

落花生平衡含水率曲線滯後現象之研究

The Study on Hysteresis Phenomenon of EMC Curves for Peanuts

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摘 要

本研究在以動態方式量取落花生莢、仁與殼在乾燥與回水時之平衡含水率，試驗結果顯示仁與殼獨立時可在24小時內達到平衡，整粒的莢須五日方能至平衡點，所量得之結果，以修正之 HENDERSON 模式進行迴歸分析，相關係數在 0.99，標準誤差在 0.05，HENDERSON 模式與試驗結果吻合。

滯後現象存在於落花生的吸濕與脫水平衡含水率曲線間，兩曲線之差一般在 1% 以內，滯後係數為吸濕曲線含水率與脫水曲線含水率之比值，滯後係數與平衡含水率具有良好的線性關係。滯後係數之迴歸公式可與脫水之平衡含水率模式共用以預測吸水之平衡含水率。

ABSTRACT

This study was to develop the dynamic method to measure the EMC of peanut pod, kernel, and hull. Kernel and hull could reach the equilibrium within one day, if the air could pass over them directly. The pod needed 5 days to be at equilibrium. The modified Henderson equation was used to simulate the experimental results. Most of the correlation coefficients were above 0.99, and the standard errors were below 0.05. Therefore, the modified Henderson model was suitable to simulate the EMC of peanut.

The hysteresis phenomenon did exist between the adsorption isotherm and desorption isotherm by inspecting the experimental data. The hysteresis value was defined as the difference between two curves. Most of the hysteresis values were less than 1%. There was a good linear relationship between the hysteresis values and desorption EMC. Using the hysteresis equation and EMC equation together can estimate the EMC of adsorption accurately.

Introduction

After harvesting and processing, effectively drying and storing for agricultural products are important. Storage at high initial moisture content or exposure to adverse environment conditions, which are at high temperature and relative humidity, will be rapidly spoiled. The moisture content of biological hygroscopic materials, which include agricultural products, is of major concern in their proper drying and safe storage. In order to provide suitable moisture condition for a material, it is often necessary to dry or wet the material. An understanding of this wetting or drying process requires a knowledge of the equilibrium moisture content (EMC) of the material in the surrounding environment. The equilibrium moisture content is particularly important in drying, because it states the limiting value for given humidity and temperature conditions. A knowledge of the equilibrium moisture content of a biological material is essential for the efficient design and operation of systems for drying, or storing the material.

A hygroscopic biological material is contacted continuously with air at constant temperature and humidity until equilibrium is reached, the material will attain a definite moisture content which is known as the equilibrium moisture content (Perry, 1963). The equilibrium moisture content for a given environment may be defined as the moisture content which the material would approach if left in that environment for an infinite period of time. A graphic expression of the relationship between the equilibrium moisture content of a material and the corresponding relative humidity of air is termed the equilibrium moisture content curve (Henderson, 1952), or the moisture sorption isotherm. The mathematical descriptions of the curves are known as sorption isotherm equations. An adsorption or desorption isotherm is a curve of equilibrium moisture content versus relative humidity at a given temperature for a material which has been subjected to a drying or wetting environment.

Many researchers have experimentally determined EMC for peanut and other grains, and also developed the corresponding adsorption and desorption isotherms. It is known that a hysteresis exists between the sorption isotherms

of drying and wetting processes. Hysteresis refers to the difference of EMC between the adsorption and desorption curves. Thus, when obtaining equilibrium data, the moisture sorption and desorption history of the material under investigation must be known and stated. Since several researchers including Babbitt (1945), Hubbard et al. (1957), Breese (1955), and Young and Nelson (1967), found a hysteresis between the sorption isotherms curves for wetting and drying processes, sometimes it is necessary to define both adsorption and desorption isotherms respectively.

One of the objectives of this study was to experimentally determine the EMC of peanuts for the range of temperatures and relative humidities most likely to be encountered in Taiwan for the drying process. The way to measure EMC can be done either by bringing air to equilibrium with a sample of fixed moisture content (ERH method), or by bringing a sample of peanut to equilibrium with air of fixed relative humidity (EMC method). The EMC method was adopted in this work. The other objectives of this study were to experimentally determine adsorption and desorption isotherms for Spanish Type peanut kernel, hull, and pod at selected temperatures, also to use the experimentally determined data to evaluate the parameters of modified Henderson equation and to discover the phenomenon of hysteresis.

Literature Review

EMC definition

When a biological hygroscopic material is exposed to atmospheric conditions, it loses to or gains moisture from the atmosphere, until it is at equilibrium. The moisture content at equilibrium is called the equilibrium moisture content (EMC). In other words, the EMC of a material is that moisture content which a material will reach and maintain when it is exposed to a steady controlled environment. There is an obvious need to know the equilibrium moisture contents of agricultural products in handling their drying and storage processes. This information can help predicting the drying rates of products under various drying conditions. It can also be used to predict what moisture levels would be necessary for long-term safe storage. The process of

transferring moisture between a material and the atmosphere is named sorption which includes adsorption and desorption. The adsorption and desorption are used to describe the process of taking up or giving off water for the material. The equilibrium moisture content varies with the relative humidity and temperature of the air surrounding it. The most important factor which influences the EMC of peanut is the relative humidity of the surrounding air.

The problem of EMC has been studied to a considerable extent as is evident from the hundreds of related publications. Almost all EMC of agricultural products, which must be determined with experiments, are temperature dependent. The determination needs extensive testing to a normal encountering range of values of temperature and relative humidity. Temperature affects the EMC of biological hygroscopic materials in two ways: the immediate effect of temperature and the effect of temperature history. The immediate effect of temperature is to reduce the hygroscopicity of peanut at a given relative humidity. Exposure of biological materials to high temperatures for various lengths of time causes a permanent decrease in hygroscopicity. Most of the decrease in hygroscopicity is probably due to the decomposition of the constituents. Ayerst (1965) and Pixton and Warburton (1971) found that if the relative humidity remained constant, the moisture content of wheat decreased approximately 0.6 to 0.7% per 10°C rise in temperature.

It is known that the EMC varies from one variety of agricultural products to another. This is the result of a number of factors such as the different proportions of the major constituents. It should be remembered, however, that the EMC for the constituents might be different in the gross agricultural product than in the isolated constituents because of the effect of extracting the constituents and also because of the interrelationships among the constituents. Coleman and Fellows (1925) studied the EMC of cereals. They equilibrated various grains with the atmosphere of known relative humidities. It was reported that the experimental moisture contents of all cereals in equilibrium with the same relative humidity were much the same. Flaxseed, however, had a lower moisture content. The results showed that the equilibrium moisture

content relationship of starchy cereal grains differed only slightly, and they differed from oilseeds. The evidence suggested that the oil content of a product simply acted as a weighting factor. The reasonably comparable results for oilseeds might be expected if the moisture content was expressed on a fat-free basis.

