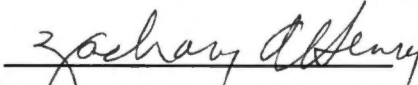


To the Graduate Council:

I am submitting herewith a dissertation written by Samuel Gaither McNeill entitled "Effects of Delayed Harvest on the Moisture Sorption Properties of Soybeans." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Agricultural Engineering.


Dr. Zachary A. Henry, Major Professor

We have read this dissertation
and recommend its acceptance:







Accepted for the council:


Associate Vice Chancellor and
Dean of The Graduate School

**DELAYED HARVEST EFFECTS ON THE
MOISTURE SORPTION PROPERTIES OF SOYBEANS**

A Dissertation

Presented for the

Doctor of Philosophy

Degree

University of Tennessee, Knoxville

Samuel Gaither McNeill

December 1996

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Thesis
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DEDICATION

This dissertation is dedicated to my parents

Peter Thurman McNeill, Jr. and Anna Lou Planck McNeill

who taught me the value of an education and how to live by their example.

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ABSTRACT

Absorption and desorption characteristics were determined for three varieties of soybean seeds that were harvested over 16 weeks in two crop years. Harvest began at physiological maturity and extended well beyond a normal harvest period. Fully exposed absorption tests were followed by desorption tests in all cases under near constant temperature and air flow conditions. Experimental data were analyzed by empirical, theoretical, and statistical models.

An investigation of the morphological features of soybean seeds led to sorption tests with two soybean varieties which included covering the hilum area (approximately 10% of the total surface area) with wax. It was concluded that the hilum area did not provide a preferential route for moisture vapor exchange with the atmosphere during absorption or desorption.

The empirically based modified Page equation was used to estimate the moisture equilibrium value by non-linear regression and found to adequately describe both absorption and desorption behavior. Equation parameters k and n were used to generate two descriptive parameters, k^n and k^m , for each replication of variety and week of harvest to help identify the effects of field weathering. The n and k^m parameters were found to be more sensitive to harvest moisture conditions for absorption than the k and k^n parameters but this was not repeated in both years or found for desorption in either year.

The level of protein, oil, free fatty acids, harvest moisture, and seed size were merged with the variables found by regression from the modified Page equation that characterized the absorption and desorption responses. The statistical model that accounted for most of the variation in k values for 1989 contained the covariates of harvest moisture and free fatty acid, while the corresponding model in 1990 contained the covariate of oil. Also in 1989, the desorption EMCR value was correlated to seed size.

These findings suggested that the role of chemical components on the rate and extent of moisture transfer in seeds or other grains requires further investigation. It is suggested that non-

destructive technique be used to facilitate measurements with the same sample during a moisture transfer cycle, which occurs every year in the field, in storage environments, and during transport where seeds are fully exposed to a wide range of environmental conditions.

The cellular diffusion model was paired with a selected set of sorption data to determine estimates for the theoretical parameters (Biot number and diffusion term) by regression. The diffusion model produced estimates for the moisture ratio that were in very good agreement with the data but were slightly less accurate than those produced by the modified Page equation. The most important result from this comparison was that the Biot number had a similar effect on the relationship that describes the rate of moisture transport (for both absorption and desorption) as the n value in the modified Page equation.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
1.1. Background	1
1.2. Purpose and Objectives	5
II. LITERATURE REVIEW	6
2.1. Mathematical Models for Grain Conditioning	6
2.1.1. Theoretical Models	7
2.1.2. Semi-theoretical Models	13
2.1.3. Empirical Models	16
2.2. Moisture Equilibrium Studies	20
2.2.1. Temperature Effects	21
2.2.2. Hysteresis	22
2.2.3. Methods of Measuring EMC	24
2.2.4. EMC-ERH Models	26
2.3. Drying Studies	32
2.3.1. Drying Studies for Soybeans	33
2.3.2. Drying Studies for Other Oilseeds	38
2.3.3. Related Drying Studies for Cereal Grains	40
2.4. Wetting Studies	43
2.5. Delayed Harvest/Field Weathering Studies	47
2.5.1. Potential Problems Associated with Weather Exposure	47
2.5.2. Field Moisture Studies and Predictive Models	49
2.5.3. Predictive Models for Imbibition	51
III. PHYSICAL AND CHEMICAL DESCRIPTION OF SOYBEAN SEEDS	53
3.1. Morphology of Soybean Seed Components	53
3.2. Chemical Composition	57
3.3. Influence of Structure and Composition on EMC and Conditioning Properties	59
IV. MATHEMATICAL ANALYSIS	65
4.1. Partition of Diffusion Resistances	65
4.2. Principle of Homogeneity	66
4.3. Assumptions	66
4.4. Governing Equation, Boundary Conditions, and Solution	68
4.5. Application of the Analytical Solution	76
4.6. Model for Homogeneous Materials	81
4.7. Development of a New Component Model	82

V. EXPERIMENTAL PROCEDURES	89
5.1. Experimental Design	89
5.2. Material Procurement, Handling, and Processing Procedures	90
5.3. The Absorption-Desorption System	91
5.4. The Absorption-Desorption Tests	94
5.5. Data Collection	94
5.6. Conditioning Tests with Wax Covered Hilum	95
VI. RESULTS AND DISCUSSION	98
6.1. Harvest Data for the Field Weathering Study	98
6.2. Comparative Sorption Through the Hilum Area	100
6.3. Sorption Tests with Field Weathered Soybeans	103
6.3.1. Absorption Tests	105
6.3.1.1. Initial moisture content	106
6.3.1.2. Chamber conditions	108
6.3.1.3. Predicted parameters	111
6.3.1.4. Comparison of the modified Page equation with the diffusion equation	115
6.3.2. Desorption Tests	118
6.3.2.1. Initial moisture content	118
6.3.2.2. Chamber conditions	121
6.3.2.3. Predicted parameters	122
6.3.2.4. Comparison of the modified Page equation with the diffusion equation	126
6.4. Effect of Chemical Components	127
6.4.1. Absorption Tests	128
6.4.2. Desorption Tests	128
VII. SUMMARY AND CONCLUSIONS	132
REFERENCES	135
APPENDICES	150
A. Harvest Data and Chamber Conditions for Field Weathered Soybeans	151
B. Chamber Conditions and Moisture Ratio Graphs for Wax Treated Soybeans	160
C. Experimental Results and Predicted Parameters for Sorption Tests with Weathered Soybeans	163
D. Comparison of Empirical and Theoretical Models	208
E. Computer Program and Sample Output for Theoretical Model	214
VITA	220

LIST OF TABLES

TABLE		PAGE
3.1.	Composition of the component parts of soybean seeds (Markley, 1950)	58
4.1.	Physical and diffusive properties of soybean seed components at 20° C	78
4.2.	Beta values for soybean seed components at different moisture content levels at 20° C .	80
5.1.	Statistical design for field weathered soybean seed conditioning tests	89
5.2.	Statistical design for wax covered soybean seed conditioning tests	96
6.1.	Experimental values and predicted variables under absorption conditions for Tn4-86 and Tn6-90 soybeans with a wax coated hilum and uncoated control	101
6.2.	Experimental values and predicted variables under desorption conditions for Tn4-86 and Tn6-90 soybeans with a wax coated hilum and uncoated control	101
6.3.	Summary of the analysis of variance for the initial moisture content and predicted variables from wax treated absorption tests with Tn4-86 and Tn6-90 soybeans	102
6.4.	Summary of the analysis of variance for the initial moisture content and predicted variables from wax treated desorption tests with Tn4-86 and Tn6-90 soybeans	103
6.5.	Classification of variables used in the statistical analysis for each year of study.	104
6.6.	Hours of exposure for absorption conditioning tests during 1989 and 1990	106
6.7.	Summary of observed and predicted parameters for each variety with 1989 and 1990 soybean absorption data	107
6.8.	Analysis of variance model statements used to test correlations among the observed and predicted variables for absorption and desorption tests in 1989	109
6.9.	Summary of the analysis of variance results for observed and predicted variables for the absorption experiment in 1989	109
6.10.	Analysis of variance model statements used to test correlations among the observed and predicted variables for absorption and desorption tests in 1990	110
6.11.	Summary of the analysis variance results for observed and predicted variables for the absorption experiment in 1990	110

6.12.	Comparison of empirical and theoretical model parameters for selected absorption and desorption tests (harvest week 6) in 1989 and 1990	117
6.13.	Hours of exposure for desorption conditioning tests during 1989 and 1990	118
6.14.	Summary of observed and predicted parameters for each variety with 1989 and 1990 soybean desorption data	119
6.15.	Summary of the analysis of variance results for observed and predicted variables for the desorption experiment in 1989	120
6.16.	Summary of the analysis of variance results for observed and predicted variables for the desorption experiment in 1990	121
6.17.	Summary of the analysis of variance for selected variables and the significant terms from the 1989 and 1990 desorption experiments	129
A1.	Harvest dates during each week of study for soybean varieties Tn4-86, Essex, and Leflore during the 1989 season	152
A2.	Harvest dates during each week of study for soybean varieties Tn4-86, Essex, and Leflore during the 1990 season	152
C1.	Summary of observed and predicted variables for Tn4-86 soybeans under absorption conditions in 1989	164
C2.	Summary of observed and predicted variables for Essex soybeans under absorption conditions in 1989	165
C3.	Summary of observed and predicted variables for Leflore soybeans under absorption conditions in 1989	166
C4.	Summary of observed and predicted variables for Tn4-86 soybeans under absorption conditions in 1990	167
C5.	Summary of observed and predicted variables for Essex soybeans under absorption conditions in 1990	168
C6.	Summary of observed and predicted variables for Leflore soybeans under absorption conditions in 1990	169
C7.	Summary of observed and predicted variables for Tn4-86 soybeans under desorption conditions in 1989	170
C8.	Summary of observed and predicted variables for Essex soybeans under desorption conditions in 1989	171

C9.	Summary of observed and predicted variables for Leflore soybeans under desorption conditions in 1989	172
C10.	Summary of observed and predicted variables for Tn4-86 soybeans under desorption conditions in 1990	173
C11.	Summary of observed and predicted variables for Essex soybeans under desorption conditions in 1990	174
C12.	Summary of observed and predicted variables for Leflore soybeans under desorption conditions in 1990	175

LIST OF FIGURES

FIGURE	PAGE
2.1. Desorption moisture ratio for canola, corn, soybeans, and wheat	19
2.2. Absorption moisture ratio for canola, corn, soybeans, and wheat	19
3.1. Morphological features of a typical soybean seed	54
3.2. A sketch of the microscopic structure of the soybean seed coat and cotyledon	54
4.1. Beta values for soybean seed components at different moisture levels (represented by the slope of each bold line segment)	80
5.1. Schematic diagram of the environmental control system used for moisture conditioning tests with field weathered soybeans	92
A1. Cumulative rainfall and weekly mean temperature and relative humidity levels during the 1989 harvest season	153
A2. Cumulative rainfall and weekly mean temperature and relative humidity levels during the 1990 harvest season	153
A3. Harvest moisture content for Tn4-86, Essex, and Leflore soybeans during the 1989 harvest season by calendar days	154
A4. Harvest moisture content for Tn4-86, Essex, and Leflore soybeans during the 1990 harvest season by calendar days	154
A5. Moisture content for Tn4-86, Essex, and Leflore soybeans during the 1989 harvest season with weeks overlaid	155
A6. Moisture content for Tn4-86, Essex, and Leflore soybeans during the 1990 harvest season with weeks overlaid	155
A7. Mean relative humidity, temperature, initial moisture content, EMCH, and EMCR during the 1989 absorption tests	156
A8. Mean relative humidity, temperature, initial moisture content, EMCH, and EMCR during the 1990 absorption tests	156
A9. Mean relative humidity, EMCH, and EMCR for each chamber during the 1990 absorption tests	157

