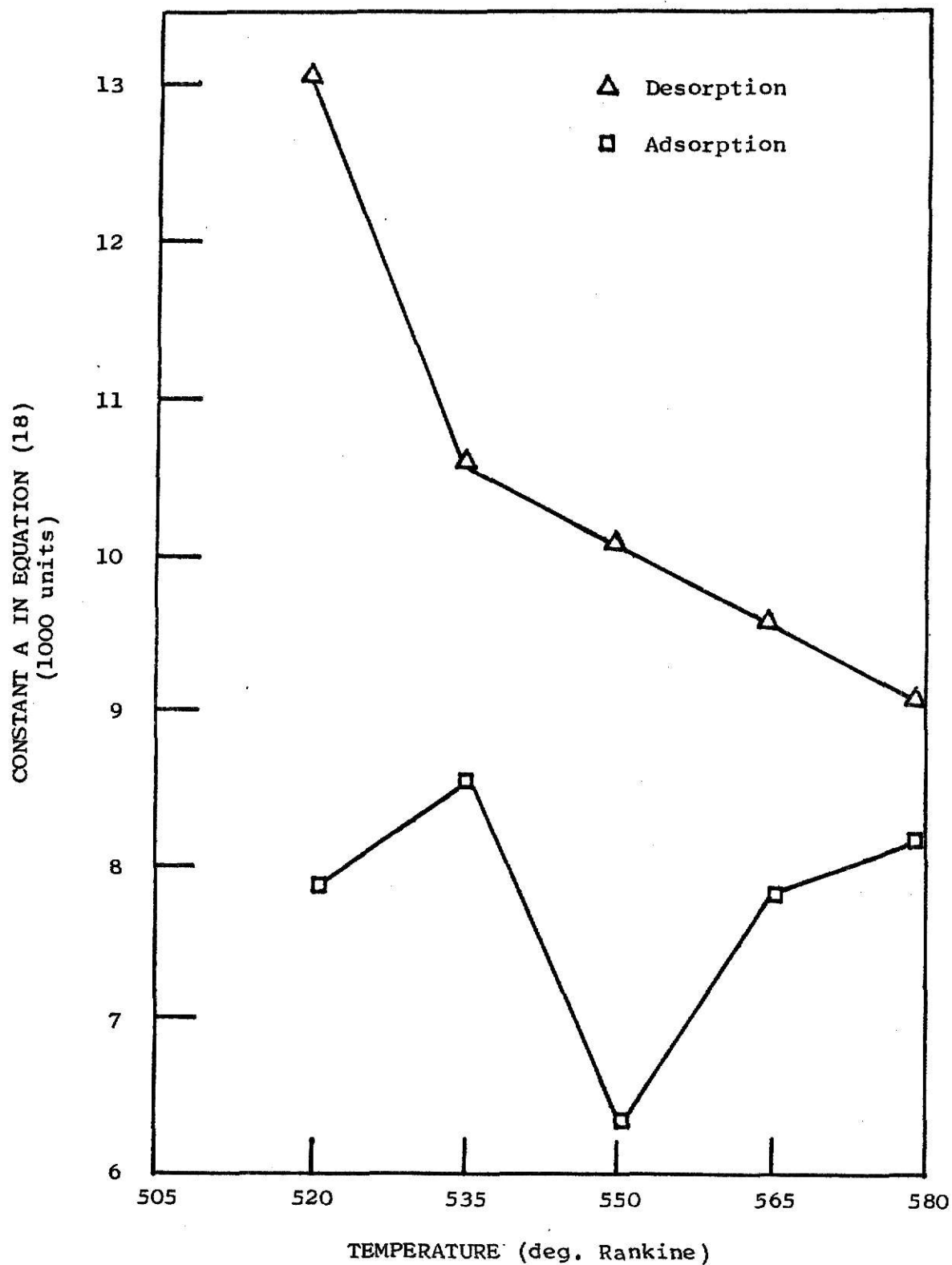


Figure 22. Temperature dependence of Chung and Pfost's constant A.

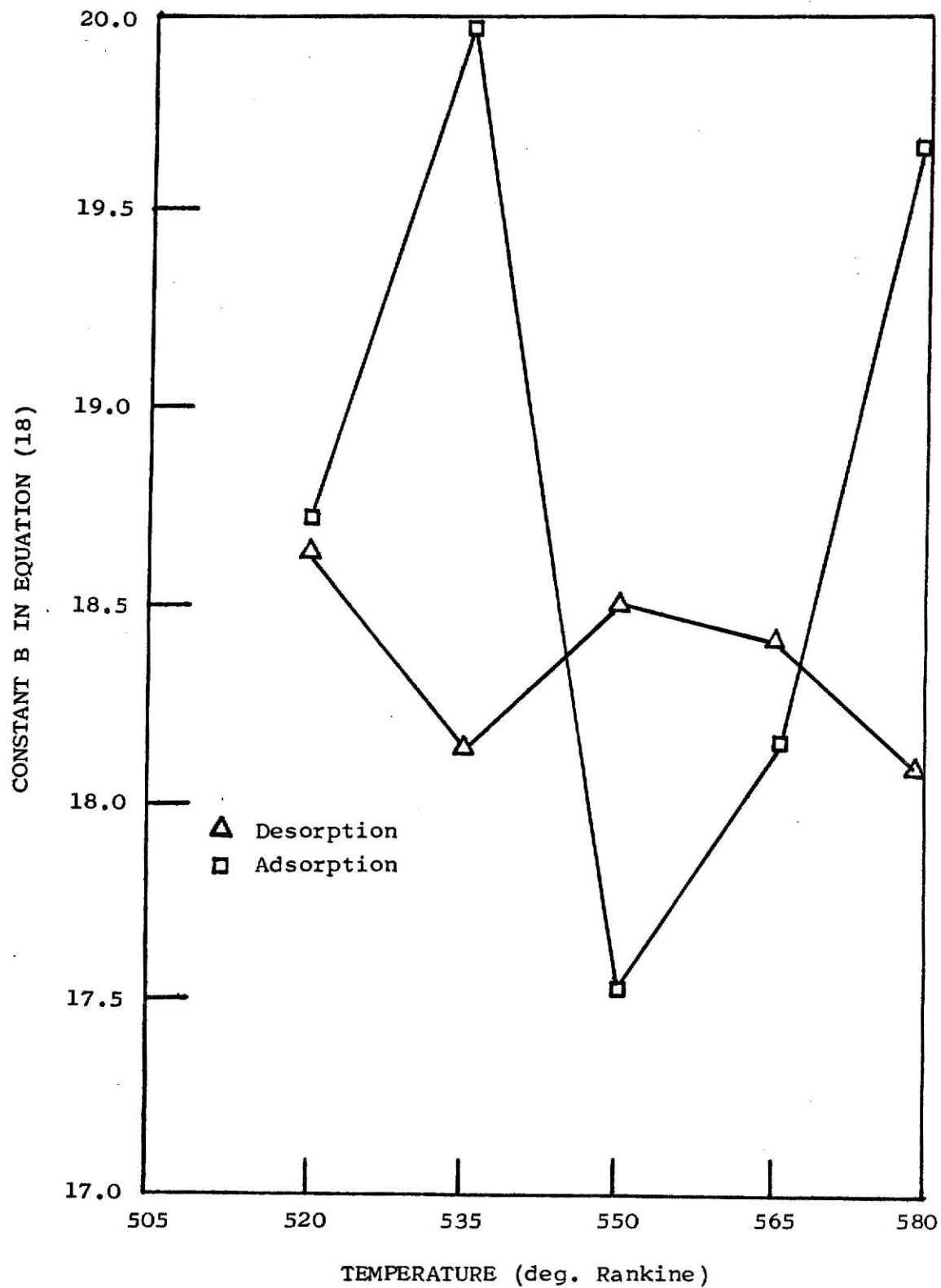


Figure 23. Temperature dependence of Chung and Pfost's constant B.