Sorption isotherm

A sorption isotherm is a graphic expression to describe the equilibrium moisture content of a product at a particular constant temperature as a function of the relative humidity. The moisture content of a product in equilibrium with a given relative humidity may have two values, one when the material is adsorbing moisture, and the other when it is desorbing water or drying out. A sorption isotherm may, therefore, be an adsorption or a desorption isotherm. It is important when quoting EMC data to state to which the data refer. The sorption isotherms of agricultural products usually are described as sigmoid curves. The sigmoid shape, described as the type II isotherm according to the classification of Brunauer et al. (1938). In the low humidity range the curve is concave to the humidity axis; in the mid range it has a region of inflection which is approximatedly linear; and in the high humidity range the curve is concave to the moisture content axis. The researchers have experimentally determined the sorption isotherms for peanut and grains, and they were smooth sigmoid curves.

Young (1976) showed the experimental data for desorption and adsorption respectively of peanut kernel and hull. The temperature effect on the adsorption and desorption isotherms was relatively small as compared with the effect for cereal grains. He found the desorption isotherm for kernels had lower equilibrium moisture contents at higher temperatures when the relative humidity was low and a reverse effect or no effect of temperature at relative humidities above 70 percent. He also pointed out that the data for hulls had more variation than for kernels.

Strohman and Yoerger (1967) stated that the technique of measuring EMC at high relative humidity is not accurate enough to prove the existence of a finite equilibrium moisture content at 100 percent relative humidity. The asymptotic behavior of sorption isotherm is more

usable for mathematical derivation.

Keen (1968) mentioned that the corresponding stable saturated vapor pressure of selected saturated salt solution at referred temperature could be used to define the experimental relative humidity. Two ways were adopted to finding the equilibrium moisture content of a material. In the static method, a small sample was placed in an environment of controlled relative humidity. The sample was weighed continuously until the attainment of a steady weight which was recorded to be the EMC. This method was time consuming; several weeks might elapse before equilibrium was reached. The other method, a faster technique, was the dynamic method, in which humidified air was blown to pass over the sample. The time for equilibrating was 10 hours or less. If the testing system was not calibrated well, the accuracy was somewhat less than with the static method. A well-calibrated dynamic method was adopted in this study.

In addition to sorption isotherms, EMC models which are mathematical equations are commonly used to describe the relationship of equilibrium moisture content, relative humidity and temperature. After reviewing published EMC models, Van den Berg (1985) suggested the following requirements for EMC models: (1) the equation should have a relatively simple form with temperature dependent parameters, (2) the model should be developed for practical applications such as drying and storing, (3) the model should include the influence of hysteresis. A number of theoretical, semi-theoretical, and empirical equations have been suggested to model the equilibrium moisture content isotherms. Young and Nelson (1967) combined the BET equation and Smith equation to build their EMC model which seemed to include the advantage of both and fit the isotherm fairly well. Young (1976) used the model to simulate the desorption and adsorption isotherms of Virginia-type peanut. He pointed out that the model could be used to describe both sorption and desorption with same parameter values for each process. The report showed the deviation was less than 2%. The predicted EMC difference between adsorption and desorption was much smaller than the experimental results.

Due to the accuracy and convenience, semi-empirical equations have been adopted in

practical application. Modified Henderson equation was investigated in this study. Henderson (1952) derived the equation of sorption isotherm for biological materials from Gibb's adsorption equation. Henderson (1952) presented his best known equation of sorption isotherm for biological materials as:

$$1 - RH = (-A * T * M^B)$$

Where;

- RH : relative humidity, decimal,
- Ta : absolute temperature (R),
- M : moisture content, d.b.,%.
- A,B : constants.

Chang (1988) modified the procedures to derive the Henderson equation to show its physical and mathematical meanings. The equation can be transferred to become linear for variables A and B. Then, the parameters can be determined by linear regression procedures. Since A and B are constants, the equation cannot use to correct the shift of the isotherms as the temperature changes. Many researchers have used different values of A and B of the EMC equation at different temperatures.

Young (1976) compared five EMC equations as: BET equation, Smith equation, Chung-Pfost equation, Henderson equation and Young-Nelson equation. Henderson equation was simple but did not fit as well as that of Young and Nelson at high relative humidities. And he also found the constants were temperature dependent. Since Henderson equation is temperature dependent, Thompson et al. (1968) modified the Henderson equation to include the temperature term which improved the predictions of the equation.

$$1 - RH = (-A * (T+C) * M^B)$$

- T: Temperature (F),
- C: Constant.

The modified Henderson equation is the most widely adopted EMC equation. Young did not make a comparison between modified Henderson equation and Young-Nelson equation. Chen (1988) selected four sorption equations, as modified Henderson equation, Chung-Pfost equation, modified Halsey equation, and modified

Oswin equation, to compare in his study of equilibrium relative humidity. In his report, the modified Henderson equation had the best prediction for peanut hull.

The modified Henderson equation has been found by other investigators to adequately describe the equilibrium moisture contents of peanut and grains. The equation is nonlinear and involves three parameters. Since the equation can not be transferred into the linear form, the parameters must be estimated using the nonlinear regression technique. Parameters were computed for the EMC equation of adsorption and desorption respectively.

The adsorption and desorption isotherms for most agricultural products are not necessarily the same. The equilibrium moisture content corresponding to a given relative humidity may have two values, depending on whether the material is adsorbing or desorbing moisture. For agricultural products, the equilibrium moisture content with a given relative humidity is higher for desorbing than for adsorbing. The difference of EMC between desorption and adsorption isotherms is called the phenomenon of hysteresis. Young (1967) stated that a difference of as much as to 5% in the equilibrium moisture content. Friesen (1974) reported that there was not much difference in the two sorption isotherms at low relative humidities; however, the difference was gradually to increase at higher relative humidities.

Hysteresis Phenomenon

Presently, there is no easy and effective method to predict the equilibrium moisture content within a hysteresis loop. Skaar (1972) developed a procedure for determining the equilibrium moisture contents of biological materials within their hysteresis loops. The procedure was developed with the aid of experimental data and took into account the history of a material's previous equilibrium moisture content. The hysteresis was history dependent. The EMC in adsorption was higher when a dry sample was exposed to a given humidity in one single step than when it was brought to the same humidity through a series of adsorption steps. Undoubtedly this phenomenon was a significant factor in determining the effect of the hysteresis at any given humidity. The findings of Christensen and Kelsey (1957) have been substantiated by

Prichananda (1966), who showed that the adsorption isotherm for yellow birch in air for single-step adsorption from the dry condition was higher than that obtained from the usual multistep process. The magnitude of the hysteresis was larger for the single-step than for multistep adsorption curves.