A10.	Mean temperature and initial moisture content for each chamber during the 1990 absorption tests	157
A11.	Mean relative humidity, temperature, initial moisture content, EMCH, and EMCR during the 1989 desorption tests	158
A12.	Mean relative humidity, temperature, initial moisture content, EMCH, and EMCR during the 1990 desorption tests	158
A13.	Mean relative humidity, EMCH, and EMCR for each chamber during the 1990 desorption tests	159
A14.	Mean temperature and initial moisture content for each chamber during the 1990 desorption tests	159
B1.	Mean temperature and relative humidity levels during the absorption tests with wax covered and uncovered control soybeans	161
B2.	Mean temperature and relative humidity levels during the desorption tests with wax covered and uncovered control soybeans	161
B3.	Observed and predicted absorption moisture ratios plotted against time for Tn4-86 and Tn6-90 soybeans with a wax covered hilum (W) and uncovered control ©	162
B4.	Observed and predicted desorption moisture ratios plotted against time for Tn4-86 and Tn6-90 soybeans with a wax covered hilum (W) and uncovered control ©	162
C1.	Observed and predicted moisture ratios for absorption tests during harvest week 3 for Tn4-86, and week 2 for Essex and Leflore soybeans in 1989	176
C2.	Observed and predicted moisture ratios for absorption tests during harvest week 6 with Tn4-86, Essex, and Leflore soybeans in 1989	177
C3.	Observed and predicted moisture ratios for absorption tests during harvest week 11 with Tn4-86, Essex, and Leflore soybeans in 1989	178
C4.	Observed and predicted moisture ratios for absorption tests during harvest week 16 with Tn4-86, Essex, and Leflore soybeans in 1989	179
C5.	Observed and predicted moisture ratios for absorption tests during harvest week 2 with Tn4-86, Essex, and Leflore soybeans in 1990	180
C6.	Observed and predicted moisture ratios for absorption tests during harvest week 6 with Tn4-86, Essex, and Leflore soybeans in 1990	181

C7.	Observed and predicted moisture ratios for absorption tests during harvest week 11 with Tn4-86, Essex, and Leflore soybeans in 1990	182
C8.	Observed and predicted moisture ratios for absorption tests during harvest week 16 with Tn4-86, Essex, and Leflore soybeans in 1990	183
C9.	Observed and predicted moisture ratios for desorption tests during harvest week 3 for Tn4-86, and week 2 for Essex, and Leflore soybeans in 1989	184
C10.	Observed and predicted moisture ratios for desorption tests during harvest week 6 with Tn4-86, Essex, and Leflore soybeans in 1989	185
C11.	Observed and predicted moisture ratios for desorption tests during harvest week 11 with Tn4-86, Essex, and Leflore soybeans in 1989	186
C12.	Observed and predicted moisture ratios for desorption tests during harvest week 16 with Tn4-86, Essex, and Leflore soybeans in 1989	187
C13.	Observed and predicted moisture ratios for desorption tests during harvest week 2 with Tn4-86, Essex, and Leflore soybeans in 1990	188
C14.	Observed and predicted moisture ratios for desorption tests during harvest week 6 with Tn4-86, Essex, and Leflore soybeans in 1990	189
C15.	Observed and predicted moisture ratios for desorption tests during harvest week 11 with Tn4-86, Essex, and Leflore soybeans in 1990	190
C16.	Observed and predicted moisture ratios for desorption tests during harvest week 16 with Tn4-86, Essex, and Leflore soybeans in 1990	191
C17.	Comparison of mean regression equilibrium moisture content (EMCR) values with values predicted by the modified Halsey equation (EMCH) for 89 (a) and 1990 (b) absorption tests	192
C18.	Variations in the regression equilibrium moisture content (EMCR) values by harvest week and variety for 1989 (a) and 1990 (b) absorption tests	193
C19.	Mean k values for each harvest week and variety for 1989 (a) and 1990 (b) absorption tests	194
C20.	Mean n values among harvest week and variety for 1989 (a) and 1990 (b) absorption tests	195
C21.	Mean k ^a values for each harvest week and variety for 1989 (a) and 1990 (b) absorption tests	196

C22.	Mean k^m values among harvest week and variety for 1989 (a) and 1990 (b) absorption tests	197
C23.	Comparison of regression equilibrium moisture content (EMCR) values with values predicted by the modified Halsey equation (EMCH) for 1989 (a) and 1990 (b) desorption tests	198
C24.	Variations in regression equilibrium moisture content (EMCR) values by harvest week and variety for 1989 (a) and 1990 (b) desorption tests	199
C25.	Mean k values for each harvest week and variety for 1989 (a) and 1990 (b) desorption tests	200
C26.	Mean n values among harvest week and variety for 1989 (a) and 1990 (b) desorption tests	201
C27.	Mean k^a values for each harvest week and variety for 1989 (a) and 1990 (b) desorption tests	202
C28.	Mean k^m values for each harvest week and variety for 1989 (a) and 1990 (b) desorption tests	203
C29.	Comparison of mean k values for absorption and desorption for 1989 (a) and 1990 (b) tests	204
C30.	Comparison of mean n values for absorption and desorption for 1989 (a) and 1990 (b) tests	205
C31.	Comparison of mean k^a values for absorption and desorption for 1989 (a) and 1990 (b) tests	206
C32.	Comparison of mean k^m values for absorption and desorption for 1989 (a) and 1990 (b) tests	207
D1.	Comparison of the modified Page equation and the diffusion equation for absorption tests during harvest week 6 (Rep 3) for Tn4-86, Essex, and Leflore soybeans in 1989	209
D2.	Comparison of the modified Page equation and the diffusion equation for absorption tests during harvest week 6 (Rep 1) for Tn4-86, Essex, and Leflore soybeans in 1990	210
D3.	Comparison of the modified Page equation and the diffusion equation for desorption tests during harvest week 6 (Rep 3) for Tn4-86, Essex, and Leflore soybeans in 1989	211

D4.	Comparison of the modified Page equation and the diffusion equation for desorption tests during harvest week 6 (Rep 1) for Tn4-86, Essex, and Leflore soybeans in 1990	212
D5.	Biot numbers and n values for absorption and desorption conditions for Tn4-86, Essex, and Leflore soybeans harvested during week 6 in 1989 and 1990	213
D6.	D'/R^2 and k values for absorption and desorption conditions for Tn4-86, Essex, and Leflore soybeans harvested during week 6 in 1989 and 1990	213

CHAPTER I

INTRODUCTION

1.1. BACKGROUND:

Over two and a half billion bushels of soybeans [*Glycine max* (L.) Merrill] were produced in the U. S. in 1994 (STRATSOY, 1996) with a combined contribution of approximately 90 million bushels from Tennessee and Kentucky growers (Williams, 1995). This level of production represented over \$223 and \$263 million to the gross incomes of farmers in these two states, respectively.

On average, 90 per cent of the domestic use is for oil, the most valuable component, used for cooking oil, margarine, salad dressings, mayonnaise, and other food products in the human food chain. Soybean meal, a by-product of oil extraction, is relatively high in protein and is used primarily for livestock feed by both ruminant and monogastric species. Roughly three per cent of the crop is used for seed while seven per cent goes into new products such as soy ink, soy-diesel, edible films, and construction materials (STRATSOY, 1996).

Grain quality standards have been established for trading purposes by the United States Department of Agriculture Federal Grain Inspection Service and are described by the Official Grades for Soybeans. Test weight, damaged kernels (splits or heat damage), and seed color are specified, however the relationship of these grade factors to oil and protein content (quality factors) is not clearly defined.

The present marketing system theoretically provides an incentive for farmers to deliver the best quality grain possible by offering premiums for No.1 grade. Premiums are actually influenced by the demand for various end uses of soybeans, competition from other countries, and global politics. Presently, it behooves producers to be knowledgeable of the factors that influence soybean quality so that they can take advantage of marketing opportunities when they become available. Quite often the producer is unaware of the final destination of the crop after it has been sold to the

elevator. Consequently, the producer has a narrow view of the factors that influence the end use product quality. Ironically, the first processor (i.e., the farmer) has a strong influence regarding raw product quality but usually has little control of the final product destination.

Some investigators have attempted to relate bean quality factors to bean grade factors (Sidhu, 1992; Hurburgh et al., 1987, and Overhults, 1975) and even to crop value (Hurburgh et al., 1990). Yet these findings have not been widely embraced by the trade, probably because of the added time required to grade each lot prior to a transaction.

Moisture content remains a trade consideration for local elevators because of its strong indication of condition and storability. Moisture content has been identified as the single most important parameter for preventing mold growth in stored grain (Ross et al., 1990; Pomeranz, 1992). Other important factors are seed temperature throughout storage and soundness of individual seeds in the lot at the beginning of storage. Hence, moisture management is vitally important throughout the harvesting, drying, and storage phases of production and during transport if product quality is to be maintained as the crop moves from the field to the final domestic or foreign processor.

Soybeans are traditionally harvested several weeks after physiological maturity (PM) when the moisture content of the bean is in the 10-25% (d.b.) range (DeBusk, 1987). Harvest is delayed primarily to reduce drying costs, but this practice can create an added (though subtle) expense if beans are exposed to extreme dry or wet weather periods. Dry weather can cause excessive shatter losses during harvest which reduces yield and profits. Wet field conditions can delay harvest. This prolongs exposure of the seed to environmental conditions that promote mold growth and causes a reduction in the quality of the bean and its end use products. The added costs of delayed harvest are not always evident until the crop is marketed, which can be several months later. By then, many other factors that effect bean quality (i.e., handling, drying, and storage conditions) come into play and the effects of delayed harvest may be compounded or masked altogether.

This study was prompted by an occurrence of adverse weather which delayed soybean harvest. In the fall of 1984 and 1985, the lower Mississippi River valley was inundated with heavy

rains from hurricanes that entered the Gulf of Mexico just prior to harvest. Many farmers were kept out of their fields until late November especially in fields along rivers and streams. During these two years and oftentimes in many isolated areas in other years, artificial drying has been necessary in lieu of field drying for high quality soybean production.

Numerous studies have been conducted on the drying and storage of cereal grains (corn, rice, and wheat) and much of the developed theory can be extended to oilseed products. However, only a few studies have dealt with moisture properties of oilseeds. Limited recent studies conclusively show that oilseeds exhibit unique moisture equilibrium and transport properties. Parameters used to describe the drying rate in prediction models have often been expressed in terms that are easily measured such as the temperature and humidity of the outside air and seed moisture.

Accurate models for product-specific equilibrium moisture content values are essential to the design engineer who requires such information to predict the exposure time needed to dry to a target level. Additionally, drying and aeration models are needed to assist grain storage managers with fan control strategies to avoid over drying the bottom layer of soybeans in a bin and under drying the top layer. Over dried soybeans can lead to significant economic losses to the producer. For example, when soybeans are valued at \$7.50/bu, water is worth 12.5 ¢/lb or \$1/gallon. If soybeans are unintentionally dried to 11% (d.b.) moisture content by mismanagement of the drying or aeration fan, they will have 3.8% less water (2 lbs/bu) than if sold at 14.9% (d.b.) which elucidates to a 25 ¢/bu loss to the farmer! Under drying the top layers in a bin can be just as devastating because the area just below the top 6 to 12 inches is most likely to spoil by microbial activity if moisture is not controlled. Typical situations that can create such problems are placing a load of wet soybeans directly from the field in the middle of a bin of dry soybeans, not filling the bin with a distributor or spreader especially if the seeds are not cleaned prior to binning, and not inspecting the crop or monitoring temperatures below the surface frequently during storage.

A package of Windows-based computer programs (called GRANARY) has recently been made available to predict the time and energy required to dry grain with natural air, low temperature,

stirring equipment or high speed commercial dryers (Lower et al., 1994). Factors considered in these models are initial temperature and moisture of the air and grain, desired final product moisture, and air flow rate. Outputs from these programs include not only the drying time, energy, and cost estimates but the moisture and temperature profile within the bed. Low temperature system evaluations also include a dry matter loss accumulation subroutine as an indicator of product quality. The convenience and versatility of these programs greatly enhance a producers ability to compare dryer performance of different manufacturers and manage a particular dryer as crop moisture and environmental conditions change, yet not all of the drying models in the program package include sufficient information for soybeans.

Both engineers who design grain dryers and operators who manage them must recognize the physical differences in cereal grains and oilseeds in order to protect product quality. Presently no models have been developed to take into consideration the effects of oil, protein, carbohydrates or other chemical properties on the moisture transfer rates and equilibrium values for soybeans. If any of these variables are shown to influence drying or wetting rates or the extent of moisture transfer for soybeans, then a new model may be needed which can more accurately describe the moisture holding capacity and mass transfer phenomena of these materials.

Tests in the University of Tennessee Agricultural Engineering Department have indicated a marked difference between moisture sorption and desorption rates of soybean seeds. There are indications that when soybeans move through wetting and drying cycles in the field they have progressive increases in damage as indicated by wrinkles and cracks in the seed coat. Additionally, food scientists (Melton, 1989; Hulbert, 1996) have indicated that this increased physical damage may produce an end product of lower quality.