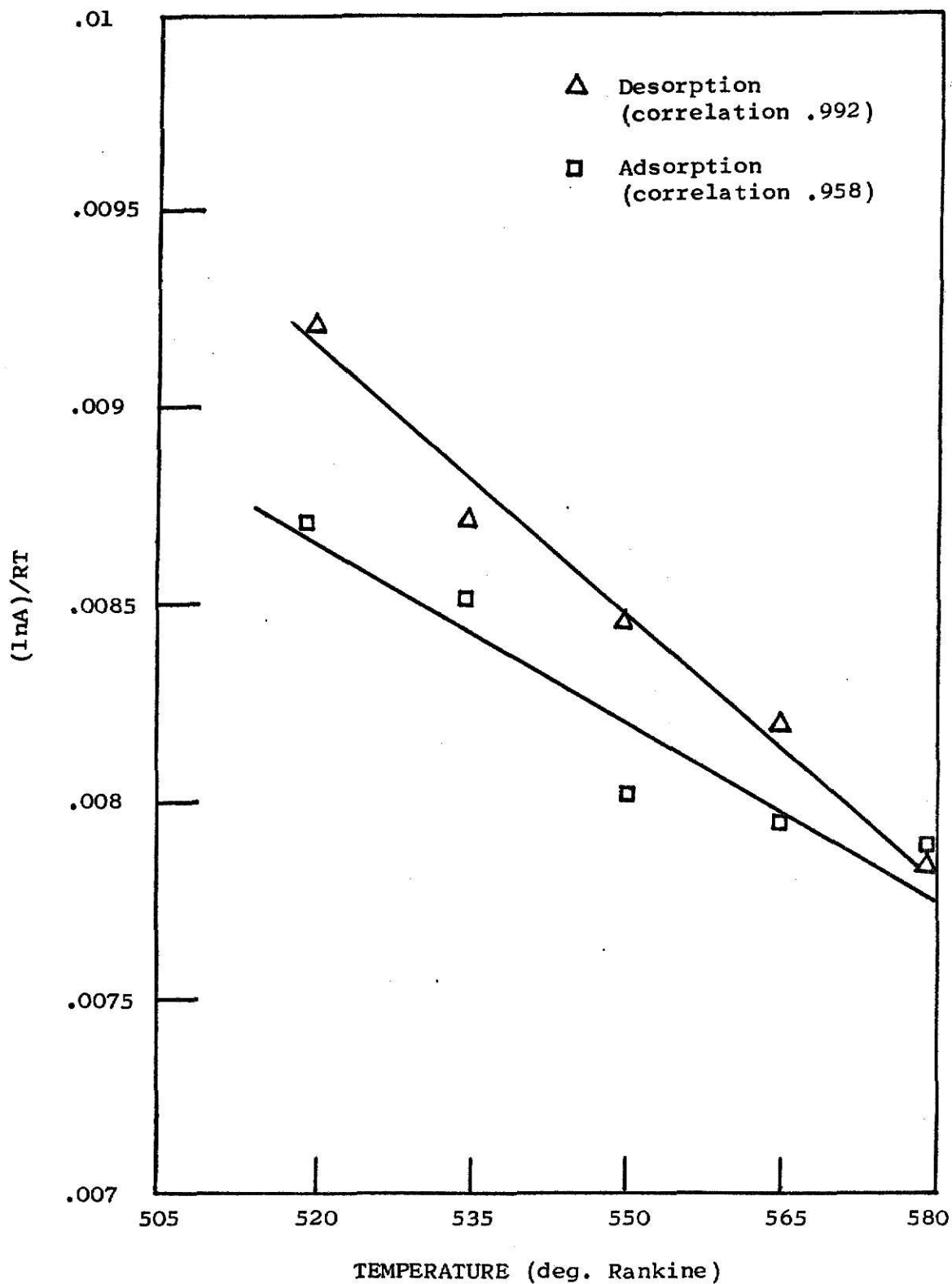


Figure 24. The linear regression line found when the temperature dependence of the Chung and Pfoest constant A is described.

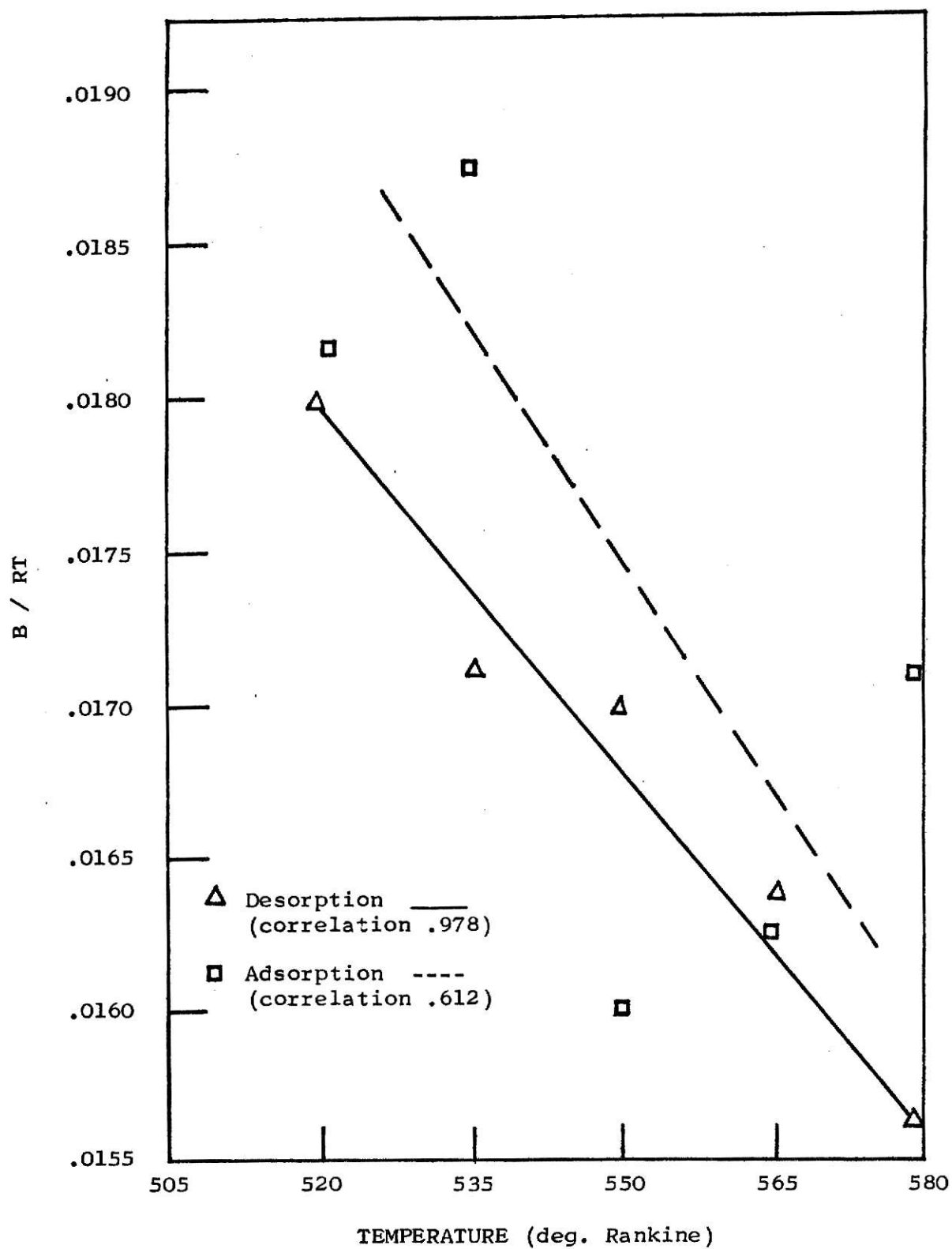


Figure 25. The linear regression line found when the temperature dependence of the Chung and Pfof constant B is described.

dispersion, yields results that are poor in comparison to those of desorption. This poor correlation has little effect on the final predicted isotherms, however. The four constants C, D, E, and F from Equations (30) and (31) are given in Table 4, along with the same constants for the data by Rodriguez-Arias (1956). Correlation coefficients with the Rodriguez-Arias data were .997 and .878, respectively, for Equations (30) and (31). These results show that the extended Chung and Pfof equation developed is applicable to other cereal grains.