Babbitt (1949) was one of the first workers to demonstrate the effect of hysteresis in sorption and desorption of water from wheat and flour. He observed that hysteresis was not as pronounced with flour as with whole wheat, inferring that the structure of the biological material had an influence. Pierce and Smith (1950) suggested that the hysteresis resulted from energy changes which took place in the system when water, had deposited first at active centers, merged to form a layer covering the adsorbing surface. Hubbard et al. (1975) investigated this phenomenon for wheat and corn. Ayerst (1965) observed that when products were exposed to an atmosphere of controlled relative humidity until a state of constant weight was attained, the observed hysteresis was large (1.5 to 2.0% moisture content). Both Ayerst and Pixton and Warburton (1971), using the same technique found that with prepared samples the hysteresis effect was in the order of 0.5 to 1.0% moisture content. Keen (1968) found that the declined trend or pattern of hysteresis appears for biological materials with increasing temperature.

Becker and Sallans (1956) pointed out that the side effects of drying would cause the hysteresis occurrence. The effect of case hardening after drying could make a nearly impermeable outer layer, which prevented moisture transfer between the material and atmosphere. Therefore, the equilibrium moisture content was higher in a desorption than in an adsorption. The irreversible loss of ability to rehydrate was the other side effect. The process of rehydration after drying could never be a simple reversal of the drying mechanism. Some of the changes produced by drying were irreversible, which put severe stresses on the outer layers. The irreversible changes of the colloidal constituents of both animal and plant tissue did occur when the material was held for a period of time at high temperature. It reduced the ability of rehydration of the tissue. Keen (1968) stated

that the elasticity of cell walls and the swelling power of starch gel, both important for rehydration of biological materials, were reduced in a drying process.

Young and Nelson (1967) studied EMC of wheat which lead to hysteresis relationship and found the effect of temperature upon the hysteresis. They observed the hysteresis phenomenon by using saturated salt solutions to control relative humidity. An approximate 5% EMC difference was observed between desorption and adsorption. Hart (1964) conducted EMC tests for wheat through drying and wetting. Desorption moisture content was higher than adsorption moisture content. Repeated wetting and drying tended to decrease the hysteresis effect. Chung et al. (1967) used the dynamic method to study the hysteresis of wheat. The maximum deviation of desorption and adsorption was nearly 2% moisture content. No deviation was reported after the third cycle with both curves.

Numerous researchers have studied hysteresis and have postulated theories for its presence. There is no single, adequate theory explaining the hysteresis. Many researchers have proposed mechanisms to explain hysteresis. Luikov (1966) suggested that the phenomena of evaporation and condensation were not reversible for a hygroscopic capillary material. In adsorption a dry material became sodden, the capillary walls were covered by a layer of liquefied vapor, but a meniscus was not formed until the adsorbed layers were close enough to touch and blocked the pores at the narrowest section. Thus, at the same ambient humidity, the equilibrium moisture content for desorption would be greater than that for adsorption. The above explanation of hysteresis was defined as the bottle and neck effect by Chen (1988) and Labuza (1985). Henderson (1970) stated that the pores of a capillary hygroscopic material were irregular in shape and size, which inhibited filling and emptying of the pores in a manner. The milled rice was dried and rehydrated, and a hysteresis was noted. The process was then repeated and, at the end of the third trial, no hysteresis was present.

McBain (1935) offered the other explanation was that impurities such as permanent gases - particular air- adsorbed on the pore or capillary walls restricted the attachment of water

molecules. As the water vapor pressure was raised and more water filled the capillary space during the adsorption, foreign material was displaced. No foreign material was present during the desorption process, so the vapor pressure and moisture content relationship was different and hysteresis resulted. Henderson (1970) reported a small hysteresis did exist, less than one percent moisture, which tended to disappear as the material repeated through hysteresis loops. Since a biological material is a combination of many biological cells, three mechanisms were hypothesized by which water was held by the material (Young and Nelson, 1967). First, there were unimolecular layers of water molecules bound to the surface of the cells. Second, there were multimolecular layers of molecules stacked on top of the first layer. Third, there were moisture within the cells. It was known from past experimentation that the heat of adsorption of the water decreased as the moisture content increased. It could be explained that the first layer of water molecules was bound to the surface of the cells by forces in excess of those which would bind the water molecules to each other in normal condensation. Then it was assumed that the second and higher layers of moisture were condensed with a normal heat of condensation. When the moisture content of the material was very low, practically all of the adsorbed moisture would be in the first layer, and would have a higher heat of adsorption. As the moisture content increased, more and more of the moisture adsorbed would be in the second or higher layers where the condensation was normal, and thus the average heat of adsorption would decrease. The difference of heat could cause a hysteresis.

If the adsorption and desorption processes were completely reversible, the amount of moisture in the products at equilibrium conditions should be the same, regardless of whether the equilibrium was reached through a drying or wetting process. But many EMC studies showed the existence of the hysteresis; therefore, the hysteresis effect had to be due to the adsorbed moisture. If a dry, biological material was subjected to a wetting environment, moisture in a unimolecular layer first adhered to the surface of the cells. When a layer of molecules built up on the surface, the diffusional forces tended to

transfer moisture into the cell. However, the surface molecules of the cell exerted binding forces on the water molecules inhibited moisture moving into the cell. As more and more water molecules were accumulated on the surface, the diffusional forces exceeded the binding forces and allowed some moisture to transfer into the cell. In a drying environment, there was no force to pull the moisture out of the cells until all the moisture had been removed from the surface. The diffusional forces again caused the moisture to move out of the cell. Thus a hysteresis effect occurred between the drying and wetting processes.

Friesen (1974) defined the two R terms, moisture ratios for adsorption and desorption, and developed a procedure to determine the equilibrium moisture contents to account for the effect of hysteresis that varied according to the range of changes in relative humidities of the environment. He reported that no data concerning the effect of temperature on the moisture history within the hysteresis loop were found. Henderson (1970) applied his EMC model with different parameters for adsorption and desorption to describe the hysteresis loop. The model worked very well in his study. Young and Nelson (1967) presented their model to predict the hysteresis loop by combining BET equation and Smith equation. The parameters of their model were estimated respectively for adsorption and desorption. The model worked for both wheat and peanut.