Sidhu (1992) provided an evaluation of the influence of the field environment on end use quality. Such an evaluation should be coupled with more complete knowledge of the wetting and drying mechanisms of soybeans, whether these are influenced by delayed harvest, varietal differences

or other factors and whether the physical and chemical nature of the bean effects these processes. A study should be conducted, therefore, to provide insight for such an evaluation.

1.2. PURPOSE AND OBJECTIVES:

The overall purpose of this study was to investigate the effects of delayed harvest and varietal differences on the rate of moisture gain and loss by soybean seeds when exposed to extreme humidity conditions. Specific objectives were to:

1. Develop an analytical model to describe the moisture absorption and desorption rates of soybean seed.
2. Compare the analytical model to an empirical model using sorption data from soybeans exposed to field weathering after maturity and to simulated field atmospheric conditions.
3. Evaluate the absorption and desorption data to establish descriptive parameters from the empirical model to test functional relationships with the chemical components and diffusive properties of the material.

CHAPTER II

REVIEW OF LITERATURE

Many engineers have conducted studies to gain a better understanding of the factors that determine the rate of mass transfer and the moisture holding capacity of grains and oilseeds. Researchers have recently focused on the physical processes that exist between a product and its environment. Existing models have been improved to describe the mechanisms that govern the rate of moisture transfer to and from cereal grains and oilseeds for different temperature and humidity conditions. Yet, more information is needed to develop new relationships that accurately describe moisture sorption rates and equilibrium moisture levels for specific products across the entire humidity range that is observed in nature. This review has addressed the areas of mathematical model development for grain conditioning, equilibrium moisture content investigations and their associated mathematical treatments of the sorption phenomena, pertinent grain drying and rewetting studies, and reports that relate quality factors in soybean seeds to delayed harvest.

2.1. MATHEMATICAL MODELS FOR GRAIN CONDITIONING:

Mathematical models that have been used to describe the moisture transfer rate in cereal grains and oilseeds can be categorized into three general groups; theoretical, semi-theoretical, and empirical. Diffusion models have been widely used because of their emphasis on moisture transport theory. Closed form solutions or numerical techniques have been employed to solve the partial differential equation based on appropriate boundary conditions of the problem, although neither solution can be solved quickly without the aid of a computer. Semi-theoretical models are slightly varied or truncated mathematical expressions that are theoretically based and are less mathematically rigorous. Empirical models are purely derived from curve fitting or statistical procedures from existing data and are generally the most mathematically straightforward. Theoretical models have been developed primarily by academic and industrial researchers and used to select significant

parameters for the operation of interest. The later two types of models are widely used for process control algorithms in industry but any valid model is beneficial to the grain trade.

2.1.1. Theoretical Models:

Soybeans are comprised of two distinct structural components-the cotyledon and seed coat. The cotyledon is a relatively homogeneous body as compared to the seed coat which is comprised of a variety of cellular tissue with different orientation, structural integrity, and intercellular space. The morphological features of each seed component are given in more detail in Chapter III, but are mentioned here because the discussion that follows relates to these unique physical features.

Brooker et al. (1992) listed the following mechanisms that govern moisture movement in capillary porous bodies such as grains and oilseeds during the falling-rate drying period: capillary action, liquid diffusion, surface diffusion, vapor diffusion, hydrodynamic flow, and thermal diffusion. Other mechanisms that may be considered are flow by shrinkage pressures and flow by vaporization-condensation sequences although these may be a combination of the first four mechanisms listed. These mechanisms apply to both absorption and desorption conditions but are presented in the context of soybean drying.

Capillary action is liquid movement due to surface forces which occurs through the micro pores between the cellular tissue. As moisture is removed from the seed coat surface of a soybean seed, a void space is created which is filled with liquid from within the adjacent cells by capillary action. This mechanism may only be important in the high moisture range.

Liquid diffusion is movement due to differences in moisture concentration. When moisture is removed from the seed surface a moisture gradient is created in the outer region of the seed that progresses towards the center as drying ensues. This action causes moisture from within the cell to move outside the cell since it is permeable to liquids. Yet because of the resistance offered by the cell wall, this mode of diffusion may not occur until after the capillaries are void of water.

Surface diffusion is liquid movement due to diffusion of moisture on porous surfaces and is due to the moisture gradient at the surface. This may result in a local difference of equilibrium moisture properties of the various cells and capillaries within the seed coat tissue.

Vapor diffusion is the movement of moisture vapor due to differences in moisture concentration. Vapor will also diffuse by moisture concentration differences along with liquids. This mode of transport will cause the high moisture inner cell to dry by diffusing vapor through cell walls by a concentration gradient driving force. Due to the widespread selection and success as a drying model, this mechanism may be the most dominant of all those listed for grains and oilseeds.

Hydrodynamic flow is liquid movement due to gravitational forces which may cause moisture movement between specific cells with relatively large intercellular porous regions at high moisture conditions. This has not been shown to be significant when applied to grain drying, probably because of the chemical bond between the water molecules and the cellular tissue even with several layers of water molecules between the cells. Hydrodynamic flow is significant only at extremely high temperatures but these are not intentionally reached when drying soybeans on the farm or at an elevator/processor.

Thermal diffusion is vapor movement due to temperature differences within a seed. This mode of transport can create moisture movement by thermal diffusion in the form of latent heat in certain situations. The driving force for this mode is purely due to a temperature gradient; for example, a steeping or dryeration phase when drying corn at high temperatures to minimize thermal and moisture stresses within the seed. Such a process is not normally applied when drying soybeans because of the relatively fragile nature of the seed coat. In addition, shrinkage pressure may be caused by cellular contraction during drying which may create a force within the seed sufficient for moisture transport. Simultaneous liquid and vapor movement can also occur due to total pressure differences.

Mass transport within a seed cannot be described by a single mechanism. Instead, all of the mechanisms listed may occur individually, collectively, or in a particular combination that depends

on the condition of the grain and its environment. For these reasons one equation that includes all possible modes of transport would be so complex that it would not be solvable or useful. Several simplifying assumptions must be made before a tractable model can be developed and will be presented as the selection of an appropriate model is discussed.

Luikov (1966) and his associates developed a set of three differential equations to describe the moisture movement within capillary-porous bodies based on the mechanisms listed above, which were:

$$\frac{\partial m}{\partial t} = \nabla^2 K_{11} m + \nabla^2 K_{12} T + \nabla^2 K_{13} P \quad (2.1)$$

$$\frac{\partial T}{\partial t} = \nabla^2 K_{21} m + \nabla^2 K_{22} T + \nabla^2 K_{23} P \quad (2.2)$$

$$\frac{\partial P}{\partial t} = \nabla^2 K_{31} m + \nabla^2 K_{32} T + \nabla^2 K_{33} P \quad (2.3)$$

where m = moisture content, dry basis decimal
 t = time, h
 T = product temperature, C
 P = total pressure, kPa
 K_{11}, K_{22}, K_{33} = phenomenological coefficients
 $K_{12}, K_{13}, K_{21}, K_{23}, K_{31}, K_{32}$ = coupling coefficients

These equations have not been applied in their entirety to cereal grain or oilseed drying or rewetting. To obtain a useful model, a few simplifying assumptions were made to reduce the form of these equations. The first assumption was that the pressure terms were negligible. This was reasonable because significant pressure gradients are created only at very high temperatures, which do not exist in typical grain conditioning situations. Shrinkage pressures were also neglected. This reduces the set of equations to the following:

$$\frac{\partial m}{\partial t} = \nabla^2 K_{11} m + \nabla^2 K_{12} T \quad (2.4)$$

$$\frac{\partial T}{\partial t} = \nabla^2 K_{21} m + \nabla^2 K_{22} T \quad (2.5)$$

These two equations were applied to corn drying by Husain et al. (1972), who concluded that the coupling effect between temperature and moisture was negligible for corn. Assuming this applies to soybeans as well, the equation set reduced to:

$$\frac{\partial m}{\partial t} = \nabla^2 K_{11} m \quad (2.6)$$

$$\frac{\partial T}{\partial t} = \nabla^2 K_{22} T \quad (2.7)$$

The temperature of the product usually reaches steady state much faster than the moisture content. Especially for low temperature systems, most of the drying occurs without a temperature gradient in the product which lead to the use of equation (2.6) alone to describe moisture transport in capillary-porous bodies.

If the flow of moisture within a seed is assumed to take place by liquid or vapor diffusion or a combination of these transport mechanisms, the phenomenological coefficient K_{11} can be replaced by an average diffusion coefficient D' , yielding:

$$\frac{\partial m}{\partial t} = \nabla^2 D' m \quad (2.8)$$

This is Fick's law which has been used extensively throughout the literature (as reviewed by Jayas, et al., 1991; and Parry, 1985) to describe the sorption and desorption rates for many different agricultural products. Some examples are canola (Crisp and Woods, 1994), corn (Chu and Hustrulid, 1968b; Hamdy and Barre, 1969; Pabis and Henderson, 1962; Parry, 1985; Walton et al., 1988), peanuts (Whitaker and Young, 1972), rice (Steffe and Singh, 1982), soybeans (Lee, 1959; Osborn et al., 1991), tobacco (Chirnoksorn, 1992; Walton and Casada, 1988; Walton et al., 1976), and wheat (Babbitt, 1949; Becker and Sallans, 1955; Casada, 1994; Simmonds et al., 1953). The versatility of this equation obviously provides considerable latitude for a variety of products with vastly different particle size, cellular structure, and chemical composition.

A solution to equation (2.8) begins by assuming an appropriate shape of the body under investigation. Some investigators have derived successful models from geometric shapes that do not necessarily represent the physical representation of the material. For example, Becker and Sallans (1955) chose a spherical model to describe the wheat kernel as did Steffe and Singh (1982) for rice. While both grains actually resemble a cylinder, both models accurately depicted the observed diffusion rates quite well. This does not suggest that diffusion coefficients are interchangeable between products with different shapes. In fact, Sokhansanj (1987), Walton et al. (1988) and Syarief

et al. (1987) caution against this practice. Hence, diffusion coefficients that are determined from experimental data are product and shape dependent.

The following assumptions were made to apply equation (2.8) to soybean drying and wetting conditions:

- 1) seeds were regular in shape and uniform in size throughout the moisture conditioning process (such as a non-shrinking sphere)
- 2) moisture was uniformly distributed within all seeds initially
- 3) moisture transport was not temperature driven (isothermal)
- 4) the permeability of each component within the seed was uniform and constant
- 5) moisture transport was symmetrical within each homogeneous sub-component

These assumptions permit equation (2.8) to be rewritten in terms of the average moisture content, m , as:

$$\frac{\partial m}{\partial t} = D' \nabla^2 m \quad (2.9)$$

Solutions to this equation depend on the specified initial conditions and boundary constraints. For the initial condition ($t = 0$) a uniform average moisture content is generally assumed which implies that

$$m(r,0) = m_0 \quad (2.10)$$

where r is the radial distance from the center and m_0 is the average initial moisture content (decimal).

The boundary condition at the center of the body assumes a symmetric moisture profile which presupposes no change in moisture with time, or

$$\left. \frac{\partial m}{\partial t} \right|_{r=0} = 0 \quad (2.11)$$

The boundary condition at the surface of the body depends on the amount of resistance to mass transport. If one assumes there is a negligible resistance to moisture gain or loss during rewetting or drying, the surface moisture is assumed to reach equilibrium instantaneously upon exposure to the environment, i.e.:

$$m(R) = m_e \quad (2.12)$$

where $m(R)$ is the surface moisture content and m_e is the equilibrium moisture content.

Crank (1975) solved equation (2.9) by employing the condition of negligible resistance at the boundary layer (equation 2.12) and by assuming that the internal diffusion coefficient does not vary within the homogeneous material. His evaluation yielded the following solution:

$$MR(t) = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(-D' \left(\frac{n\pi}{R} \right)^2 t \right) \quad (2.13)$$

where $MR(t)$ is the average moisture ratio of the material at any given time which is defined by:

$$MR(t) = \frac{m(t) - m_e}{m_0 - m_e} \quad (2.14)$$

This solution has been tested by several researchers for soybean drying studies (Lee, 1959; Overhults, 1975; Mensah et al. 1979; Saurez et al. 1980a, Kitic and Viollaz, 1984) and wetting studies (Osborn et al. 1991) with mixed success reported. It has been used much more extensively in some form for other grain products including canola (Crisp and Woods, 1994), corn (Chu and Hustrulid, 1968), cotton seed (Farinati and Saurez, 1984), lintels (Tang and Sokhansanj, 1993), peanuts (Young and Whitaker, 1971a; Whitaker and Young, 1972), rice (Steffe and Singh, 1980a), sorghum (Saurez et al., 1980b) sunflower seed components (Rovedeo et al., 1993) and wheat (Becker and Sallans, 1955; and Jaros et al., 1992). Although it will not be incorporated in this study, it is mentioned because it has obviously been used extensively in the literature and provides a basis for comparison between two analytical solutions that have been applied to grain and food products. It will be referred to as the spherical diffusion equation in the discussion that follows to distinguish this equation from the second solution that will be presented.