Equation (30) can be put into the form

$$A = \exp RT(C + D T) \quad (32)$$

and Equation (31) can be put into the form

$$B = RT(E + F T). \quad (33)$$

Substitution of Equations (32) and (33) into Equation (18) (Chung and Pfof),

$$\ln P/P_0 = \frac{-A}{RT} e^{-BM}, \quad (18)$$

yields the final equation

$$\frac{\ln(RT \ln P_0/P)}{RT} = X - YM, \quad (34)$$

where X is equal to C + DT and Y is equal to E + FT. The predicted

Table 4. The calculated constants in the extended Chung and Pfost equation.

Constant	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	$-3.599(10^{-5})$	$-3.101(10^{-5})$	$+2.873(10^{-5})$

* Rodriguez-Arias (1956)

Corrected 1-28-75 De. Do Sup Chung

A = 6500
B = 16.2

moisture contents for this equation can be found by putting Equation (34) into the form

$$M = \frac{\frac{\ln(RT \ln P_0/P)}{RT} - X}{-Y}. \quad (35)$$

To test this equation two isotherms were predicted at 80 and 100 F for the constants given in Table 4. The predicted isotherms are shown in Figures 26 and 27 and tabulated in Table 5. Two isotherms for adsorption and desorption at 80 and 100 F were found experimentally by the sulfuric acid method used earlier. These are also tabulated in Table 5 and plotted in Figures 26 and 27 to compare with the predicted values. Figures 26 and 27 show that there is a good comparison between the experimental and predicted. To further prove the applicability of Equation (35) the predicted values are compared statistically to the experimental values. Student's t-test is used to test the hypothesis $U_1 - U_2 = 0$ against the alternate $U_1 - U_2 \neq 0$, where U_1 and U_2 are the true means of predicted and experimental data respectively. The t distribution is

$$t = \frac{(x_1 - x_2) - (U_1 - U_2)}{S_{x_1 - x_2}}, \quad (36)$$

where x_1 and x_2 are the sample means of group 1 (experimental) and group 2 (predicted), and $S_{x_1 - x_2}$ is the sample standard error or difference between means. $S_{x_1 - x_2}$ can be found by the equation

$$S_{x_1 - x_2}^2 = \frac{\sum x_1^2 + \sum x_2^2}{n(n-1)}, \quad (37)$$

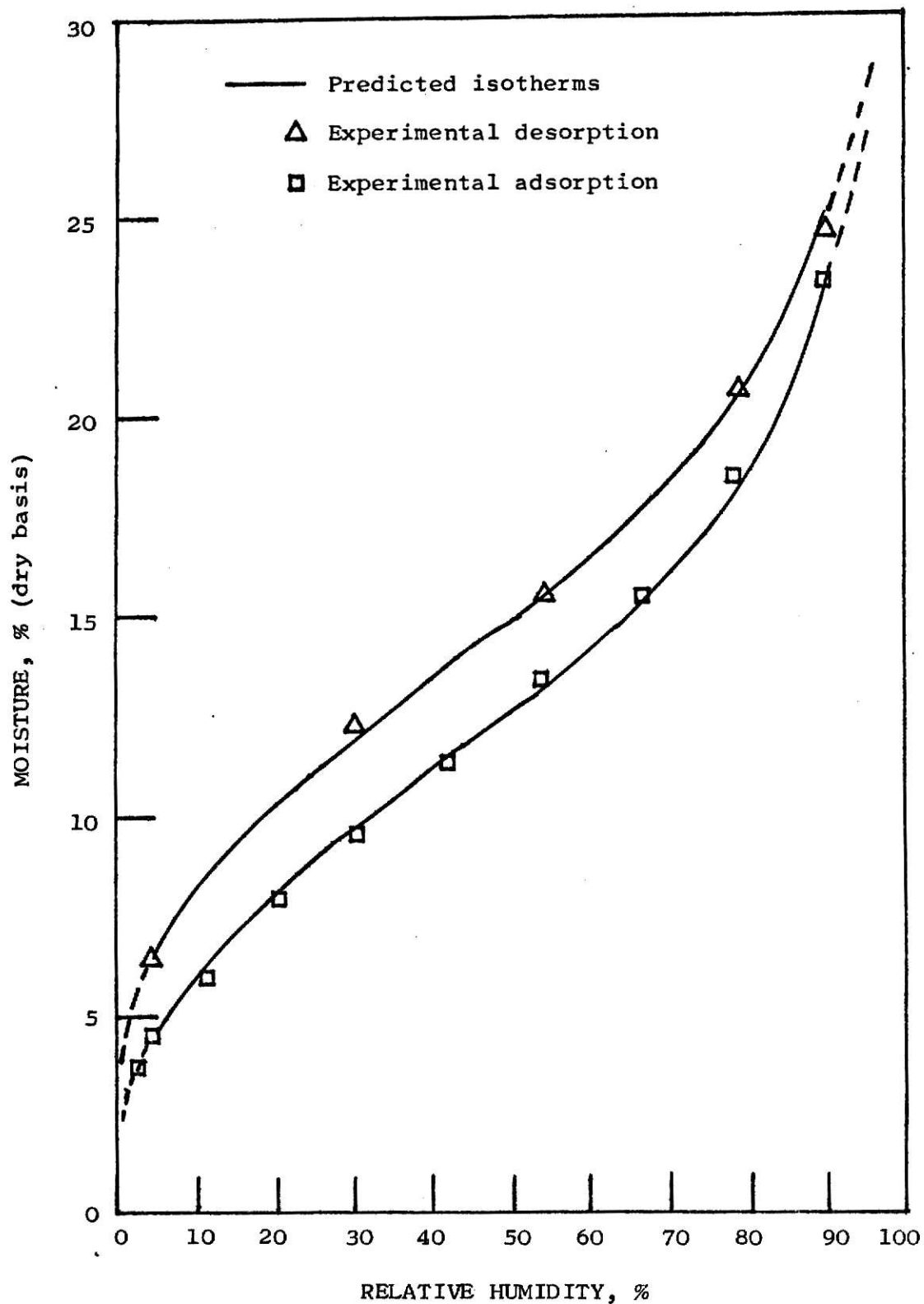


Figure 26. Comparison of the predicted isotherms by the extended Chung and Pfoest equation to the experimental isotherms at 80 F.