Skaar (1972) defined the hysteresis coefficient, A/D, as the ratio of the EMC for adsorption to that at desorption for any given temperature and relative humidity. From his investigations, he found that in a complete adsorption-desorption cycle the hysteresis coefficient ranges about 0.8 to 1.0. According to Weichert (1963), the hysteresis decreased with increasing temperature and disappeared at temperatures of 75 and 100°C. Kelsey (1957) also showed a reduction in hysteresis between 25 to 55°C. The hysteresis ratio would be used to represent the degree of hysteresis in this study, and the relationship with temperature would be derived and discussed.

Babbit et al. (1945) reported a significant hysteresis when wheat was moved through a single desorption and adsorption cycle when observations were conducted in the absence of

air. Houston (1952) reported a true hysteresis with a 1 percent moisture content deviation. Breese (1955) used the same procedure on rough rice. He found that 60 days were required for equilibrium and that the hysteresis (1 cycle) deviation varied from 1.8% at the 50% relative humidity point to nearly zero at 10 and 90 percent. Bushuk et al. (1957) studied hysteresis in wheat flour and its fractions. They ran the materials through two desorption and adsorption cycles and observed a maximum hysteresis differential of approximately 1.5% moisture content for each material.

Instrumentation and Experimental Procedures

Equilibrium moisture content data of peanut hull, kernel, and pod would be determined for both desorption and adsorption conditions for two temperatures (35 and 45°C) and five relative humidities from 10% to 90%. This research included both adsorption and desorption processes. Fresh wet sample peanuts were put into sealed bags for later desorption tests. Dry sample peanuts, used in adsorption tests, were made of fresh peanuts which were dried with a vacuum dryer for 3 days at 15°C. When the samples were dried to moisture content less than 2%, dry peanuts were put into sealed bags. All sample bags were placed inside air-tight plastic containers. A freezer was used to store sample bags at temperature of -5°C. Before running the tests, sample bags were moved from the freezer to room for 24 hours to normalize the sample temperature.

The testing system was mainly composed of an environmental chamber, a solution box, a sample box, an air pump, a cooling fan, and a hygrometer. The air was bubbled into the saturated salt solution in the solution box to have air with saturated humidity referring to a specified temperature. Five different salt solutions were selected to make air have the desired relative humidities. The air was blown to pass over the samples in the sample box. According to the mass transfer principle, the rate of moisture transfer between samples and air could be speeded up by increasing the air velocity; then, the time to reach the equilibrium can be reduced. The

samples were hung inside the sample box with screen bags. With the pump, the air was drawn out of the sample box and entered the solution box again to complete a cycle. The solution and sample boxes were placed inside the environmental chamber where temperature was defined. The pump was located next to the chamber. A fan was used to cool the pump and air through the pump. A measuring header of a hygrometer was placed in the sample box to monitor the relative humidity and temperature changes in tests.

Peanut pod, kernel and hull were tested separately. The samples were measured for moisture contents everyday, until the values did not change in three continuous measurements. The oven method, 130°C for 6 hours, suggested by Young et al. (1982) was adopted in this study. Part of pods were put into the oven to determine the moisture content. Some pods were split into kernels and hulls, to measure moisture contents separately. These moisture contents were used by comparing with the EMC of kernel and hull which were tested individually to prove the accuracy of experimental procedures.

Results and Discussion

To conduct the EMC tests by blowing the air, of which humidity is referring to selected saturated salt solution and specific temperature, to pass over samples is called the dynamic method. The fact that kernel and hull could reach the equilibrium in one day showed the dynamic method was really able to accelerate the moisture exchange between sample and air. But pods still needed five days to be at equilibrium. By testing pods, shelling pods and measuring moisture contents of kernel and hull separately, it was found that the hull still could reach the equilibrium within one day, and the kernel took much longer period to get the equilibrium. When running tests for pods, because kernels were inside hull, the air, blocked by the hull, could not penetrate the hull and exchange moisture with kernels directly; therefore, the kernel required more time to have EMC. However, the testing time was reduced a lot, if comparing with the static method. The criterion to justify pods to be at equilibrium was the moisture contents of kernel and hull to be equivalent with the data which were tested individually. Figure 1 and 2

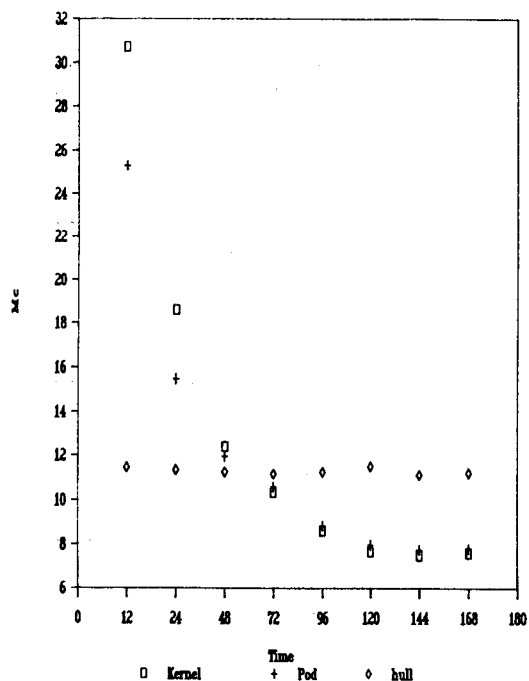


Figure 1. Historical moisture contents of peanut pod, kernel, and hull in a desorption process.

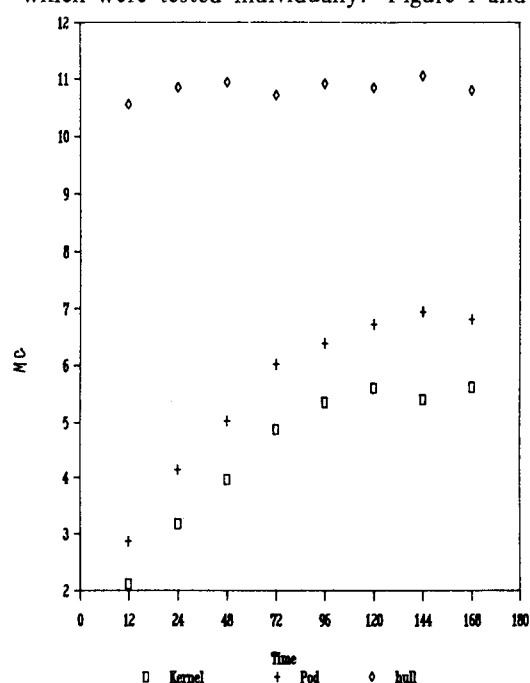


Figure 2: Historical moisture contents of peanut pod, kernel, and hull in an adsorption process.

showed the historical moisture contents of pod, kernel, and hull in testing runs of desorption and adsorption.