The rate of moisture transferred to the surface must equal the rate of moisture flowing from the surface when there is a finite resistance to moisture transport at the surface and is stated mathematically as:

$$-D' \frac{\partial m(R,t)}{\partial r} = h_m (m(R,t) - m_e) \quad (2.15)$$

where

R = average radius for spheroid, cm

D' = mass diffusion coefficient based on moisture content gradient, cm^2/h

h_m = convective mass transfer coefficient, cm/h

By applying this boundary condition in place of equation (2.12) a much different solution results, as shown by Crank (1975):

$$MR(t) = 6 \sum_{n=1}^{\infty} \frac{(\sin \lambda_n R - \lambda_n R \cos \lambda_n R)^2}{(\lambda_n R)^3 (\lambda_n R - \sin \lambda_n R \cos \lambda_n R)} e^{-\frac{D'}{R^2} (\lambda_n R)^2 t} \quad (2.16)$$

where

$$\begin{aligned} D' &= \text{effective mass diffusion coefficient, cm}^2/\text{h} \\ \lambda_n R &= \text{eigenvalues from the equation} \\ \lambda_n R \cos(\lambda_n R) &= (1 - \text{Bi}_m) \sin(\lambda_n R) \\ \text{Bi}_m &= \text{Biot number for mass transfer} = h_m R / D \end{aligned} \quad (2.17)$$

Osborn et al. (1991) found that equation (2.16) produced less prediction error than equation (2.13) when compared with their experimental data for soybean absorption. Walton et al. (1988) also successfully applied this equation to white corn drying data from White et al. (1973). This equation has not been previously tested against soybean drying data, consequently it was selected as a candidate model in this study. The equation has been fully derived in a subsequent chapter and applied to the conditions of this study. This solution of the diffusion equation will be referred to as the cellular diffusion model in the discussion that follows to distinguish it from the spherical model.

Truncation of the series solution or alternative treatments of the diffusion term have been widely employed with varying degrees of success by several authors to simplify the spherical model. Brooker et al. (1992) suggested that equation (2.13) be used with a diffusion coefficient that is dependent on temperature and moisture content in an Arrhenius form. Tolaba et al. (1990) and Jaros et al. (1992) confirmed this conclusion but derived a slightly different relationship for the diffusion term. These recent reports emphasize that more information is needed to gain a better understanding of the diffusion phenomena for grain and oilseed products.

2.1.2. Semi-theoretical Models:

To simplify the mathematics of the solutions that have just been discussed Brooker et al. (1992) suggested that only the first term of the full series may be used with an error of less than 5% during the first portion of a drying test whenever the following constraint occurs:

$$D' \pi^2 t / R^2 > 1.2 \quad \text{or} \quad t > 0.122 R^2 / D'. \quad (2.18)$$

This suggestion is useful as long as these properties are known, but is difficult to implement otherwise. For example, when conditioning thin slices of the soybean cotyledon, Mensah et al. (1979) observed that the moisture diffusivity varied according to temperature and humidity conditions. Their prediction equation may be extrapolated for a conditioning temperature of 20° C to estimate the mass diffusivity for drying of 0.000156 cm²/h and for wetting of 0.00476 cm²/h. Assuming an average seed radius of 0.35 cm, the corresponding time estimates for conditioning soybeans to avoid excessive errors with a simplified, single term semi-theoretical model are 96 and 3.1 hours for the drying and wetting tests, respectively. The time estimate for the wetting condition seems reasonable but the estimate for the drying condition seems excessively long when considerations are given to the broad use of the diffusion model for so many different crop materials.

An analogous equation from heat transfer applications has been taken from Newton's second law of cooling. This analogy, which was first presented by Lewis (1921) and later discussed by Henderson and Pabis (1961), states that the rate of moisture transport during the falling rate period for hygroscopic materials is proportional to the difference between the moisture content at any given time and the equilibrium moisture content. Mathematically, this expression is written as:

$$dm/dt = -k'' (m - m_e) \quad (2.19)$$

In addition to the previously stated assumptions, this equation implies that all of the resistance to moisture movement is in a thin layer near the surface of the body as opposed to being equally distributed as in the diffusion model (Overhults, 1975). The equation may be solved by combining like terms, assuming k'' to be independent of time and moisture, integrating and applying the initial condition (equation 2.10) to solve for the integration constant which yields the exponential model:

$$MR = \exp (-k'' t) \quad (2.20)$$

Note that the only difference between this equation and the first term of equation (2.13) is the $6/\pi^2$ coefficient (when $k'' = D' \pi^2 / R^2$), which diminishes in significance as time increases. Of more importance is the implication that the k'' variable is related to the diffusion coefficient and the size

of the body, yet, few researchers have correlated these two parameters. Chu (1966) and Crane et al. (1959) were among the few investigators who studied the effect of kernel size on the drying rate of shelled corn, yet, both concluded that neither size nor shape significantly affected the drying rate. The exponential model has been used to successfully describe the drying rates of barley, corn, and wheat in thin layer experiments (Jayas et al., 1988; Ross and White, 1972; Bruce, 1985).

Chung et al. (1972) measured the wetting and drying rates of yellow shelled corn in the 15 to 27° C temperature range with 30 to 80% relative humidities. Sound kernels were tested with heat damaged and broken kernels from one year of study. Results for the desorption condition revealed a faster drying rate for broken kernels, while sound and heat damaged kernels dried at nearly the same rate (27° C; 30%). However, each material had slightly different desorption equilibrium values (within 0.5 percentage point). Absorption tests showed faster transfer rates for broken kernels, followed by heat damaged kernels then sound kernels. This was attributed to the fact that broken kernels have more surface area exposed to the conditioning air and heat damaged kernels have stress cracks which create less resistance to moisture movement than intact kernels. Also, equilibrium moisture levels for broken kernels were 1.3 percentage points higher than sound kernels but 1.2 percentage points lower for heat damaged kernels when all sorption conditions were averaged. The authors combined equation (2.20) with the first term of equation (2.13) to establish a moisture ratio model based on the two primary modes of moisture transport, namely surface adsorption and diffusion, respectively, which can be written as:

$$MR = \frac{6}{\pi^2} e^{-Kt} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-D' n^2 t) \quad (2.21)$$

The K and D' values were computed by regression from experimental data and shown in the report to range from 0.022 to 0.124 and 0.00099 to 0.126, respectively. Although this model was shown for only one sorption condition (21° C; 80%), it was reported to have performed exceptionally well for all materials and conditions tested.

In a previous study with the same material, Park et al. (1971) measured the rate of moisture regain using the same temperature and humidity conditions but different initial moisture levels and shorter exposure times (11 to 12.5 hours). Data from these tests were evaluated by trial and error solution to determine four empirical parameters that were required for their abbreviated kinetic model for each initial moisture level. They concluded that their model was adequate for these relatively short exposure times within the range of conditions for which the parameters were selected, but cautioned against their use for extended periods when the moisture level approaches equilibrium. They suggested that the diffusion equation should be applied for such cases, which was accomplished by Chung et al. (1972).

2.1.3. Empirical Models:

Page (1949) modified the exponential equation by adding an exponent to the time variable to improve the fit of his drying data for corn and is given by:

$$MR = \exp(-k' t^n) \quad (2.22)$$

where t = time from beginning of diffusion process, hr

k', n = product specific constants

The k' value for any product contains a combination of the moisture diffusivity and a shape factor, which is often expressed as an Arrhenius-type equation (Brooker et al., 1992) in terms of the environmental conditions. The n value adds some 'flexure' to the empirical drying model and thereby compensates somewhat for the simplified solution which replaces the infinite series that results from the analytical solution. Numerous studies have since adopted Page's equation which is listed in ASAE Standard S433 (1996) along with prediction equations for k' and n that are often expressed as functions of the environmental conditions. The fact that they are considered to be product dependent variables implicates their dependence on product composition, yet, no one has reported such a correlation.

Sokhansanj et al. (1987) reviewed numerous investigations that have employed the semi-theoretical model for cereal grains and oilseeds and concluded that its current use is obsolete because it does not perform as well as other models that may be derived by today's powerful statistical software packages. Jayas et al. (1988) suggested that the logarithmic model be used for short duration experiments to determine the equilibrium moisture level and the k value while the Page equation could be used for long duration tests to determine the k and n values once the equilibrium moisture content was established.

Page's equation was first modified for drying conditions by Overhults (1975) and later employed by Osborn et al. (1988) for wetting conditions to compare the rates of moisture loss or gain for soybeans. The modified form of Page's equation is given by:

$$MR = \exp(-(kt)^n) \quad (2.23)$$

where t = time from beginning of diffusion process, hr
 k, n = product specific constants

This presentation of the equation simplifies the units of k , maintaining continuity with the logarithmic model (i.e., the reciprocal of time). Note that, by comparing equation (2.22) with (2.23), k' can be equated to k^n .

Diffusion coefficients (or k and n values) are not the same for both wetting and drying conditions. The reasons are not entirely clear, yet this area has received little attention among researchers. Differences may be attributed to the transport mechanism within the material which perhaps influences hysteresis as well. Many suggest that vapor diffusion is the primary mechanism when drying cereal grains (Jaros et al. 1992) while others state that both liquid and vapor transport play equally important roles, depending on product moisture (Chinnan and Young, 1977b).

Fortes et al. (1981) developed a set of prediction equations to describe the wetting and drying rates of wheat based on non-equilibrium thermodynamics. This model was tested over a typically encountered range of temperature ($27 \leq T \leq 88^\circ \text{C}$), relative humidity ($5.6 \leq RH \leq 96\%$) and initial moisture ($10 \leq M_o \leq 35\%$) levels. For the lowest temperature investigated, they concluded that liquid

diffusion was the primary mode of transport in the wetter regions of the material during drying and throughout the kernel during re-wetting. Another conclusion was that liquid and vapor fluxes were equally important near the surface.

The time needed to reach moisture equilibrium for different cereal grains and oilseeds under the same environmental conditions depends on seed size, cellular composition, and diffusive properties. An example of the drying response by two different oilseeds and cereal grains is shown in Figure 2.1 for arid conditions ($T = 20^{\circ}\text{C}$, $\text{RH} = 20\%$ and an air flow rate of 0.51 m/s). These curves were constructed from ASAE Standard D245.5 (1996) for moisture equilibrium values and S344 (ASAE, 1996) for the drying parameters for Page's equation (2.22). This plot portrays a visual comparison of the different response to seed size and seed type. Observe that the smallest seed, canola, dries much faster than the other seeds during the first 5 hours of exposure; whereas wheat dries slower than canola and soybeans initially ($<3\text{ h}$) then dries much faster than corn and soybeans after continued exposure to these conditions. Corn and soybeans approach equilibrium at nearly the same rate throughout the entire exposure. A slightly different response would be expected for different drying conditions. Bakker-Arkema and Maier (1987) produced similar response curves at different temperatures for corn, wheat, and rice by using diffusivity values that varied with air/product temperature and moisture content.

A similar plot for the absorption condition ($\text{RH} = 85\%$) is shown in Figure 2.2 for the same products, air temperature, and air flow. Note that canola, corn, and wheat respond in a similar manner but that soybeans are quite different for these conditions.