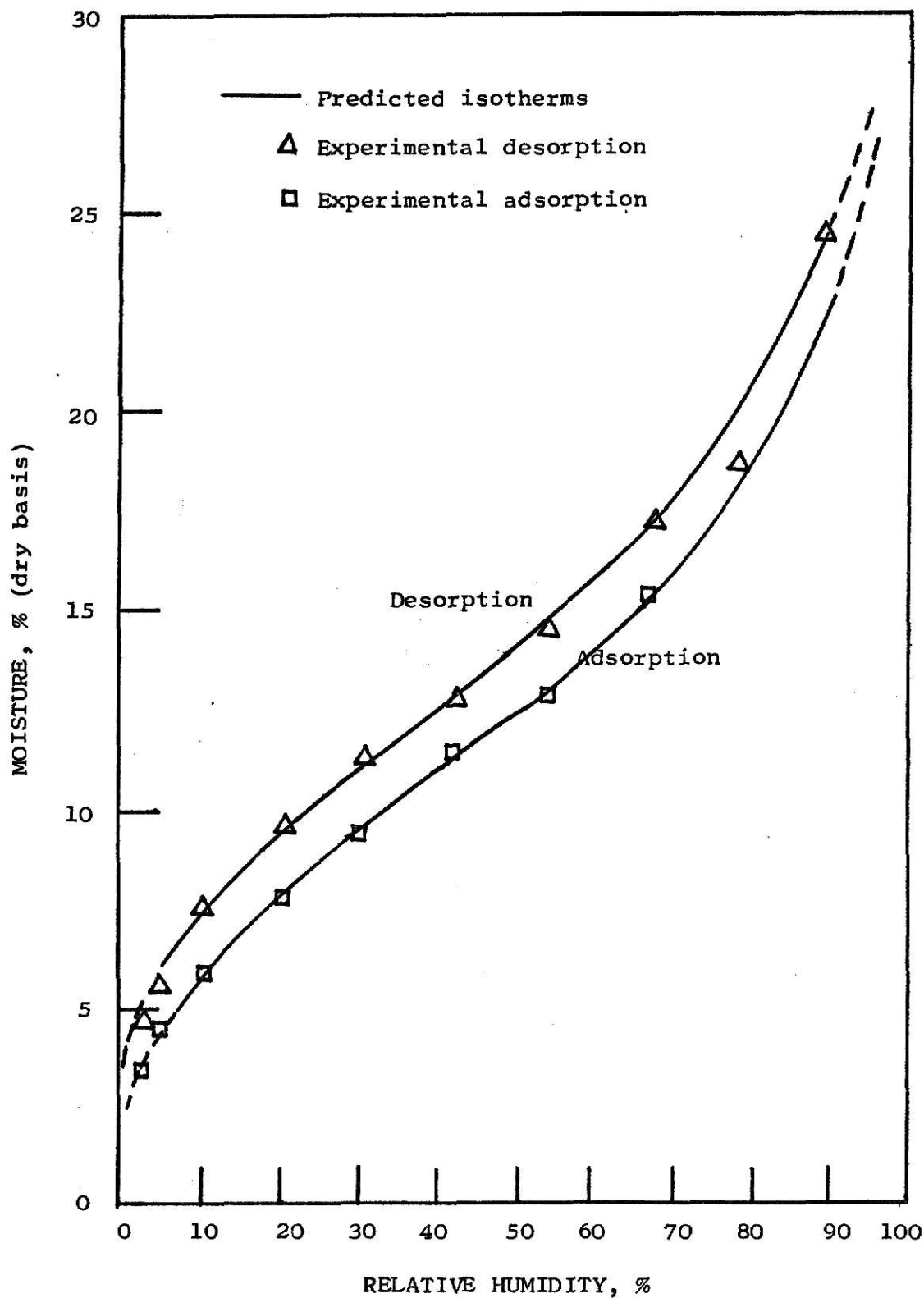


Figure 27. Comparison of the predicted isotherms by the extended Chung and Pfoest equation to the experimental isotherms at 100 F.

Table 5. Experimental and predicted data to test the extended Chung and Pfost equation.

Experimental

Temperature (deg. Fahr.)	Relative Humidity** (%)	Moisture Content, % (dry basis)	
		Desorption	Adsorption
80	2.33	----	3.68
	4.97	6.43	4.40
	11.77	----	5.85
	21.13	----	7.94
	31.17	12.17	9.55
	42.86	-----	11.32
	53.70	15.37	13.28
	66.78	-----	15.23
	78.12	20.37	18.25
	88.98	24.22*	23.03*
100	2.37	4.59	3.53
	5.00	5.52	4.32
	11.86	6.79	5.97
	21.27	9.51	7.83
	31.38	11.27	9.46
	43.16	12.92	11.28
	53.65	14.46	12.93
	67.31	17.07	15.33
	78.57	18.55	18.08
	89.41	24.01*	-----

* Grain treated with propionic acid to inhibit mold growth.

** Calculated to these values from Greenwalt (1925).

Predicted

80	5.00	6.76	4.62
	10.00	8.21	6.02
	20.00	10.13	7.92
	30.00	11.71	9.47
	40.00	13.22	10.92
	50.00	14.74	12.40
	60.00	16.37	14.02
	70.00	18.32	15.93
	80.00	20.85	18.43
	90.00	24.93	22.42
100	5.00	6.00	4.41
	10.00	7.44	5.81
	20.00	9.39	7.72
	30.00	10.98	9.26

Table 5 (cont.)

100	40.00	12.47	10.71
	50.00	14.00	12.19
	60.00	15.67	13.81
	70.00	17.63	15.72
	80.00	20.19	18.21
	90.00	24.30	22.20

where n is the number of observations in each sample. $\sum x_1^2$ and $\sum x_2^2$ are found by the expression

$$\sum x^2 = \sum X^2 - \frac{(\sum X)^2}{n}, \quad (38)$$

where X is the value of the observation or predicted value in each case. The calculated t values, error differences, and theoretical t values at $\alpha = 0.1$ are given in Table 6 showing the acceptance of the hypothesis that $U_1 - U_2 = 0$, or the failure to reject $U_1 - U_2 = 0$.

An equation which defines all of the isotherms between 60 and 120 F for grain sorghum has now been developed. The equation developed is statistically sound and can be applied to grain sorghum and corn.

The equation developed needs only four points to predict any isotherm. Knowing any four equilibrium conditions the four constants C , D , E , and F can be found. The equation developed has a minimum of parameters when compared to equations by Chen, and Young and Nelson, and others, who have developed equations that account for temperature dependence of equation constants.

Dynamic Versus Static Equilibrium

A limited study of dynamic versus static equilibrium was made. Table 7 shows four dynamic equilibrium moistures at equilibrium compared to the static values taken from Figures 12 and 13. The dynamic values tend to be higher than the static. The dynamic value was found as the asymptote of the drying curve, as shown in Figure 6. The time used to determine a

Table 6. Statistical values used to test the hypothesis $U_1 - U_2 = 0$ for the extended Chung and Pfoest equation.

Temperature*	A80	A100	D80	D100
Degrees of Freedom	18	16	10	18
Standard Error Difference	2.73	2.32	5.16	2.74
Calculated t values	.0264	.0060	.0030	.1080
Theoretical t values at $\alpha = 0.1$	1.73	1.75	1.81	1.73
Hypothesis ($U_1 - U_2 = 0$)	accept	accept	accept	accept

* A-Adsorption
D-Desorption

Table 7. Dynamic equilibrium moisture versus static equilibrium moisture for grain sorghum at a few environmental conditions.

Temperature (deg. Fahr.)	RH %	Dynamic Moisture (%, dry basis)	Static Moisture (%, dry basis) from Figures 12 & 13
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

dynamic value is very small compared to that for a static value. The dynamic values were found at about 36 hours compared to three weeks for the static values. If the dynamic tests were extended to three weeks, would the difference in equilibrium moisture be less? Because of the limited data no major statement or comparison can be made between static and dynamic equilibrium moistures. The difference could be a variation in water distribution in the sample. No research was done to verify this statement.

Volumetric Hysteresis

Bushuk and Hlynka (1960) found volumetric hysteresis in wheat samples during desorption and adsorption. They found that curves were sigmoid in shape when volumes were plotted versus relative humidity. The volumetric hysteresis was greater than the moisture equilibrium hysteresis. Although their study was with static conditions, volumetric hysteresis should occur with dynamic conditions and take a much shorter time. For this reason, a dynamic study was made.

Figures 10 through 14 show that moisture hysteresis decreases with an increase in temperature. Chung and Pfof found a decrease in hysteresis in successive moisture desorption and adsorption trials. In conjunction with Figures 10 through 14 and Chung and Pfof successive dynamic desorption and adsorption trials were made on 440 kernels of grain sorghum at an initial moisture content of 30.55 percent, dry basis. The changes in weight and volume were recorded over the successive trials. The results of this study are given in Figures 28 and 29, and Table 12.