The modified Henderson model of EMC was applied to simulating the experimental measurements. The non-linear regression technique, at least square method (Draper and Smith, 1980), was used to estimate the parameters of the model. When using the non-linear regression procedures, it may oscillate widely or not converge at all; therefore, the underrelaxation method was used to help solving the problem of divergency. Table 1 presented calculated parameters and correlation coefficients (R-square) of EMC models for adsorption and desorption of peanut pod, kernel, and hull. The experiments were conducted at 35 and 45°C, which was the recommended temperature range to dry peanuts in Taiwan. Besides the adsorption EMC curves, the values of correlation coefficient were above 0.99. The standard errors of EMC in Table 1 were high when comparing

with ASAE Standard D245.4 (1987) and other published data. Since only five values, the means of three runs, were used to compute three parameters, the small sample size would exaggerate the standard error. By inspecting experimental data, three measurements were so close at a specific experimental condition. All three data were used to run the regression would help reducing the standard error, but it did not improve the model. It is a constructive suggestion that to test more EMC data at different relative humidities then to simulate the model would improve the model and standard errors. Figure 3 described the good relationship between the experimental data and EMC equation. Every computed EMC equation had the similar relationship with the testing results.

Figure 4 showed the EMC curves of desorption for hull, pod, and kernel at 35°C. The hull had higher EMC than the others, and the curve of kernel was below the other two. Because the structure of hull was highly porous, it was capable of retaining more moisture; therefore, at the

Table 1: Estimated constants, correlation coefficients, and standard errors of EMC models.

		A	B	C	R ²	S.E.
35°C Adsorption	Kernel	0.00056248	1.7997	13.6180	0.9852	0.0544
	Pod	0.00032170	2.0163	4.5205	0.9827	0.0589
	Hull	0.00012957	2.1974	-4.8432	0.9949	0.0318
35°C Desorption	Kernel	0.00016702	2.0680	28.5270	0.9958	0.0290
	Pod	0.00019665	2.1408	4.3266	0.9938	0.0352
	Hull	0.00016702	1.9851	0.3567	0.9948	0.0032
45°C Adsorption	Kernel	0.00031594	1.8279	39.6450	0.9924	0.0328
	Pod	0.00065653	1.7372	-2.3146	0.9836	0.0556
	Hull	0.00019814	1.9931	0.3979	0.9982	0.0184
45°C Desorption	Kernel	0.00038857	1.8899	5.5898	0.9906	0.0423
	Pod	0.00028605	1.8703	15.4360	0.9910	0.0041
	Hull	0.00022423	1.9586	-5.2990	0.9983	0.0179

A, B, C: constants of modified Henderson equation

R² : correlation coefficient

S.E. : standard error of EMC

same temperature and relative humidity, it had higher EMC than kernel and pod. Chen (1988) stated that the product containing more oil content would have lower equilibrium relative humidity (ERH). It implied that the EMC of kernel should be lower than the value of hull. The results of this work showed the coincidence with Chen's report. The EMC of pods were the mixed results of kernel and hull. The EMC curve of pod had to be located in the middle of the curves of kernel and hull, which was also presented in Figure 4.

Almost all the EMC papers reported that the higher EMC at lower temperature than the values at higher temperature. The same results were found in Figure 5. Young (1976) conducted the EMC study of Virginia-Type peanuts, and found the unclear temperature effect. Most of his data followed the rule. Figure 6 showed the experimental and Young's curves of EMC. The experimental results were higher than the Young's predictions. Keen (1968) had mentioned that the dynamic method could save time to get the equilibrium, but lost the accuracy. This might be one of the reasons to explain the difference between two curves. For agricultural products, the different species would have different major constituents, which had their own EMC equations. Spanish-Type peanuts was the selected variety in this study, and Virginia-Type peanuts were used in Young's report. The experimental EMC curve of pod was examined with the model presented in ASAE Standard D245.4 (1987) in Figure 7. Two curves were cross with each other. The experimental results had lower readings at low relative humidity and higher values at high relative humidity.

It is the hysteresis phenomenon that the EMC curve of desorption is above the curve of adsorption. Usually, the curves of desorption and adsorption will form a closed loop is named as a hysteresis loop. Figure 8 illustrated a hysteresis loop of kernel at 35°C. The differences between desorption and adsorption EMC data were smaller at both ends in the range of experimental relative humidities comparing with the differences in the middle of the range. The similar relationship were found for kernels and pods in this study. Although the desorption curve was still above the adsorption curve for

hull, the difference between two curves was getting larger as increasing the relative humidity (Figure 9). The structure difference of kernel and hull was the main reason. The porous hull was capable of keeping more water, no matter which process was proceeded. The hysteresis value, defined as the difference between adsorption and desorption data, for hull was relatively small. Henderson (1970) tested the hysteresis phenomenon for rice, and reported the similar conclusion in this paper. Because rice is not an oil-rich product, the shape of its hysteresis loop should be closer to hull than kernel. Most of the experimental hysteresis values were less than 1%. When a product is dried in a vacuum dryer, it has the better ability to adsorb moisture. Since the dry samples for adsorption tests were prepared with a vacuum dryer in this work, the ability of adsorption might be increased and the hysteresis values were decreased.

The hysteresis ratio, A/D , is defined as the ratio between the values of adsorption and desorption. Table 2 presented all the values of hysteresis ratios computed from experimental results and simulated EMC data. Experimental hysteresis ratios were scattered within the range of 0.73 to 0.99. By inspecting the ratios carefully, to draw a worthy conclusion from the data was difficult. When testing at a low relative humidity, the value of EMC was quite small. The small deviation in measurement, which could not be totally avoided, was divided by the denominator, a relatively small EMC, the experimental hysteresis ratio was exaggerated. The hysteresis loop is temperature dependent. The higher temperature should have less effect of hysteresis, it can be checked by examining the hysteresis ratios. Table 2 did not demonstrate the temperature effect on hysteresis. The hysteresis ratios of EMC models showed the linear relationship with computed EMC values. Table 2 also presented the R-square's and standard errors of the first order linear regression equation to simulate the relationship between the computing hysteresis ratios and EMC. Although all R-square's were above 0.9, they still could be improved to 0.99, if using the second order linear regression equation. Figure 10 presented two curves: one was drawn for the computed values from the equations of EMC model of desorption and hysteresis ratio, and the other was the curve

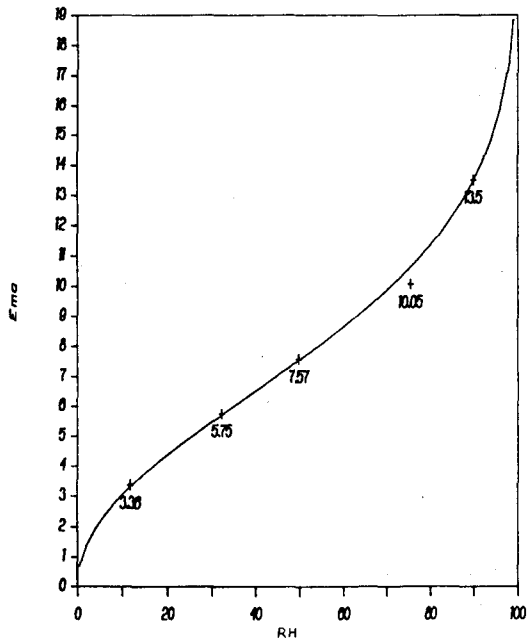


Figure 3: Experimental data and computed modified Henderson equation.