A change in transport mechanisms (liquid versus vapor) could affect the magnitude of the diffusion coefficient between wetting and drying conditions. Nevertheless, the diffusion equation proposed earlier accounts for both modes of transport and should be capable of accurately predicting the rate of moisture change with time for a product provided that correct boundary conditions are selected. A multi-disciplinary approach for the development of an improved model that involves the expertise of engineers, seed physiologists, cereal chemists, and perhaps microbiologists might be

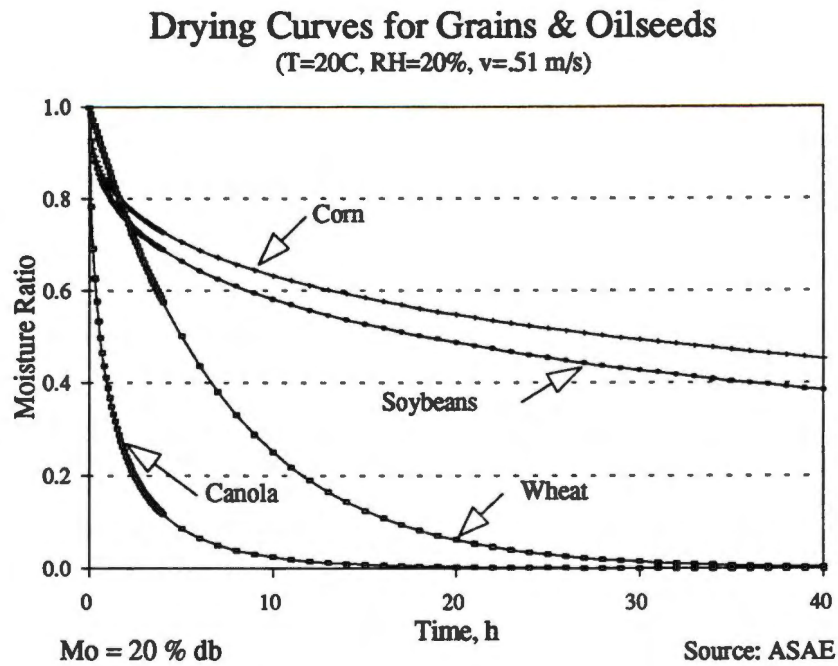


Figure 2.1. Desorption moisture ratio for canola, corn, soybeans, and wheat.

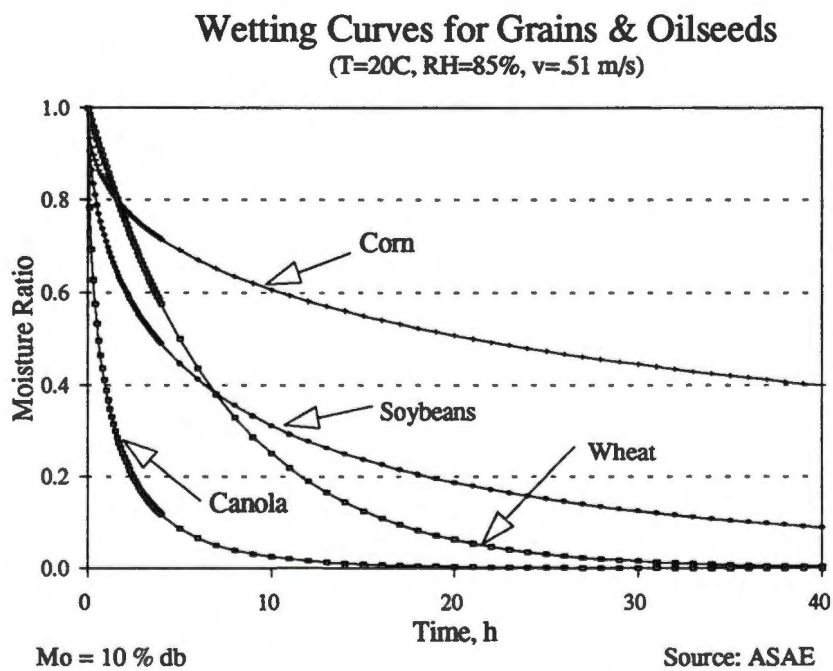


Figure 2.2. Absorption moisture ratio for canola, corn, soybeans, and wheat.

most expedient considering all that has been accomplished to date in this important area of research. Such a team of highly trained specialists could hopefully advance this important area of physiological science beyond its current stage of maturation. Until such a model is developed, all will struggle as piece-meal steps are made within individual disciplines towards this lofty goal with the hope that each step along the progression will lead toward a better understanding of the functional relationships that encompass all biological materials of economic importance.

2.2. MOISTURE EQUILIBRIUM STUDIES:

Equilibrium moisture is the constant moisture attained by a product after sufficient exposure to constant environmental conditions. Equilibrium moisture content (EMC) levels determine the extent to which drying or wetting can occur and to some degree the rate of sorption. For this reason, accurate estimates for equilibrium moisture are essential for predicting the storage life of a product as well as for drying and aeration management decisions and the algorithms that are used to predict the time required to condition grain products.

Difference in vapor pressure between the product and its environment is the driving potential for moisture transfer. Equilibrium moisture content values are strongly affected by the vapor pressure (P_v), which is more commonly identified by the relative humidity (RH) or water activity (AW) of the surrounding environment and the air and product temperature. ASAE Standard D245.5 (1996) presents a graphical relationship of EMC versus RH/AW for many commercially important grain and oilseed crops including soybeans. These are temperature dependent sigmoidal-shaped curves (isotherms) for most grains which increase sharply with humidity initially ($0 < RH < 20\%$), then flatten to a linear form with moderate humidities ($20 < RH < 60-70\%$) and rise sharply again in the high humidity region ($RH > 80\%$).

Ngoddy and Bakker-Arkema (1970), Pixton and Howe (1983), and Young and Nelson (1967a) suggested that the three distinct sections of an isotherm are governed by the energies that bind moisture to the material which weaken with increases in moisture. From 0 to 20% relative

humidity, a single layer or mono-layer of water molecules is formed on the cellular surfaces within the product. From 20 to near 70% relative humidity, additional layers of water molecules are added, and above this region moisture penetrates the cell wall and gradually fills the inner voids to approach saturation. At this level, the binding forces are very weak and a small increase in RH creates relatively large increases in moisture content. By comparing the isotherms in ASAE Standard D245.5 (1996), this phenomena is more pronounced in soybeans than corn possibly because of the structural features of the seed.

Equilibrium moisture values for grains and oilseeds are product dependent and may be influenced by variety, maturity, moisture history, degree of deterioration, composition and other biological variables (ASAE Standard D245.5, 1996). For example, at the same temperature soybeans exhibit lower EMC values than corn or wheat for relative humidity levels below 80% but above 90% soybean EMC values exceed those for both grains. However, when soybean EMC values are plotted against the equilibrium relative humidity (ERH) on an oil free basis, the sigmoidal curve responds similarly to these cereal grains (Pixton and Warburton, 1971). This implies that the oil component within a seed might also affect the moisture sorption properties as well and will be discussed further in Chapter IV. Sorption isotherms for soybeans are similar to peanut kernels in the low ERH range (~20%), however the slope of the isotherm is much higher than for peanuts above 20% RH.

2.2.1. Temperature Effects:

Equilibrium moisture values are inversely affected by the temperature of the environment for a given product. Specifically, for a given relative humidity/water activity level the EMC decreases with increases in temperature. This observation holds true for cereal grains and oilseeds (ASAE Standard D245.5, 1996) and agrees with logical reasoning from a psychometric viewpoint (the warmer the air along a constant relative humidity line, the higher the saturation vapor pressure, vapor pressure, and moisture holding capacity of the surrounding air and consequently the drier the

product). Temperature effects are not as pronounced for soybeans as for corn or soft winter wheat, but are nearly the same as durum wheat.

Temperature effects on desorption isotherms were reported by Chen and Clayton (1971) for nine different cereal grains. Material dependent parameters were generated by regression for each grain but no attempt was made to relate these empirical parameters to their chemical composition. Osborn et al. (1989) tested the Chen and Clayton (1971) equation on soybeans but found that it gave a poorer fit to the sorption data compared to other models that were tested.

2.2.2. Hysteresis:

When moisture is added to a dry product the moisture level obtained at a constant relative humidity condition is usually lower than the level observed for the same humidity during desorption (Brooker et al., 1992). This difference is called a hysteresis effect and has been reported to varying degrees when rewetting grain and food products that have been previously dried. Hysteresis is the difference between moisture levels at the same environmental conditions depending on whether the product is gaining or losing moisture. This phenomenon is most easily explained by the “ink bottle” theory (Labuza, 1968; Ngoddy and Bakker-Arkema, 1970; Rao, 1941;) which considers the cellular tissue of hygroscopic material to behave in a manner similar to a large diameter vessel with a small diameter neck or spout. During desorption, the spout controls how fast the vessel is emptied and, thus, controls the level of activity. During absorption, equilibrium is not reached until the activity of the larger diameter vessel is satisfied, which occurs at a lower level than during desorption. The extent of hysteresis is dependent on the type of product, the isotherm location, and the moisture history of the product to some extent, (Pixton and Warburton, 1971; Young and Nelson, 1967b).

Young and Nelson (1967a) provided a thorough explanation of the hysteresis effect in sorption behavior of biological materials and derived an equation that relates the three modes of energy to each phase of the isotherm namely monomolecular bound moisture, condensed moisture and absorbed moisture. This equation was verified by Young and Nelson (1967b) with wheat in a

wide range of temperatures ($10 \leq T \leq 40^\circ \text{C}$) and relative humidities ($11.4 \leq \text{RH} \leq 96.2\%$), though it is based on the pore size and the distribution of the pore size that are very difficult to measure directly. Hence, in their development these parameters were estimated by regression from their experimental data.

Some researchers (Alam and Shove, 1973; Pixton and Warburton, 1971; Saravacos, 1969) have observed a hysteresis effect of as much as 0.5 per cent moisture for soybeans below a relative humidity level of 50 per cent. Osborn et al. (1989) reported no hysteresis effect for one variety that were tested under absorption conditions and compared with desorption data for another variety (Sulaiman, 1986). Even though these studies were conducted under the same environmental conditions ($10 \leq T \leq 35^\circ \text{C}$; $5 \leq \text{RH} \leq 82\%$) and no statistical differences were observed in the prediction parameters, both tests should have included both varieties before stating that hysteresis was not observed.

Saravacos (1969) found a hysteresis effect for relative humidities below 60% ($T = 30^\circ \text{C}$) when two soybean varieties were tested in a vacuum sorption chamber ($P = -0.1 \text{ mm Hg}$). Materials for this study included thin slices (1 mm thick) of the cotyledon, dehulled beans, and whole beans. Isotherms for each variety and all forms of the test material were the same, although response times varied from 12 to 24 hours, 2 to 6 days and 1 to 3 weeks for each material, respectively. One interesting conclusion from this study was that the seed coat had no effect on the equilibrium moisture level of the intact seed. The author suggested that the slower sorption rate for intact beans compared to beans with the hulls removed was due to an added resistance by the seed coat or because it created a longer path for moisture molecules since it held the cotyledons together. In a companion study, the author compared the sorption isotherms of defatted soybean cotyledon slices with unprocessed slices and found that EMC values were higher for the defatted material for all humidity levels. He postulated that once the oil was removed from the material more receptor sites were available for water molecules and hence the higher the moisture holding capacity, which agrees with

the results reported by Pixton and Warburton (1971) and further suggested that the oil content might also effect the rate of moisture transport, as well.

2.2.3. Methods of Measuring EMC:

Neuber (1980) provided an extensive review of moisture sorption studies that were conducted throughout the world for cereal grains and suggested that researchers fully define the factors that are known to influence EMC curves. He listed the following attributes that should be described when conducting moisture sorption studies:

- 1) Description of material should include species, variety, stage of maturity, grain dimensions, kernel density and crop year;
- 2) Chemical and physical composition of material, including protein, oil, fiber, sugar, starch, ash content, kernel size, specific density, and porosity;
- 3) Sample preparation, including post-harvest processing, handling, storage time, original moisture content, temperature and relative humidity history, and method of rewetting, if applicable;
- 4) Determination of dry matter in the sample;
- 5) Method of measuring equilibrium conditions;
- 6) Tempering method for the apparatus; and
- 7) Frequency of measurements.

Neuber (1980) identified as many of these variables as possible from 27 different authors and discovered a wide range of EMC values for the same product at nearly equal ERH/AW and temperature conditions. He attributed many of these variances to the different techniques and procedures described within those factors listed above and suggested that a common (inert) material be included in all tests as a means of comparing the results of different workers.