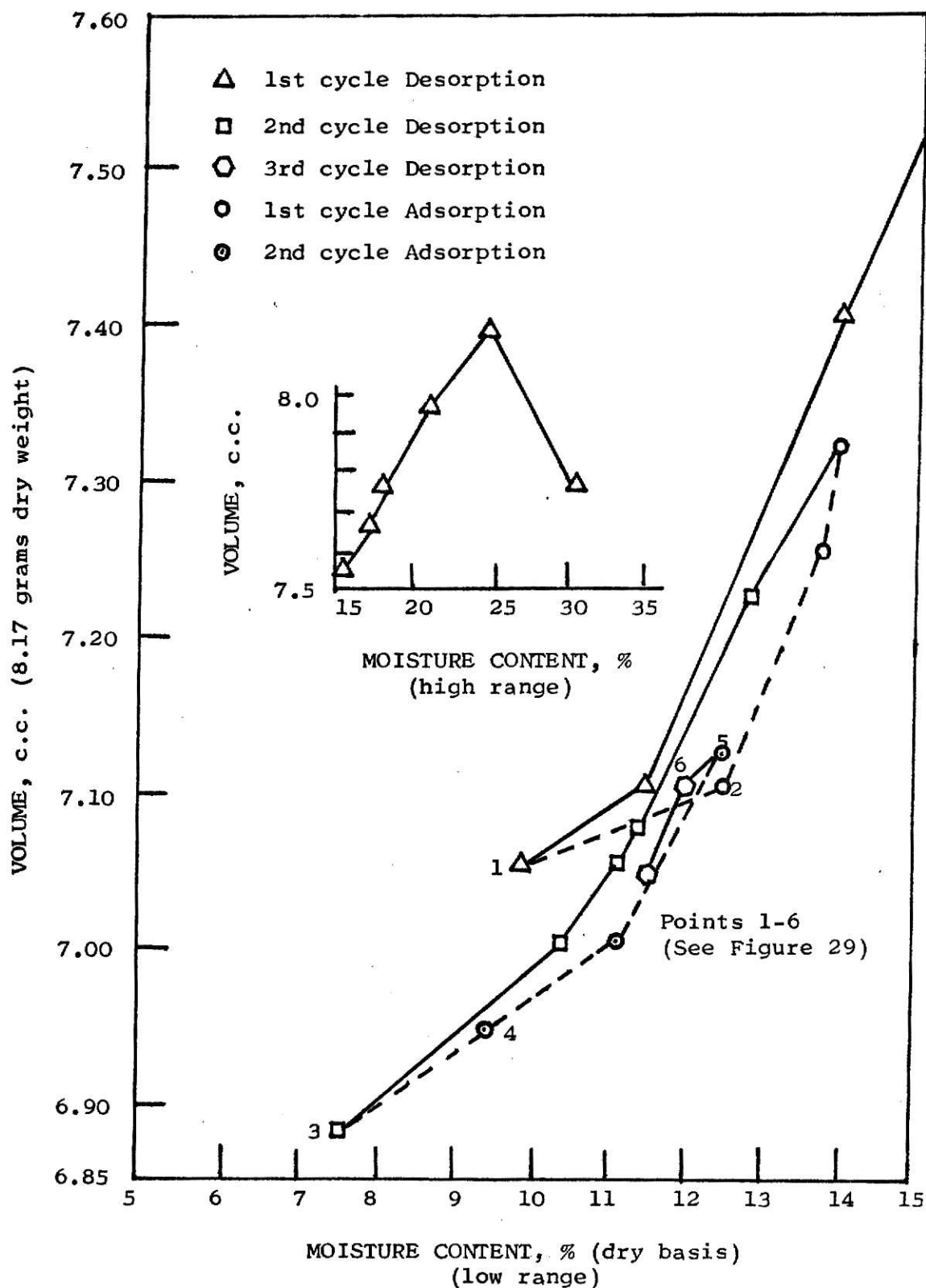


Figure 28. Successive dynamic desorption and adsorption curves for grain sorghum showing a decrease in volumetric hysteresis.

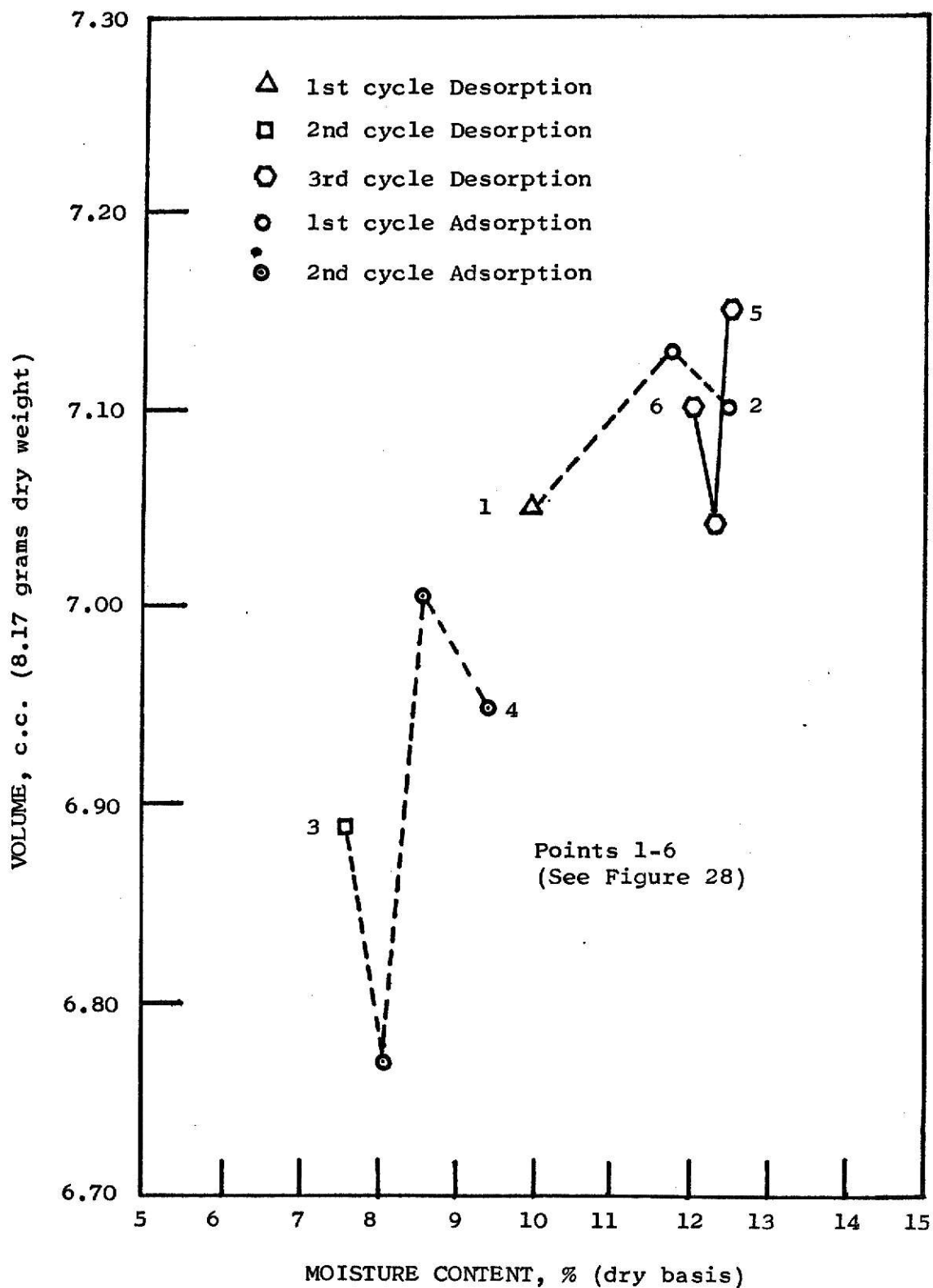


Figure 29. Volume fluctuations for the transition regions between desorption and adsorption for grain sorghum.

The volume increased initially in the higher moisture contents and decreased gradually as shown in the small insert in Figure 28. This can be explained as either 1) the method of measurement or 2) pressure change.