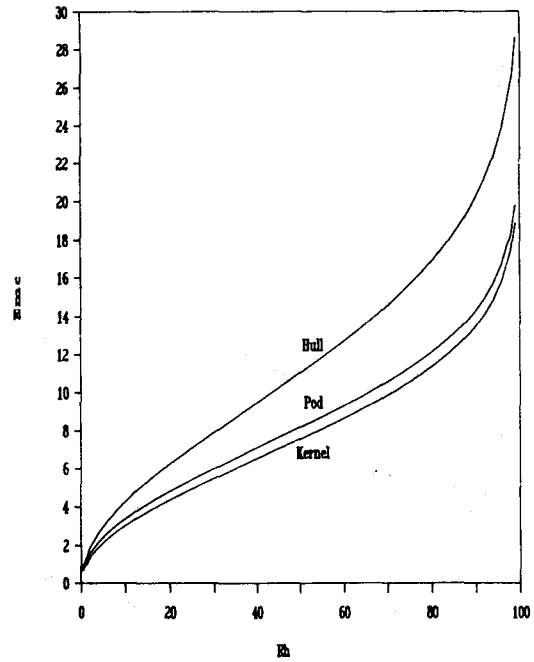


Figure 4: EMC curves of desorption for pod, kernel, and hull at 35°C.

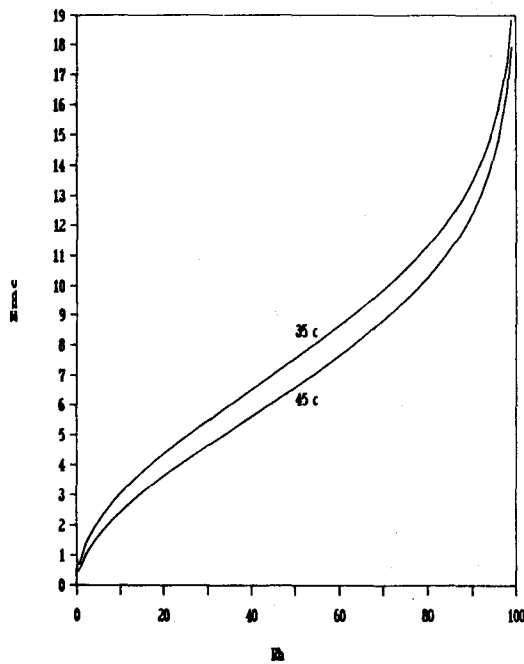


Figure 5: The EMC curve at 35°C is above the EMC curve at 45°C.

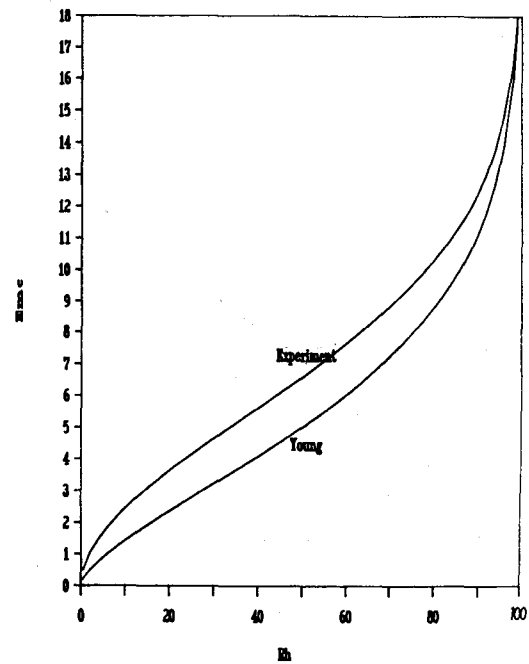


Figure 6: The comparison of experimental data and Young's data for kernel.

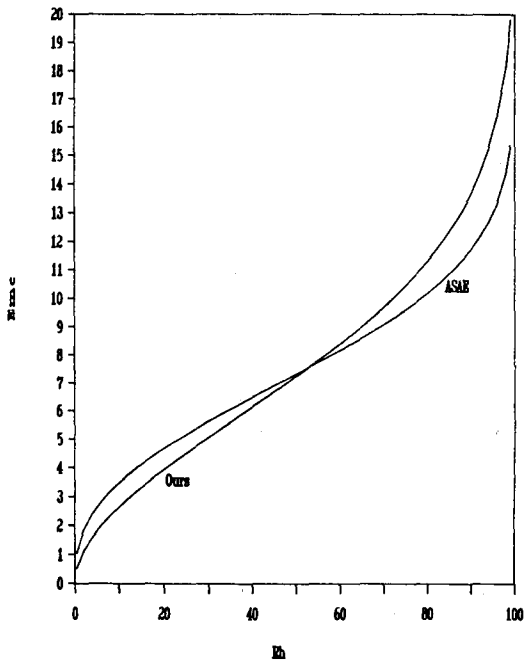


Figure 7: The comparison of experimental data and ASAE data for pod.

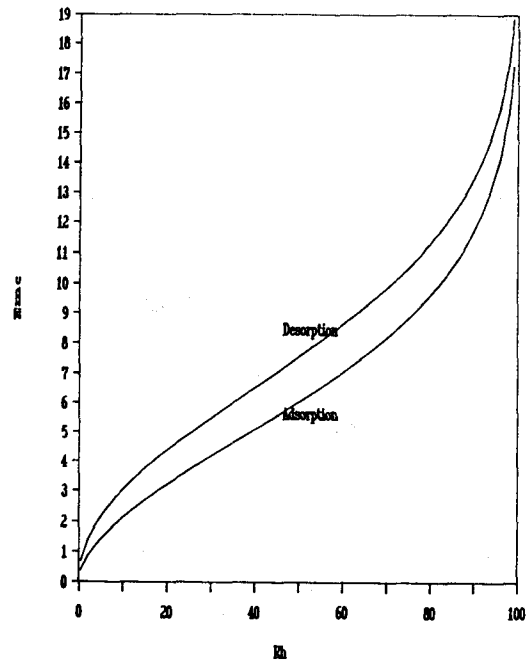


Figure 8: The hysteresis loop of kernel at 35°C.