Three primary methods have been used to measure equilibrium moisture levels in grain and food products, namely the static method, dynamic method, and constant dew point method (Pixton and Warburton, 1973). Different environmental conditions (RH/AW and temperature) are used within each method to establish a range of conditions that are typical for drying and storage environments. After sufficient exposure, the moisture gain or loss between the seed and its surrounding environment stabilizes (the vapor pressure differential is zero) and there is no net mass

transfer, thus, equilibrium is achieved and can be easily measured. Ideally, a series of tests is required for several different humidity and temperature levels to establish enough data to develop a useful relationship. Mathematical models derived from such test conditions are used to interpolate /extrapolate the data to temperature and relative humidity levels within/beyond test conditions and are, in fact, incorporated into microprocessors that are used to control grain drying and aeration systems.

The static method employs sealed containers that are held at a constant temperature and relative humidity level. Varying concentrations of salt solutions or sulfuric acid are generally used in each container to provide the desired range of humidity levels. Product samples held within the containers are exposed for a sufficiently long period until the weight change is negligible. Unfortunately, the time required to reach moisture equilibration with this method can take several weeks or even months depending on the conditions (White, 1990). Because this method is inherently slow, it has been used to a diminishing degree in recent years. In the high relative humidity range some products may spoil from microbial growth before reaching equilibrium. Because it was the only method available in early research, much of the data obtained by this method was incorporated in the development of the modified-Henderson model currently used in ASAE Standard D245.5 (1996). Alam and Shove (1973), Larmour et al. (1944) and Ramstad and Geddes (1942) applied this method when studying soybean desorption.

The dynamic method is similar to the static method with the important difference that some type of device is added to the conditioning chamber or apparatus to stir the air and thereby increase the rate of moisture transfer between the product and its environment. This slight difference in technique greatly reduces the time required to reach equilibrium for most conditions and has consequently gained in popularity among researchers. Chung and Pfof (1967) used this method to develop mathematical models to describe the hygroscopic properties of various grains which are included in the ASAE Standard D245.5 (1995). Alam and Shove (1973) noted that this method re-

duced the time required to reach equilibrium for soybeans absorption by one-half to one-third the time necessary for stagnant air tests.

The dew point method is similar to the dynamic method except that a relatively small amount of air is continuously circulated through the sample chamber in a closed loop to facilitate monitoring the dew point temperature. This method uses a relatively small amount of air compared to the material which helps to reduce process time. When the dew point temperature stabilizes, equilibrium is achieved and can be recorded. Recent studies have chosen this method to establish equilibrium moisture levels for soybeans, popcorn, corn cobs, canola and canola meal (Pixton and Warburton, 1971; Sulaiman, 1986; Osborn, 1988; Flood and White, 1984; White et al., 1985; Sokhansanj et al., 1986; and Jayas et al., 1988, respectively).

Sample preparation prior to conditioning tests is an important consideration for equilibrium studies. Pixton and Warburton (1973) reported the influence of three techniques for adjusting sample moisture during preparation of EMC tests with wheat. They determined that method of preparation had an effect on the desorption isotherm but no effect on the absorption isotherm. They reported a maximum difference between isotherms of 0.8% moisture at 35% RH and pointed out that numerous differences exist among published research which includes moisture measurement methods, sample preparation, and experimental technique. They listed the following minor factors that could influence EMC-ERH relationships: particle size, variety, equilibration time, and age of sample.

2.2.4. EMC-ERH Models:

Theoretical, semi-theoretical, and empirical mathematical models have been developed to describe moisture isotherms for many agricultural products. Early researchers spent considerable effort developing and refining models that were based on kinetic adsorption, capillary condensation, and potential energy fields to accurately predict the EMC-ERH phenomena (Brooker et al., 1992). They obviously did not have access to the powerful statistical computer packages available to today's engineer/scientist, nevertheless, they identified theories to substantiate their data. As more products

were tested and as extreme conditions were encountered for the previously tested products, these theories required modifications to describe new data. Part of the inherent problem with this area of study is that biological materials are not consistent from year to year. The moisture holding capacity of a particular product is influenced by many factors including the variety (genetics), growing conditions (weather), post-harvest handling and processing. Hence, mechanisms involved for determining the equilibrium conditions are not always consistent for the same product.

Labuza (1968) provided a succinct review of the theories that govern the three distinct curvature sections of the moisture isotherm, as it progresses from low to high moisture levels, which are kinetic energy, potential energy and capillary condensation, respectively. He concluded that each theory had unique advantages and limitations, none of which describe the entire shape of the curve completely which severely restrict their application. Young and Nelson (1967a) and Ngoddy and Bakker-Arkema (1970) have separately derived isotherm equations that stem from these theories. Both solutions require knowledge of the pore size and pore size distribution within the material which is difficult to determine. In the case of Young and Nelson (1967a), these parameters were estimated from their isotherm data, whereas, Ngoddy and Bakker-Arkema (1970) determined these directly.

The two models that have emerged for many grain conditioning studies are the modified-Henderson and the Chung-Pfost equations, as discussed below. Both models are based on theoretical considerations, have become the standard equations by which other models are tested for goodness of fit, and have been previously used for soybean sorption studies. Other models have been shown superior to these equations for soybeans and other crops and will be presented later.

The semi-theoretical isotherm model developed by Henderson (1952) is based on the thermodynamic relationship for absorption (which was first proposed by Gibbs) after applying equation fitting terms that matched specific products. His equation has been used extensively for many grain crops:

$$(1 - P_v/P_{vs}) = \exp(-a T_K M_{eq}^b) \quad (2.24)$$

where P_v = vapor pressure of the air at T_K
 P_{vs} = saturated vapor pressure of the air at T_K

T_K = ambient temperature, K
 M_{eq} = equilibrium moisture content, % dry basis
a and b = product constants

Henderson (1952) tested this model for several different materials, including clay, corn, cotton, dried prunes, and peaches, flaxseed, leather, raisins, sorghum, wheat, wood, and soybeans giving the values for $a=3.2 \times 10^{-5}$ and $b=1.52$ for soybeans.

This equation was modified by Thompson et al. (1968) to improve the predicted results in his development of a computer model for drying shelled yellow corn. Hence the modified-Henderson equation was written as:

$$(1 - P_v/P_{v_s}) = \exp(-K (T + C) M_{eq}^N) \quad (2.25)$$

where K, C, and N are product constants. ASAE Standard D245.4 (1995) gives the following values for soybeans: $K=3.053 \times 10^{-4}$, $C=134.14$ and $N=1.216$ with a standard error for moisture of 1.73% dry basis.

Chung and Pfof (1967) developed an empirical equation to predict the EMC values of grain in the following form:

$$\ln(rh) = (A/R_g T_K) \exp(-B m) \quad (2.26)$$

where rh = equilibrium relative humidity, decimal
 R_g = universal gas constant
 T_K = absolute temperature, K
 m = equilibrium moisture content, dry basis decimal
 A and B = temperature and product dependent constants

Pfof et al. (1976) modified this equation slightly to yield the following form:

$$rh = \exp[-A / (T + C) \exp(-B m)] \quad (2.27)$$

where $A = 328.3$; $B = 13.917$; and $C = 100.288$ for soybeans with a standard error for moisture of 1.91% dry basis (ASAE Standard D245.5, 1995).

Mensah et al. (1979) conducted equilibrium moisture experiments with thin slices from the cotyledon and small sections from the soybean seed coat over a moderate temperature (25 to 55° C) and relative humidity (10 to 80%) range. They tested the Henderson and Chung-Pfof equations but found them to give a poorer fit than other models that were tested for these materials and

environmental conditions. They then tested the Smith equation (as given by Young, 1969) and developed an empirical model using statistical procedures to accurately portray the EMC isotherms of each material. The Smith equation was selected as slightly superior to their empirical equation for the moisture content of seed coat material and was given as:

$$M = a - b \ln(1 - rh) \quad (2.28)$$

where a and b = material constants that are temperature dependent.

At 25° C the values for a and b were 4.838 and 8.560 for the seed coat, and 4.115 and 7.585 for the cotyledon, respectively.

Mensah et al. (1979) also developed a three-term empirical model that was slightly superior to the Smith equation for the moisture content of cotyledon material which was:

$$M = 33.13 - 0.927T_K - 8.92 rh - 11.31 \ln(1 - rh) \quad (2.29)$$

where all equation variables have been previously defined. The empirical EMC equation for the seed coat material was of the same form except that the coefficients were 36.12, -0.1035, 0 and -7.764 (from left to right) . Equation parameters were determined by a stepwise regression technique that selected values based on the correlation coefficient (R^2 value).

Halsey (1948) derived the following two parameter equation to depict the mechanisms involved with moisture equilibrium phenomena:

$$P / P_o = \exp(- (a / RT) \chi^r) \quad (2.30)$$

where

- a and r are curve fitting parameters
- P = vapor pressure exerted by the material
- P_o = vapor pressure of pure water for a specified temperature
- R = universal gas constant
- T = temperature, C
- χ = ratio of X/X_m
- X = equilibrium coverage, g sorbed / 100 g solid
- X_m = monolayer value, g sorbed / 100 g solid

Iglesias and Chirife (1976) tested the Halsey equation using corn desorption data from Chen and Clayton (1971) and adsorption data for spices, meats and other food products from various

authors. They discovered that the equation was satisfactory after a slight modification to account for temperature effects and proposed the following equation form:

$$P / P_o = \exp(- \exp (b T + c) M^{-r}) \quad (2.31)$$

where b, c and r are product constants and other variables have been previously defined. This equation is referred to as the modified Halsey in the following discussion.

Alam and Shove (1973) conducted adsorption and desorption experiments for soybeans in the ambient to moderate temperature range (5 to 55° C) across a wide humidity range (10 < RH < 95%) and reported that the Henderson equation gave a poor fit for relative humidity values above 80%. They also tested the Sabbah (1968) equation which gave a reasonable fit above 70% humidity and the Strohman and Yoerger (1967) equation which fit their data in the 20 to 85% humidity range. Since none of the previously reported equations accurately depicted their data across the entire humidity range, a third order polynomial equation was developed for insertion into a computer program that predicted soybean drying characteristics. They found that the following polynomial equation provided a better fit than either of the other models or a second order polynomial equation which was also tested:

$$\begin{aligned} M = & C_1 + C_2 RH + C_3 T_F + C_4 RH T_F + C_5 H^2 + C_6 RH^2 T_F + C_7 T_F^2 \\ & + C_8 RH T_F^2 + C_9 RH^2 T_F^2 + C_{10} RH^3 + C_{11} RH^3 T_F + C_{12} RH^3 T_F^2 \\ & + C_{13} T_F^3 + C_{14} T_F^3 + C_{15} RH^2 T_F^3 + C_{16} RH^3 T_F^3 \end{aligned} \quad (2.32)$$

where the coefficients were:

$C_1 = 2.98306$	$C_2 = 0.29107$	$C_3 = -0.10662$	$C_4 = 0.012514$
$C_5 = -6.551E-03$	$C_6 = -3.4487E-04$	$C_7 = 1.31125E-05$	$C_8 = -1.8787E-04$
$C_9 = 5.206E-06$	$C_{10} = 7.5358E-05$	$C_{11} = 2.3991E-06$	$C_{12} = -3.6882E-08$
$C_{13} = -4.801E-06$	$C_{14} = 6.8246E-07$	$C_{15} = -1.9123E-08$	$C_{16} = 1.3494E-10$

Alam's (1972) desorption data are presented in the ASAE Standards (D245.4, 1995) along with the modified Henderson and Chung-Pfost equations (2.25) and (2.27), respectively.

Osborn et al. (1989), after establishing that hysteresis was statistically negligible, combined their absorption data with Sulaiman's (1986) desorption data and analyzed three equilibrium models for soybean isotherms, namely, the modified Henderson, Chung-Pfost, and modified Halsey equations (2.24, 2.25, and 2.30) respectively. They determined that the standard errors for EMC for each of

these models were 1.16, 1.50, and 0.41% dry basis, respectively, and consequently suggested that the modified Halsey equation should be used for conditions in the range of their experiments ($10 \leq T \leq 40^\circ \text{C}$; $10 \leq \text{RH} \leq 85\%$). Equation parameters a , b , and r for the recommended equation (2.30) were determined by non-linear regression to be -0.0053636 , 2.86653 , and 1.37875 , respectively.

Collective data from all three experimental methods mentioned previously are provided in the ASAE Standard D245.5 (1996) for many cereal grains and oilseeds. Recent studies suggest that the modified Halsey equation should be added to this widely used standard to more accurately describe the EMC/ERH relationship for soybeans and oilseeds.