- 1) The air pycnometer used to measure the volume measures the outer sealed volume. Voids that are sealed would be recorded as part of the volume. At the start of desorption the water molecules would start to move out of the kernel. If the pores are sealed a larger volume would be read.
- 2) Another possible occurrence could be a change in pressure. When the outer surface molecules are removed the inner pressure is then the greatest and it may cause expansion of the kernel. Either of these processes could explain the expansion.

The successive desorption and adsorption processes resulted in a decrease of the hysteresis loop as shown in Figure 28. Chung and Pfoest explained that there is a difference in sorptive area which causes hysteresis. During successive desorption and adsorption processes the hysteresis loop decreases, which is caused by molecular shrinkage and crack formation. The sorptive areas for desorption and adsorption approaches the same value as molecular shrinkage and crack formation stabilize. This explanation can be verified by the results shown in Figure 29. For the same moisture content the volume decreased in the second cycle of desorption and increased in the second cycle of adsorption. The sorptive area changed to that the volume for desorption approached that in adsorption.

Grain volumes are plotted for selected moisture contents (designated by numbers 1 through 6 in Figure 28) in Figure 29. It was found that at the time the sample was adjusting from desorption to adsorption or vice

versa that large volume fluctuations occurred. These fluctuations could be the closing and opening of pores which cause different readings by the air pycnometer or stress changes that affected the volume of the kernel. It stands to reason that an immediate change from desorption to adsorption would cause a change in the moisture distribution in the kernel. This change in distribution could cause large stress changes. During successive desorption and adsorption trials in a static environment the long period would enable the stress changes to stabilize before the volume was determined. In this dynamic test, fluctuations occurred for about 15 minutes before a smooth curve, as in Figure 28, resulted. These fluctuations, possibly caused by stress changes, could be the major cause of molecular shrinkage and crack formation.

The actual process involved within molecular shrinkage and crack formation that causes moisture hysteresis can be explained by diffusional characteristics described by Young and Nelson (1967). During adsorption the water that is first adsorbed onto the surface forms a unimolecular layer. The surface molecules of the cell exert binding forces on the molecules preventing them from moving inward. As the amount of water builds up diffusional forces exceed the binding forces and allow some of the molecules to move to the interior. During desorption there is no force to pull the moisture out of the cell until all of the moisture has been removed from the surface. Thus at the same environmental condition there would be moisture hysteresis caused by binding forces exceeding diffusion forces, which cause the void space to be different in adsorption and desorption. During successive adsorption and desorption cycles the molecular shrinkage and crack formation described by Chung and Pfost

changes the pore structure and volume to decrease the difference in void space on successive adsorption and desorption cycles.

The shape of the isotherm, as well as hysteresis, can be explained by this diffusion process. At the start of adsorption the molecules on the surface prevent movement to the inside. The build up of molecules on the surface explains the lower part of the sigmoid curve which is concave to the pressure axis. When the build up is great enough for the molecules to be forced to the inside, the curve becomes linear with diffusion as the limiting process. When diffusion is complete, a build up on the surface causes the curve to be convex to the pressure axis.

Both volume change, caused by molecular shrinkage and crack formation, and diffusion, which were discussed for hysteresis, help to explain the failure of the BET and Smith equations. The BET and Smith equations do not account for volume changes in the adsorbent. The Bradley equation and Chung and Pfoest equation deal only with the energy of adsorption which is not limited by diffusion. The same amount of energy is required to adsorb water no matter what process governs the quantity adsorbed. The Henderson equation, as discussed earlier, is purely empirical so no theoretical discussion can be made.

Although this study of hysteresis is far from complete, it does lead to a little more insight into the process involved. Further study in this area should further the understanding of the concepts.

CONCLUSIONS

From the results of this study the following conclusions were made:

1. The type II isotherm or sigmoid isotherm for grain sorghum is consistent with those for other grains by earlier researchers.
2. The equilibrium moisture content for grain sorghum increases with an increase in relative humidity.
3. The equilibrium moisture content for grain sorghum decreases with an increase in temperature.
4. Moisture hysteresis, for grain sorghum, decreases with an increase in temperature.
5. The BET equation was applicable for grain sorghum equilibrium moisture contents in the 2 to 43 percent relative humidity range.
6. The Smith equation was applicable for grain sorghum equilibrium moisture contents in the 45 to 90 percent relative humidity range.
7. The equations by Henderson, Bradley, and Chung and Pfof were applicable to the entire range of equilibrium moisture data for grain sorghum.
8. The constants for each of the equations tested were temperature dependent.
9. The most important conclusion is that the extended Chung and Pfof equation will predict the equilibrium moisture of grain sorghum for temperatures of 60 to 120 F over the 2 to 90 percent relative humidity range.
10. The extended Chung and Pfof equation was found applicable for corn data by Rodriguez-Arias.

11. The heat of desorption for grain sorghum was found to be greater than that of the latent heat of vaporization of pure water.
12. For grain sorghum the adsorption isotherms are closer together than the corresponding desorption isotherms for the same temperatures.
13. Successive desorption and adsorption for grain sorghum leads to a decrease in the hysteresis loop.
14. Hysteresis was postulated to be caused by molecular shrinkage and crack formation in combination with diffusion.
15. Molecular shrinkage and crack formation is possibly caused by stress changes that occur when changing from an adsorption process to a desorption process or vice versa.

SUMMARY

Static equilibrium moisture contents during desorption and adsorption for grain sorghum were found by using sulfuric acid solutions to control the relative humidity in an enclosed environment at a constant temperature. Moisture contents were found for relative humidities of 2 to 90 percent at temperatures of 60, 75, 90, 105 and 120 F.

Five well known equations were applied to the experimental data and discussed. These included equations by Chung and Pfoest, Bradley, Henderson, Smith, and the equation by Brunauer, Emmett, and Teller. The equation by Chung and Pfoest was extended to account for all the experimental moisture contents. All of the equations applied contained constants that varied for each test temperature. The extension of the Chung and Pfoest equation involved an empirical approach which described the temperature variance of it's constants. The final Chung and Pfoest equation contained four constants. The four constants extended the equation to account for all the moisture contents for all the temperatures between 60 and 120 F and for the 2 to 90 percent relative humidity range.

A study of dynamic equilibrium moisture was made and compared to static equilibrium moisture. Because of limited data, no major conclusions were drawn.

A dynamic equilibrium moisture study of successive desorption and adsorption was made. The volumes of grain sorghum were studied during adsorption and desorption. The original difference in volume between desorption and adsorption decreased in three successive trials to a very small difference. Large fluctuations in volume were found in the transition period between desorption and adsorption.

SUGGESTIONS FOR FUTURE WORK

The following suggestions are recommended for future work:

1. Test the extended Chung and Pfoest equation for other cereal grains such as wheat, rice, etc.
2. Study the fluctuations in volume that occur when changing from a desorption to an adsorption process or vice versa. These fluctuations could be the key to the decrease in the hysteresis loop during successive adsorption and desorption processes.
3. Make a more complete study of dynamic versus static equilibrium moisture content.
4. Study the effect of propionic acid or other mold inhibitors upon equilibrium moisture content, and also upon the actual sorption process. This could include a hysteresis study and many other characteristics that are important in the storage of cereal grains when a mold inhibitor is required.

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APPENDIX

Table 8. Published equilibrium moisture data for grain sorghum isotherms.

Temp (F)	Relative Humidity (%)												Source ()
	10	15	20	30	40	45	50	60	70	75	80	90	100
77		6.4		8.6		10.5				15.2			21.9 (1)
40	6.8		8.5	9.7	11.0		12.3	13.7	15.3		17.3		(2)
70	6.0		7.7	9.1	10.3		11.5	12.8	14.2		16.0	19.0*	(2)
90	5.0		7.0	8.4	9.6		10.8	12.0	13.2		14.7	17.0*	(2)

* Unreliable because of mold growth

(1) Coleman, Rothgeb, and Fellows (1928)

(2) Fenton (1941)

Table 9. Constants and region applicable for the five equations tested.