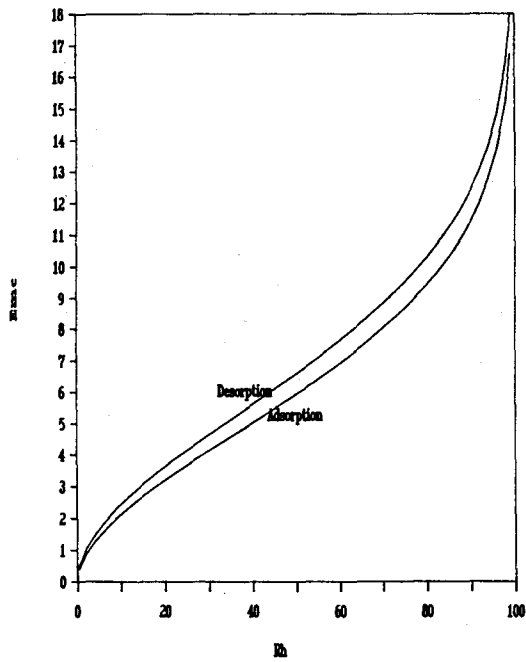


Figure 9: The hysteresis loop of hull at 45°C.

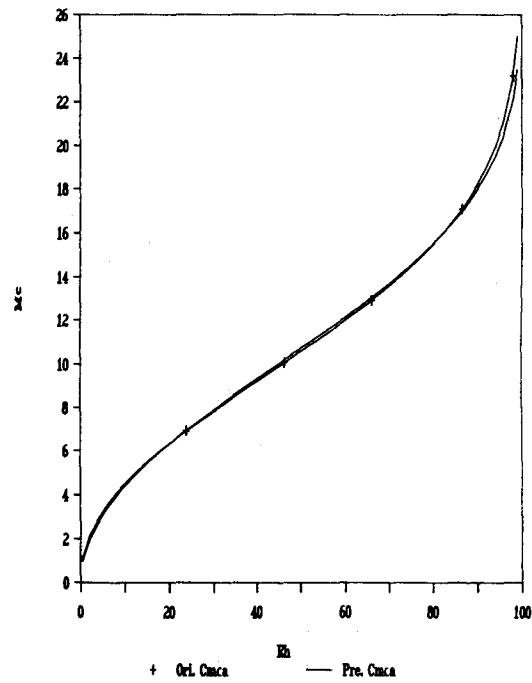


Figure 10: Using both the hysteresis ratio equation and desorption equation can predict the adsorption curve.

Table 2: Experimental and computed hysteresis ratios and their linear regression equations.

	EMC	(A/D)e	CMC	(A/D)c	1st Order	2nd Order
35°C	3.36	0.8661	3.3175	0.7066	B0 = 0.66834	C0 = 0.614277
Kernel	5.75	0.7704	5.7145	0.7663	B1 = 0.01575	C1 = 0.031354
	7.57	0.7332	7.5248	0.7984	R ² = 0.96900	C2 = -0.000921
	10.05	0.8995	10.6246	0.8405	S.E = 0.01304	R ² = 0.998710
	13.50	0.9400	13.4844	0.8709		S.E = 0.003258
35°C	4.08	0.9804	3.6920	0.8471	B0 = 0.82885	C0 = 0.801213
Pod	6.46	0.8065	6.2430	0.8751	B1 = 0.00677	C1 = 0.014137
	7.83	0.8787	8.1441	0.8895	R ² = 0.96448	C2 = -0.000405
	11.13	0.9461	11.3649	0.9080	S.E = 0.00628	R ² = 0.998505
	14.88	0.9093	14.3076	0.9210		S.E = 0.001577
35°C	5.30	0.9547	4.6856	1.0395	B0 = 1.06331	C0 = 1.119271
Hull	7.90	0.9975	8.2564	0.9841	B1 = -0.0084	C1 = -0.019544
	11.26	0.9636	10.9976	0.9572	R ² = 0.94405	C2 = 0.000440
	16.10	0.9211	15.7532	0.9246	S.E = 0.01460	R ² = 0.996799
	19.67	0.8770	20.1935	0.9026		S.E = 0.004278
45°C	3.11	0.8682	2.6292	0.8732	B0 = 0.86504	C0 = 0.848665
Kernel	4.50	0.9044	4.8012	0.8912	B1 = 0.00485	C1 = 0.010570
	6.54	0.8471	6.3181	0.8995	R ² = 0.95747	C2 = -0.000398
	9.40	0.9362	9.5061	0.9121	S.E = 0.00423	R ² = 0.997943
	12.10	0.9256	11.5481	0.9181		S.E = 0.001140
45°C	3.41	0.8915	2.8448	0.8204	B0 = 0.80247	C0 = 0.768114
Pod	5.19	0.8593	5.2279	0.8595	B1 = 0.00976	C1 = 0.020747
	7.00	0.8229	6.8993	0.8780	R ² = 0.96053	C2 = -0.000699
	9.84	0.9116	10.4251	0.9062	S.E = 0.00903	R ² = 0.998118
	12.52	0.9864	12.6904	0.9200		S.E = 0.002417
45°C	4.20	0.9333	3.8085	0.9720	B0 = 0.97677	C0 = 0.986157
Hull	6.70	0.9925	6.8094	0.9623	B1 = -0.0018	C1 = -0.004221
	8.83	0.9592	8.8748	0.9579	R ² = 0.95566	C2 = 0.000116
	13.22	0.9720	13.1629	0.9514	S.E = 0.00228	R ² = 0.997934
	16.09	0.9167	15.8816	0.9483		S.E = 0.000603

EMC : Experimental equilibrium moisture content

CMC : Computed equilibrium moisture content

(A/D)e : Experimental hysteresis ratios

(A/D)c : Computed hysteresis ratios

$$(A/D)c = B0 + B1 * CMC$$

$$(A/D)c = C0 + C1 * CMC + C2 * CMC^2$$

of adsorption model. Since both curves matched very well, the linear model of hysteresis ratio coupled with the EMC equation of desorption could be used to depict the phenomenon of hysteresis and to predict the EMC of adsorption.

Conclusions and Suggestions

It is concluded that the modified Henderson equation is capable of describing the EMC equations of peanut kernel, pod, and hull. The dynamic method can accelerate the moisture exchange process to reach the equilibrium faster. The structure difference between kernel and hull makes the EMC curves different. The porous hull has higher EMC value than the kernel.