Chen and Morey (1989) tested four equations (Chung-Pfost, modified Halsey, modified Henderson, and Oswin) for 18 different grains, seeds and fibrous products using data sets collected by others over a wide range of relative humidity and temperature conditions. They reported that no one equation adequately described the sorption isotherms for all agricultural materials and suggested specific equations for each product. A summary of their evaluation reported product-specific equations that were selected on the basis of standard error and random nature of the estimated error. In general, the modified Henderson and Chung-Pfost equations were acceptable for starchy grains and some fibrous materials (peanut and rice hulls), and the modified Halsey equation for high protein/high oil beans and seeds. No attempt was made to generate equations for beans or seeds on an oil-free basis. Since not all chemical components were reported for these materials no attempt was made to establish a correlation between those values and the EMC-ERH curves.

Sokhansanj and Yang (1996) suggested extensive changes to ASAE Standard D245.5 that have recently been incorporated to encompass 109 different products which can be classified into the general categories of high starch, high oil and protein, high fiber or feedstuffs, and agricultural byproducts. While this approach implies that the EMC-ERH relationships are dependent on the chemical components of each material, it falls short of suggesting that isotherm equations could be expressed as weighted functions of the percentages of each component (oil, protein, and fiber) with-

in a particular product. Such an approach may prove useful in the development of future models or the refinement of existing equations.

This section is summarized by noting that the processing engineer is generally more interested in how well a particular model fits the experimental data rather than how closely it adheres to a given theory. For example, an engineer who designs grain driers might program a microprocessor which has a cost-effective limit on the amount of time required to perform calculations needed to control the speed of material flow. On the other hand, the research engineer is interested in developing both empirical and theoretical models and in the refinement of existing theoretical models that more accurately depict a given process. While many theories have been developed to describe the equilibrium contents for specific products, they are often tested against scant amounts of data simply because of time, labor, and financial constraints. Obviously, the value of any equation depends on the needs of the user. It should be noted that large errors may occur if some equations are extrapolated much beyond the range of conditions for which they were generated.

2.3. DRYING STUDIES:

The primary factors that influence the drying rate of grain and oilseed products are often investigated by studying the behavior in a single layer of seed. They are moisture holding capacity of the air, product temperature, initial and final moisture contents, velocity of the airstream, and exposure time.

Air drying capacity is usually defined in terms of dry bulb temperature and either wet bulb temperature, dew point temperature, or relative humidity. Drying air temperature not only controls the extent of drying and drying rate (Henderson and Pabis, 1961) when all other variables are held constant, but also has been shown to have a significant effect on thermal conductivity, mass diffusivity, and latent heat of vaporization (Steeffe and Singh, 1980b). The higher the drying air temperature, the lower the EMC, thus, the drier the final product and the faster the drying rate in

high capacity driers. Because of the tendency of soybeans to develop cracks in the seed coat it is recommended that relative humidities for drying be held above 40%.

It is important to maintain a sufficiently high air velocity in thin-layer drying experiments so that the rate of moisture transport through the material is the limiting factor. Most researchers have performed preliminary tests for previously untested products to confirm the minimum airflow rate prior to thin-layer drying or re-wetting experiments (Osborn, 1988; Chittenden and Hustrulid, 1966; Henderson and Pabis, 1962). For some products, the k_d' and n_d parameters for Page's thin layer equation (2.22) have been expressed in terms of the drying air temperature, air velocity, initial moisture, or relative humidity (ASAE Standard S448, 1996).

Equations that have been successfully applied to thin layer grain drying in the falling-rate period have been previously discussed. This section identifies soybean drying studies that have applied these equations along with a few related investigations with other oilseeds and cereal grains. These are presented primarily in the order that matches the theoretical, semi-theoretical, and empirical models that have been previously discussed.

2.3.1. Drying Studies for Soybeans:

Several soybean drying studies have dealt with the effects of drying air temperature on seed quality as quantified by germination rating, seed vigor or viability, and seed coat cracks (Tekrony et al., 1987). Natural air drying is the first method of choice for soybeans provided that initial moisture content levels are below 16%, that ambient air conditions are above 10° C and between 40 and 70% RH, and that fan capacities are sufficient to deliver between 2 to 3 m³/min-t (Tekrony et al., 1987). Such ideal conditions provide gentle drying rates that are sufficient to dry the crop to safe storage levels before damaging mold growth is established without excessive overdrying. For soybeans above 20% moisture content, a producer has the choice of reducing grain depth in the bin to approximately 1.2 m so that air flow is increased, or adding supplemental heat if the relative humidity remains above 40% (Matthes et al. 1974).

Lee (1959) applied the spherical diffusion model (2.13) to thin-layer drying experiments and showed that the prediction of the EMC and the diffusion term was dependent on temperature and initial moisture. He concluded that the diffusion term could be accurately expressed as a function of temperature in an Arrhenius equation form. His EMC values at 32° C were 1.1 to 1.9 percentage points higher than those reported by others (Ramstad and Geddes, 1942; Larmour et al., 1944; Alam and Shove, 1973; Mensah et al., 1979; Pixton and Warburton, 1971) for temperatures in the range of 25 to 32° C and ERH between 20 and 80% (Sulaiman, 1986). Overhults et al. (1973) worked with a higher temperature and initial moisture conditions with a constant dew point and determined that the modified Page's equation (2.23) was superior to the diffusion equation (2.13) with a constant moisture condition at the surface. They identified the following correlation for the n_d value (where the subscript signifies drying):

$$n_d = 0.3964 + 0.002448 T \quad (2.33)$$

These n_d values were then used to generate predictive equations for k_d for each initial moisture test condition. For example, at $M_o = 50\%$:

$$k_d = \exp (10.375 - 3766.3/T_K) \quad (2.34)$$

Note that the n_d values increased linearly with the drying air temperature but that k_d grew exponentially with the reciprocal of absolute temperature as suggested by Henderson and Pabis (1961) in an Arrhenius form. A dynamic moisture equilibrium was determined by regression in this analysis to aid in the development of these predictive equations.

A finite element analysis was developed to describe the drying behavior of grain by Irudayaraj et al. (1992). Temperature and moisture gradients within a single kernel of soybeans, barley, and corn were estimated by two diffusion models which were based on material properties that were allowed to vary as drying progressed. The first model assumed that moisture diffused by vapor and liquid phases within the seed while the second model assumed that moisture was transferred through the body as a liquid to the outer surface of the kernel where it evaporated. An average moisture content for the body was computed by both models which were tested against available data

using a condition given by Overhults et al. (1973) for soybeans ($T = 35^{\circ}\text{C}$ and $\text{RH} = 25\%$). Since no known values existed for soybeans or other grains that adequately characterized the porous nature of the material they substituted known values for wood into their set of equations and predicted the temperature and moisture changes over time. The first model predicted a quicker time to reach temperature equilibrium than the second model for all grains, while the second model provided a better estimate of the drying curves. For soybeans, both predicted curves gave slightly higher moisture values (0.5 to 1%) during the first half of the 14 hour drying cycle but were in good agreement for the remainder of time. Both models gave better agreement than one derived previously by Haghighi and Segerlind (1988) who assumed constant material properties.

Another form of the diffusion equation (2.13) was found to adequately predict the drying rate of Amsoy soybean seed components by Mensah et al. (1979). They dried thin slices of each material separately and employed a model for an infinitely thin sheet since the width to length ratios were 1:7 and 1:50 for the cotyledon and seed coat, respectively. No other equations were tested in their report. EMC values for these materials were determined in their experiments, as described in the previous section, and used to estimate the effective diffusivities for each material using the following form:

$$D' = A \exp \left(-a / T_K + b \text{RH} - c T_K \text{RH} \right) \quad (2.35)$$

The values for A, a, b, and c were determined for the cotyledon and seed coat by regression to be 1.03×10^4 and $4.46 \times 10^2 \text{ cm}^2/\text{s}$, 7962 and 14673, 46.2 and 44.6, and 0.141 and 0.139, respectively. Their data indicate that moisture diffuses approximately 2 to 13 times faster through the cotyledon than through the seed coat, depending on the atmospheric conditions. The relationship between the environmental conditions and the effective diffusivity values provided by their study will be used as initial estimates to determine the relative resistances to moisture transport through these two major structural components of the soybean seed in the cellular diffusion drying model that is described in Chapter IV for both wetting and drying conditions.

Suarez et al. (1980a) found that the drying rate of two soybean varieties with different oil contents (15 and 21%) was influenced slightly by the level of oil in the sample. Using the spherical

diffusion equation (2.16), no significant difference was found for high air flow rates (10.5 and 12.7 m/s) from 41.5 to 71° C with an initial moisture content of 29%. Moisture diffusivities were described in an Arrhenius form by curve fitting techniques.

Kitic and Viollaz (1984) performed thin layer and fluidized bed drying tests over a similarly high range of air velocities (8 to 13 m/s). Soybeans were rewetted by soaking in distilled water for 10 to 30 minutes, removed, sealed, and refrigerated for 2 to 3 days to raise the original moisture level from 12 to 42 and 62%. Samples were then dried in the thin layer dryer at air temperatures ranging from 50 to 78° C. The spherical diffusion model (equation 2.13) was selected to represent their thin layer drying data and was used to compute the diffusion coefficient by a least squares procedure. Estimated values were combined with the ones determined by Saurez et al. (1980a) and found to be adequately described in an Arrhenius form for temperature as:

$$D' = D_o' \exp(-E_a/R_g T_K) \quad (2.36)$$

where E_a was expressed as a function of initial moisture (7.2 kcal/g-mole at $M_o = 42\%$) but D_o' was not reported. However, their plot of moisture diffusivity against the reciprocal of the absolute temperature and initial moisture was extrapolated extensively to provide a D_o' estimate of 2×10^{-7} cm²/s (at 20° C and $M_o = 42\%$). Kitic and Viollaz (1984) showed that the effective mass diffusion coefficient decreases with temperature and moisture. Their specific results were obtained out of the range of this experiment.

Tadeusz and Helena (1989) measured thin layer drying rates of soybeans at two temperatures ($T = 40$ and 60° C), two initial moisture content levels ($M_o = 18$ and 25%) and three classes of seed size ranging from 4.0 to 5.5 mm in diameter. They plotted moisture loss curves against time and found that a modification to the semi-empirical exponential model (2.20) with the following form described their data accurately:

$$M = x_1 \exp((-t^2 x_2)/x_3 + x_4) \quad (2.37)$$

where the x_i coefficients were determined for each set of drying conditions. They also concluded that

the largest seeds required more time to dry, had higher germination scores, and had more cracked seeds before and after drying at all temperature and initial moisture levels.

Alam and Shove (1973) employed an equilibrium model (which was a combination of the Henderson (1952) and Sabbah (1968) desorption equations) to describe the drying rate of soybeans with unheated or natural air at low air flow rates (1 to 2 m³/m-t). Their study more closely imitates the vast majority of post-harvest processing techniques used by soybean farmers throughout the southeast, yet their research model has not been developed beyond its initial form or incorporated into a computer program for widespread use. Additionally, the modified Halsey equation has not been tested against their data to validate the conclusions of other researchers who have conducted more recent moisture equilibrium studies for soybeans (Chen and Morey, 1989; Osborn et al., 1988).

Hutchinson and Otten (1983) reported the drying phenomena of soybeans in a somewhat narrow temperature and relative humidity range ($32 \leq T \leq 49^\circ \text{C}$; $34 \leq \text{RH} \leq 65\%$; $M_o \approx 21\%$) using the Alam and Shove (1973) predictive equation for EMC. They tested a two-term exponential model against the Page equation (2.22) and found equivalent results between the two when compared to experimental data. However they recommended the Page equation (2.22) due to its simplicity. They developed the following equations for Page's drying parameters:

$$k_d' = 0.0333 + 0.0003 T \quad (2.38)$$

$$n_d = 0.3744 + 0.00916 (T) \text{ rh} \quad (2.39)$$

Both values increase linearly with temperature and the n_d parameter contains an interaction term containing both temperature and relative humidity.