Equation - Chung and Pfof

TEMP	A	B	REGION	CORR(r)
*D 60	13128.210	-18.61279	2.10-89.63	-.9977112
*D 75	10672.790	-18.12582	2.31-88.98	-.9994595
*D 90	10117.790	-18.49677	2.37-90.05	-.9980224
*D105	9599.523	-18.36832	4.99-88.91	-.9987243
*D120	9183.430	-18.04868	5.31-67.10	-.9982179
*A 60	7862.859	-18.70064	11.59-89.63	-.9962270
*A 75	8370.410	-19.92062	21.11-78.12	-.9989948
*A 90	6306.625	-17.50517	31.42-90.05	-.9967161
*A105	7308.598	-18.16278	21.14-88.91	-.9973515
*A120	8270.730	-19.65466	21.65-89.72	-.9993565

Equation - Bradley

TEMP	K ₁	K ₂	REGION	CORR(r)
*D 60	0.82520(10 ⁻⁸)	12.7120	2.10-89.63	-.99771
*D 75	1.34290(10 ⁻⁸)	10.0450	2.31-88.98	-.99946
*D 90	0.92672(10 ⁻⁸)	9.2629	2.37-90.05	-.99802
*D105	1.05370(10 ⁻⁸)	8.5551	4.99-88.91	-.99872
*D120	1.45060(10 ⁻⁸)	7.9726	5.31-67.10	-.99822
*A 60	0.75579(10 ⁻⁸)	7.6138	11.59-89.63	-.99623
*A 75	0.22314(10 ⁻⁸)	7.8780	21.11-78.12	-.99899
*A 90	2.50700(10 ⁻⁸)	5.7738	31.42-90.05	-.99672
*A105	1.29420(10 ⁻⁸)	6.5134	21.14-88.91	-.99735
*A120	0.29113(10 ⁻⁸)	7.1802	21.65-89.72	-.99936

Equation - Henderson

TEMP	K	N	REGION	CORR(r)
*D 60	1.0387(10 ⁻⁷)	3.3839	2.10-89.63	.98243
*D 75	3.3904(10 ⁻⁷)	3.0189	2.31-88.98	.99358
*D 90	6.7372(10 ⁻⁷)	2.8073	2.37-90.05	.99779
*D105	9.7737(10 ⁻⁷)	2.6898	4.99-88.91	.99526
*D120	9.9820(10 ⁻⁷)	2.7127	5.31-67.10	.99966

Table 9 (cont.)

*A 60	2.1664(10 ⁻⁶)	2.4852	11.59-89.63	.98633
*A 75	2.5779(10 ⁻⁶)	2.4710	21.11-78.12	.99488
*A 90	7.6682(10 ⁻⁶)	2.0328	31.42-90.05	.99242
*Al05	4.3090(10 ⁻⁶)	2.2281	21.14-88.91	.99112
*Al20	4.4188(10 ⁻⁶)	2.2420	21.65-89.72	.99683

Equation - Smith

TEMP	W_b	W'	REGION	CORR(r)
+D 60	0.119520	0.059328	42.95-89.63	.99618
+D 75	0.105010	0.063946	42.92-88.98	.99740
+D 90	0.105640	0.057476	43.25-90.05	.99710
+Dl05	0.091307	0.065637	42.84-88.91	.99754
+Dl20	0.093214	0.062442	43.52-67.10	.99396
+A 60	0.077383	0.068226	42.95-89.63	.99450
+A 75	0.075950	0.065339	42.92-78.12	.99923
+A 90	0.072094	0.069294	43.25-90.05	.99863
+Al05	0.072187	0.069661	42.84-88.91	.99969
+Al20	0.077397	0.060558	43.52-89.72	.99675

Equation - BET

TEMP	C	V_m	REGION	CORR(r)
+D 60	120.460	0.087345	2.10-42.95	.99910
+D 75	82.240	0.081916	2.31-42.92	.99824
+D 90	48.913	0.080468	2.37-43.25	.99936
+Dl05	73.140	0.074834	4.99-42.84	.99893
+Dl20	44.926	0.075620	5.31-43.52	.99862
+A 60	-114.280	0.064721	11.59-42.95	.99730
+A 75	- 77.594	0.062877	21.11-42.92	1.00000
+A 90	- 23.703	0.059631	31.42-43.25	1.00000
+Al05	- 45.976	0.061701	21.14-42.84	.99779
+Al20	- 78.412	0.060370	21.65-43.52	.99852

* Equation applicable to all of the experimental isotherm data as in Figures 17 through 19.

+ Equation applicable to the linear region defined by the equation as in Figures 15 and 16.

A Adsorption

D Desorption

Table 10. Predicted equilibrium moisture contents for the five equations** tested.

TEMP	RH	C&P	B	H	BET	S	E
D 60	5	7.77	7.77	7.58	7.94	12.26	7.40
	10	9.18	9.18	9.38	9.03	12.58	9.60
	20	11.10	11.10	11.71	10.57	13.28	10.70
	30	12.66	12.66	13.45	12.24	14.07	12.70
	40	14.13	14.13	14.96	14.38	14.98	14.50
	50	15.63	15.63	16.37	17.33	16.06	16.00
	60	17.27	17.27	17.78	21.72	17.39	17.60
	70	19.20	19.20	19.27	29.01	19.09	19.50
	80	21.72	21.72	21.00	43.58	21.50	21.80
	90	25.75	25.75	23.34	87.26	25.61	25.50
D 75	5	6.67	6.67	6.49	7.00	10.83	6.40
	10	8.13	8.13	8.23	8.20	11.17	7.80
	20	10.10	10.10	10.56	9.76	11.93	10.00
	30	11.70	11.70	12.33	11.38	12.78	11.90
	40	13.21	13.21	13.89	13.41	13.77	13.40
	50	14.75	14.75	15.37	16.19	14.93	14.90
	60	16.43	16.43	16.86	20.31	16.36	16.50
	70	18.42	18.42	18.45	27.16	18.20	19.50
	80	21.00	21.00	20.31	40.83	20.79	21.00
	90	25.14	25.14	22.87	81.81	25.23	25.00
D 90	5	6.10	6.10	5.79	6.10	10.86	6.90
	10	7.53	7.53	7.48	7.55	11.17	7.30
	20	9.46	9.46	9.78	9.30	11.85	9.50
	30	11.03	11.03	11.55	10.97	12.61	11.30
	40	12.51	12.51	13.13	13.01	13.50	12.90
	50	14.02	14.02	14.64	15.77	14.55	14.30
	60	15.67	15.67	16.17	19.85	15.83	15.90
	70	17.61	17.61	17.82	26.59	17.48	17.70
	80	20.14	20.14	19.76	40.03	19.01	20.00
	90	24.20	24.20	22.45	80.29	23.00	24.00
D105	5	5.71	5.71	5.39	6.25	9.47	5.70
	10	7.15	7.15	7.04	7.40	9.82	7.00
	20	9.10	9.10	9.31	8.87	10.62	9.10
	30	10.68	10.68	11.09	10.36	11.47	10.80
	40	12.16	12.16	12.67	12.22	12.48	12.40
	50	13.68	13.68	14.19	14.76	13.68	13.80
	60	15.34	15.34	15.74	18.54	15.14	15.30
	70	17.30	17.30	17.42	24.80	17.03	17.00
	80	19.85	19.85	19.41	37.29	19.69	19.20
	90	23.94	23.94	22.18	74.72	24.24	23.60

Table 10 (cont.)