The phenomenon of hysteresis does occur in a drying and wetting cycle for peanuts. Most of the hysteresis values were within the moisture content range of 1%. A linear relationship was derived, which could be used to predict the EMC of adsorption in accompanying with the EMC equation of desorption.

From the learnings of this experiment, the following suggestions are recommended:

1. The drying temperature, recommended to use in Taiwan is within the range of 35 to 45°C. But only these two sorption isotherms are not enough to draw a safe scheme to store peanuts; therefore, the EMC curves at 15 and 25°C should be tested and determined in future.

2. Because higher air velocity to pass over samples can have higher moisture transfer rate between samples and air, it will be applied to reducing the time to elapse for EMC measurements. But the drawback of the method is the loss of the accuracy. To find the optimal velocity, which will help attaining the reliable and accurate readings, deserves further study.

3. The modified Henderson equation should work for the whole range of experimental temperatures. The parameters determined in this study are good for 35 and 45°C only, and it is too risky to recommend the parameters for extrapolative uses; therefore, more tests at other temperatures are needed.

References

ASAE DATA, 1987, Moisture Relationships of

Grains, ASAE Standards D245.4, American Society of Agricultural Engineers, St. Joseph, Michigan.

Ayerst, G., 1965, Water Activity- Its Measurement and Significance in Biology. *International Biodeterior Bulletin* 1: 13-26.

Babbitt, J. D., 1945, Hysteresis in the Adsorption of Water Vapor by Wheat. *Nature* 156: 265-266.

Becker, H. A., and H. R. Sallans, 1956, A Study of the Desorption Isotherms of Wheat at 25°C and 50°C, *Cereal Chemistry* 33: 79-91.

Breese, M. H., 1955, Hysteresis in the hygroscopic equilibria of Rough Rice at 25°C, *Cereal Chemistry* 32: 481-487.

Brunauer, S., P. H. Emmett, and E. Teller, 1938, Adsorption of Gases in Multimolecular Layers, *Journal of American Chemical Society* 60: 309-319.

Bushuk, W., and C. A. Winkler, 1957, Sorption of Water Vapor on Wheat Flour, Starch and Gluten, *Cereal Chemistry* 34: 73-86.

Chang, S. F., 1988, Modification of Henderson's EMC model and EMC Isotherms of Local Paddy and Corn, *Journal of Chinese Agricultural Engineering*, 34(1): 16-39.

Chen, C. C., 1988, A Study of Equilibrium Relative Humidity for Yellowed Dent Corn Kernels, PhD Dissertation, University of Minnesota, St. Paul, MN.

Chung, D. C., and H. B. Pfost, 1967, Adsorption and Desorption of Water Vapor by Cereal Grains and Their Products. II. Development of the General Isotherm Equation, *Transactions of the ASAE* 10(3): 551-554.

Chung, D. C., and H. B. Pfost, 1967, Adsorption and Desorption of Water Vapor by Cereal Grains and Their Products. III. A Hypothesis for Explaining the Hysteresis Effect, *Transactions of the ASAE* 10(3): 555-558.

Coleman, D. A., and H. C. Fellows, 1925, Hygroscopic Moisture of Cereal Grains and the Seed Exposed to Atmospheres of Different Relative Humidities. *Cereal Chemistry* 2: 275-287.

Draper, N. R., and H. Smith, 1980, *Applied Regression Analysis*, John Wiley and Sons, Inc., New York.

Friesen, J. A., Predicting Equilibrium Moisture Content within the Hysteresis Loop, *Transactions of the ASAE* 20(2): 339-341.

- Hart, J. R., 1964, Hysteresis Effects in Mixtures of Wheats Taken from the Same Sample but Having Different Moisture Contents, *Cereal Chemistry* 41: 340-350.
- Henderson, S. M., 1952, A Basic Concept of Equilibrium Moisture, *Agricultural Engineering* 2: 29-32.
- Henderson, S. M., 1970, Equilibrium Moisture Content of Small Grain-Hysteresis, *Transactions of the ASAE* 16(4): 762-764.
- Houston, D. F., 1952, Hygroscopic Equilibrium of Brown Rice, *Cereal Chemistry* 29: 71-76.
- Hubbard, J. E., F. R. Earle, and F. R. Senti, 1957, Moisture Relations in Wheat and Corn, *Cereal Chemistry* 34: 422-433.
- Labuza, Theodore P., 1985, Moisture Sorption: Practical Aspects of Isotherm Measurement and Use, American Association of Cereal Chemists, St. Paul, Minnesota.
- Luikov, A. V., 1966, Heat and Mass Transfer in Capillary Porous Bodies. Academic Press Inc., New York.
- McBain, J. W., 1935, An Explanation of Hysteresis in the Hydration and Dehydration of Gels, *Journal of American Chemistry Society* 57: 699-700.
- Perry, J. T., 1963, *Perry's Engineering Handbook*, McGraw-Hill Book Co., New York.
- Pixton, S. W., and S. Warburton, 1971, Moisture Content/Relative Humidity Equilibrium Relationship of Some Cereal Grains at Different Temperatures, *Journal of Stored Products Research* 6: 283-292.
- Skaar, C., 1972, *Water in Wood*, Syracuse University Press, New York.
- Strohman, R. D., and R. R. Yoerger, 1967, A New Equilibrium Moisture Content Equation, *Transactions of the ASAE* 13(3): 675-677.
- Thompson, T. L., R. M. Peart, and G. H. Forst, 1968, Mathematical Simulation of Corn Drying - A New Model, *Transactions of the ASAE* 14(3): 582-586.
- Van den Berg, 1985, *Water Activity in: Concentration and Drying of Foods*, Elsevier Applied Science Publisher, London and New York.
- Weichert, L., 1963, Investigations on Sorption and Swelling of Spruce, Beech, and Compressed Beech Wood between 20 and 100°C, *Holz als Roh-und Werkstoff* 21(8): 290-300.
- Young, J. H., and G. L. Nelson, 1967, Theory of Hysteresis between Sorption and Desorption Isotherms in Biological Materials, *Transactions of the ASAE* 13(1): 260-263.
- Young, J. H., and G. L. Nelson, 1967, Research of Hysteresis between Sorption and Desorption Isotherms of Wheat, *Transactions of the ASAE* 13(4): 756-761.
- Young, J. H., 1976, Evaluation of Models to Describe Sorption and Desorption Equilibrium Moisture Content Isotherms of Virginia Type Peanuts, *Transactions of the ASAE* 19(1): 146-150, 155.
- Young, J. H., T. B. Whitaker, P. D. Blankenship, G. H. Brusewitz, J. M. Troeger, J. L. Steele, and N. K. Person, Jr., 1982, Effect of Oven Drying Time on Peanut Moisture Determination, *Transactions of the ASAE* 28(2): 491-496.

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