D120	5	5.42	5.42	5.22	5.59	9.64	5.30
	10	6.88	6.88	6.81	7.00	9.98	6.70
	20	8.87	8.87	8.98	8.68	10.71	8.80
	30	10.47	10.47	10.67	10.27	11.55	10.60
	40	11.99	11.99	12.19	12.20	12.51	12.10
	50	13.53	13.53	13.64	14.79	13.65	13.60
	60	15.22	15.22	15.11	18.63	15.04	15.10
	70	17.21	17.21	16.72	24.97	16.84	16.80
	80	19.81	19.81	18.60	37.60	19.37	18.80
	90	23.97	23.97	21.22	75.43	23.70	22.80

A 60	5	4.99	4.99	4.65	----	8.09	5.80
	10	6.40	6.40	6.21	----	8.46	7.00
	20	8.31	8.31	8.40	8.38	9.26	8.50
	30	9.86	9.86	10.14	9.44	10.17	9.60
	40	11.32	11.32	11.72	10.93	11.22	10.80
	50	12.81	12.81	13.25	13.06	12.47	12.00
	60	14.45	14.45	14.83	16.28	13.99	14.00
	70	16.37	16.37	16.55	21.65	15.95	15.00
	80	18.88	18.88	18.60	32.54	18.72	19.00
	90	22.89	22.89	21.48	64.78	23.45	23.00

A 75	5	4.85	4.85	4.32	----	7.93	5.00
	10	6.17	6.17	5.78	----	8.28	6.20
	20	7.97	7.97	7.83	8.29	9.05	7.00
	30	9.43	9.43	9.47	9.26	9.93	9.40
	40	10.80	10.80	10.95	10.69	10.93	10.70
	50	12.20	12.20	12.39	12.74	12.12	12.20
	60	13.73	13.73	13.87	15.86	13.58	13.80
	70	15.54	15.54	15.50	21.08	15.46	15.50
	80	17.89	17.89	17.43	31.54	18.11	17.50
	90	21.66	21.66	20.14	62.97	22.64	20.30

A 90	5	3.75	3.75	3.42	----	7.56	4.00
	10	5.25	5.25	4.87	----	7.94	5.80
	20	7.30	7.30	7.04	----	8.76	7.90
	30	8.96	8.96	8.87	9.45	9.68	9.30
	40	10.52	10.52	10.59	10.61	10.75	10.70
	50	12.11	12.11	12.30	12.45	12.01	12.00
	60	13.86	13.86	14.11	15.34	13.56	13.80
	70	15.91	15.91	16.14	20.24	15.55	15.20
	80	18.59	18.59	18.62	30.13	18.36	17.50
	90	22.88	22.88	22.21	59.91	23.16	22.40

A105	5	4.28	4.28	3.93	----	7.58	4.40
	10	5.73	5.73	5.42	----	7.95	6.40
	20	7.70	7.70	7.60	----	8.77	8.10
	30	9.30	9.30	9.38	9.29	9.70	9.70
	40	10.80	10.80	10.02	10.63	10.78	10.80
	50	12.33	12.33	12.63	12.61	12.05	12.00

Table 10 (cont.)

	60	14.02	14.02	14.32	15.65	13.60	13.80
	70	15.99	15.99	16.19	20.76	15.61	15.60
	80	18.58	18.58	18.44	31.02	18.43	17.50
	90	22.71	22.71	12.66	61.85	23.26	22.00
<hr/>							
Al2O	5	4.45	4.45	3.81	----	8.05	4.00
	10	5.79	5.79	5.25	----	8.38	5.80
	20	7.61	7.61	7.33	----	9.09	7.70
	30	9.09	9.09	9.04	8.89	9.90	9.00
	40	10.47	10.47	10.61	10.26	10.83	10.30
	50	11.89	11.89	12.16	12.23	11.94	11.80
	60	13.45	13.45	13.77	15.82	13.29	13.30
	70	15.28	15.28	15.55	20.23	15.03	15.00
	80	17.66	17.66	17.70	30.28	17.49	17.50
	90	21.48	21.48	20.77	60.46	21.68	21.20

* C & P Chung and Pfost equation
 B Bradley equation
 H Henderson equation
 BET Brunauer, Emmett, and Teller equation
 S Smith equation
 E Actual or Experimental taken from Figures 10 through 14

+ D Desorption
 A Adsorption
 RH Relative Humidity (percent)

(All moisture contents percent dry basis)

Table 11. Heats of desorption at 112 F found from the desorption isotherms at 105 and 120 F.

Moisture Content (% d.b.)	Heats of desorption (10 ³) BTU/lb. - mole
5.0	29.5
6.0	24.8
7.0	24.6
8.0	22.9
9.0	21.7
10.0	21.2
11.0	20.6
13.0	19.7
14.0	19.7
15.0	19.4
16.0	19.4
17.0	19.5
19.0	19.5
20.0	19.4

Table 12. Volumes obtained in successive dynamic desorption and adsorption cycles.

Moisture Content (% dry basis)	No. used in Figures 29 and 30 to show the transition period	Volume, grain sorghum (cubic centimeters)
30.55		7.72
25.09		8.15
22.09		7.95
18.05		7.75
17.74		7.65
15.45		7.54
13.95		7.40
11.38		7.09
9.90	1	7.05
11.75		7.13
12.48	2	7.10
13.71		7.25
13.95		7.32
12.73		7.22
11.38		7.08
11.14		7.06
10.40		7.00
7.59	3	6.88
8.08		6.75
8.69		7.02
9.30	4	6.95
11.14		7.00
12.48	5	7.15
12.36		7.04
12.00	6	7.10
11.63		7.04

Dry Weight 8.17 grams
Kernels 440

ADSORPTION-DESORPTION CHARACTERISTICS OF GRAIN SORGHUM

by

Edwin Rex Dunstan, Jr.

B. S., Kansas State University, 1970

AN ABSTRACT OF A MASTER'S THESIS

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MASTER OF SCIENCE

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KANSAS STATE UNIVERSITY
Manhattan, Kansas

1972

The overall purpose of this investigation was to find the static equilibrium moisture content for grain sorghum between 60 and 120 F and to develop an equation to predict these moisture contents. Both desorption and adsorption were studied. The investigation also dealt with dynamic equilibrium moisture contents in comparison to static moisture contents and a volumetric hysteresis study that resulted in a theoretical discussion of isotherm shape and hysteresis postulation.

Five isotherm equations were tested against the experimental results. These include equations by Bradley; Henderson; Smith; Chung and Pfost; and Brunauer, Emmett, and Teller. The equations by Bradley, Henderson, and Chung and Pfost were applicable for the entire range of relative humidities of 2 to 90 percent. The equation by Brunauer, Emmett and Teller was applicable in the 2 to 45 percent relative humidity range. The Smith equation was applicable in the 45 to 90 percent relative humidity range.

The static equilibrium moisture contents were found by a sulfuric acid method. Desorption isotherms and adsorption isotherms were found at 60, 75, 90, 105, and 120 F for the relative humidity range of 2 to 90 percent. The equation developed was an extension of the Chung and Pfost equation, which involved accounting for the temperature dependence of the constants A and B in the equation,

$$\ln P/P_0 = - \frac{A}{RT} e^{-BM}, \quad (1)$$

which is the Chung and Pfost equation with P/P_0 as the relative humidity, R as the universal gas constant, T as the absolute temperature, and M as the equilibrium moisture content. The constants A and B vary with temperature, which were expressed by

$$A = e^{RT(C + DT)} \quad (2)$$

and

$$B = RT(E + FT) \quad (3)$$

which leads to the equation

$$\frac{\ln(RT \ln P_0/P)}{RT} = X - YM, \quad (4)$$

where $X = C + DT$ and $Y = E + FT$. Two additional adsorption and desorption isotherms were found experimentally by the same method to verify the equation developed. These isotherms were at 80 and 100 F. Isotherms were predicted by Equation (4) and compared to the additional isotherms found experimentally at 80 and 100 F. A graphical and statistical comparison was made. Very good correlations were found when comparing predicted and experimental results. The equation was also shown to be applicable to corn.

A limited dynamic equilibrium study was made and compared to the static case. The dynamic equilibrium moisture content used was the asymptote of the drying curve.

Volumetric hysteresis was demonstrated and it was shown that successive desorption and adsorption processes led to a decrease in the hysteresis loop. This was postulated to be caused by molecular shrinkage and crack formation which effect diffusion processes in the grain sorghum.

The crack formation and molecular shrinkage was postulated to be caused by stress changes that take place when changing from an adsorption to a desorption process or vice versa.