White et al. (1981) found that Page's modified equation (2.23) adequately described the thin-layer drying of soybeans under moderate conditions ($30 \leq T \leq 70^\circ \text{C}$; $8 \leq T_{dp} \leq 33^\circ \text{C}$; and $16 \leq M_o' \leq 24\%$). The n_d value in the modified Page equation was found to range from approximately 0.47 to 0.58 and increase with drying air temperature and relative humidity, as described in the following regression result ($R^2 = 0.58$, $\text{SE} = 0.027$):

$$n_d = 0.33 + 0.00238 \text{ RH} + 0.00276 T \quad (2.40)$$

These n_d values were used to compute the k_d values in Page's modified equation through regression using the experimental results ($0.08 \leq k_d \leq 0.5$), and were also related to the test conditions. The following relationship was determined ($R^2 = 0.96$ and $SE = 0.025$):

$$k_d = -0.207 + 0.00357 T + 0.00216 M_o' + 0.002613 RH + 3.2E-06 T M_o' \quad (2.41)$$

These k_d and n_d values adequately described the drying rate for their experiments and were further tested against the drying data from three other researchers (Lee, 1959; Overhults et al., 1973; and Pfost, 1975) who used different varieties, test procedures, and conditions. These values performed favorably for the data reported by others. They concluded that the simplicity of these prediction equations would facilitate their use in deep-bed soybean models, but cautioned against using them outside the range of test conditions for which they were developed.

2.3.2. Drying Studies for Other Oilseeds:

The spherical diffusion model (2.13) was used on drying data of whole cottonseeds and the endosperm (hulls removed) Farinati and Suarez (1984). The model perform well for the endosperm but not the whole seed. They concluded that since the hull comprises 40% of the fresh seed weight that the heterogeneous nature of the material was the primary reason for the inadequacy of the whole seed model. A cellular diffusion model was not attempted in this study.

Young and Whitaker (1971a) found no constant rate drying period with unshelled peanuts even though initial moistures were as high as 106%. Using the spherical diffusion equation (2.13) and a similar solution for a slab, infinite cylinder, and finite cylinder, they estimated the drying parameters for the exponential term ($D\pi^2/R^2$) for each drying condition by graphical interpretation. The spherical model performed slightly better than all others for each test condition. However, all of the models predicted slower initial drying and faster drying in the later stages of each test. This lead to the conclusion that a composite model needed to be developed because of the differences between the drying rates of the peanut and its shell.

Chinnnan and Young (1977a) developed two numerical solutions to the diffusion equation (2.9) for drying peanuts in the shell when modeled as a composite body by vapor or liquid transport mechanisms. Chinnnan and Young (1977b) reported on a combination of vapor and liquid transport mechanisms using a slightly modified model. A comparison of these three composite models against the drying data by Young and Whitaker (1971a) resulted in the following ranking for these models: vapor-liquid solution, vapor solution, and liquid solution.

Colson and Young (1990) developed an improved model that used two semi-theoretical equations [in a form of (2.20)] that were similar to the combined vapor-liquid model of Chinnnan and Young (1977b), but with the simplifying assumption that moisture gradients within each material component was negligible. They tested this set of equations with drying data for each component and found a good fit after selecting a dynamic EMC in place of the value computed by the Henderson (1952) equation.

Tang and Sokhansanj (1993) performed thin-layer drying experiments with lentils to estimate the diffusivity of the hilum, cotyledon, and seed coat at three temperature/relative humidity conditions (30 /30, 40 /30, and 50° C/20%). A uniform air velocity of 0.2 m/s and initial moisture (24.5% db) was used in all tests. The drying rate of intact seeds was compared with dehulled samples and with seeds that had an impermeable wax coating over the hilum. Initially the wax covered samples dried at the same rate as the control samples but slowed as drying progressed. Uncovered samples dried extremely fast (40° C) reaching near equilibrium moisture (10%) within about 6 hours, while the waxed sample required more than 100 hours to reach within 2 percentage points of the same moisture level. Diffusivity values increased slightly with temperature for each material and were determined indirectly from each drying curve and were in the order of 10^{-5} , 10^{-8} and 10^{-9} m²/h for the hilum, cotyledon, and seed coat, respectively. Moreover, the diffusivity of the seed coat decreased with moisture content by an order of magnitude for each 5 percentage points from 20 to 10%. An Arrhenius equation was successfully used to represent the diffusivity values for all materials tested.

Thin layer drying properties of rapeseed (canola) was determined by Crisp and Woods (1994) over a typical range of heated air drying temperature and humidity conditions ($40 \leq T \leq 70^{\circ}\text{C}$ and $5 \leq \text{RH} \leq 23\%$). Initial moistures were in the range of 12.5 to 26%. The spherical diffusion model (2.13) was tested against the logarithmic equation (2.20) to describe the drying data by allowing the D' value to vary with initial seed temperature in an Arrhenius form and by letting k'' vary with temperature and seed moisture. Prediction errors for all data points in 16 total experiments were 0.31 and 1.34% for the diffusion model and logarithmic equation, respectively.

2.3.3. Related Drying Studies for Cereal Grains:

Much more research has been reported on the drying characteristics for corn, wheat, and rice than for soybeans or most other oilseed crops. The following discussion focuses on those studies that were similar in either the experimental treatment, modeling approach taken or the analysis of the data collected in this study.

Purdy and Crane (1967) measured the rate of moisture loss by soaking two corn varieties in sucrose solutions with the pericarp removed and found no difference between the moisture gain or loss for either variety. Conversely, different rates of moisture loss were observed for intact kernels of the same variety under the same conditions. They summarized that drying rates were dependent on the thickness and permeability of the pericarp more than the internal processes of the kernel.

Other researchers have applied the Page equation (2.22) to rice drying. Agrawal and Singh (1977) conducted experiments for a range of temperatures and a fixed humidity and a wide range of humidities and a fixed temperature. They determined the following relationships for k_d' and n_d for short-grain rice:

$$k_d' = 0.2958 - 0.44565 \text{ rh} + 0.01215 \text{ T} \quad (2.42)$$

$$n_d = 0.13365 + 1.93653 \text{ rh} - 1.7743 \text{ rh}^2 + 0.009468 \text{ T} \quad (2.43)$$

Wang and Sing (1978) investigated the single-layer drying of medium-grain rough rice in similar conditions and applied their data to four equations. These included a modified form of the

thin-layer equation proposed by Thompson et al. (1968), the spherical diffusion equation (2.13), the Page (1949) equation (2.22) and a single term approximation to the spherical diffusion equation. Each equation performed reasonably well in the order listed. Steffe and Singh (1980) developed a modified form for Newton's law of cooling:

$$MR = A \exp(-k t) + (1-A) \exp(-B k t) \quad (2.44)$$

where, A, B, and k are arbitrary 'constants' that are applicable only for the conditions of their test.

Misra and Brooker (1980) compiled a summary of ten thin-layer drying and rewetting studies that had been reported for yellow corn and identified the Page equation (2.22) as the most promising model. They chose the deBoer equation as given by Bakker-Arkema et al. (1974) to calculate EMC values and reported that most of the drying curves tended toward these predicted values. The k_d' and n_d values were best described by:

$$k_d' = -7.1735 + 1.2793 \ln(1.8 T + 32) + 0.1378 V \quad (2.45)$$

$$n_d = 0.0811 \ln(RH) + 0.0078 M_o \quad (2.46)$$

Hence, the k_d' value for corn was a function of temperature and velocity of the drying air while the n_d value was found to vary with the initial moisture and relative humidity.

Sokhansanj et al. (1984) determined the drying parameters for barley, canola, and wheat. All grains were remoistened to near their original level (within 0.5% of moisture on average) and re-dried under the same conditions. This procedure was repeated until six drying cycles were completed. EMC values for each product were determined by extending the drying time of the last sample in the sequence to 8 hours. The Page (1949) equation (2.22) was fitted to the drying data for each cycle to generate the k' and n parameters which were used to compare the drying rates of naturally moistened versus artificially moistened grain. They observed that the drying rate for canola gradually decreased as a result of rewetting but no clear trend emerged for barley or wheat. More importantly, the largest change in the drying rate of all products tested was between naturally moistened and reconstituted grain.

Syarief et al. (1987) estimated the diffusion coefficients of the pericarp, germ, and endosperm of corn for two initial moisture levels at 40° C and verified their procedure with a known inert material. They determined that moisture diffuses approximately four times faster through the germ than through the endosperm and that the diffusivity of the pericarp is roughly one order of magnitude lower than the other components and is partially location dependent. Tolaba et al. (1990) developed a numerical solution to the spherical diffusion (2.13) equation by considering the resistance to moisture transport of the outer shell or pericarp as a separate component. They confirmed the usefulness of this solution by comparing the drying data of intact corn kernels with de-hulled kernels ($M_0 = 21\%$) in a fluidized bed dryer in the 50 to 60° C temperature range and estimated the diffusivity of each component. They concluded that the diffusivity of the endosperm and germ composite was approximately eight times higher than for the pericarp which was similar to the results obtained by Syarief et al. (1988). Augerre and Suarez (1992) developed a numerical solution to the cellular diffusion equation (2.16) using finite differences for a composite body of the inner components (endosperm and germ) and outer shell (pericarp) and tested it against corn drying data (60° C) from Tolaba and Suarez (1990). They concluded that the diffusivity of the pericarp was approximately 10 times greater for the pericarp than for the homogeneous inner sphere (endosperm and germ composite), which agrees closely with previous work (Tolaba et al., 1990).

The cellular diffusion model (2.16) was verified to describe the moisture loss for burley tobacco leaves by Walton and Casada (1986) using the data reported by Walton et al. (1976). Walton et al. (1988) applied this model to white corn drying using the data collected by White et al. (1973). Although numerous investigators have applied diffusion theory to the drying of agricultural products, as evidenced by the above discussion, the cellular diffusion equation has not been tested against soybean drying data for moderate air flow rates. For these reasons it was chosen as a candidate model in this analysis and will be fully developed in Chapter IV.

2.4. WETTING STUDIES:

Osborn et al. (1991) investigated the rewetting rates of soybeans under moderate temperatures ($10 \leq T \leq 40^\circ \text{C}$), relative humidity conditions (73 and 83%) and initial moisture levels ($9 \leq M_o \leq 14\%$). A constant air velocity of 0.51 m/s was selected for all tests. Equilibrium moisture values were computed by the modified Halsey (three parameter) equation which Osborn et al. (1989) developed for similar temperature/relative humidity conditions and used in the regression analysis. They tested five equations against their absorption data and found that Page's modified equation (2.23) was slightly superior to the cellular diffusion equation (2.16) with a finite boundary condition at the surface. Moreover, they discovered that the n_w value (where the subscript denotes a wetting condition) was a product dependent constant [0.8267] and that the k_w value varied with the air temperature and relative humidity as:

$$k_w = -0.2625 + 0.004916 T + 0.3033 \text{ rh.} \quad (2.47)$$

Two solutions to the diffusion equation in spherical coordinates were plotted by Osborn (1988) to illustrate the differences between the assumptions for the surface boundary condition when used to estimate the moisture transport of soybeans. The cellular model (2.16), which assumed a finite resistance on the surface ($Bi_m < 30$), was compared to the spherical model (2.13) which assumed a negligible resistance on the surface ($Bi_m > 50$). He concluded that the cellular diffusion model yielded a superior fit to the adsorption data for these conditions and suggested that it be tested with other products because of its versatility.

Shatadal et al. (1990) studied the rewetting behavior of canola under ambient conditions and found that Page's equation (2.22) adequately represented the absorption rate. Equilibrium moisture levels were determined experimentally for each test condition ($11.2 \leq M_{eq} \leq 17.7\%$) and were used in a non-linear regression to determine n_w and k_w' for Page's equation (2.22). The power term (n_w) was found to be a product-dependent constant (0.818) which was nearly equal to the value determined for soybeans by Osborn et al. (1991). The k_w' value was correlated through regression to the air conditions, namely:

$$k_w' = -0.0257 + 0.00094 T + 0.031 rh \quad (2.48)$$

Note that the k_w' values increase with temperature and relative humidity for soybeans (2.48) and canola (2.49) and that n_w is constant under these test conditions for both oilseeds.

A different absorption model was developed by Roa and Macedo (1976) for carioca beans and tested by Villa et al. (1978) for soybeans, to yield the following coefficients:

$$MR = \exp(-0.01448 (P_{vs} - P_v)^{0.47088} t^{0.51168}) \quad (2.49)$$

where,
 P_{vs} = saturated vapor pressure for the air temperature
 P_v = vapor pressure of the conditioning air
 t = time from the beginning of the adsorption phase

Osborn et al. (1989) tested this model against their soybean absorption data and found a different set of coefficients through regression than the ones shown above. Consequently, this equation was omitted from further considerations since the 'constants' were obviously not entirely product dependent for soybeans.

Misra and Brooker (1980) reviewed six rewetting studies for corn over a wide range of test conditions and used the de Boer equation (Brooker et al., 1974) to estimate EMC values. They selected the Page equation (2.22) to represent all rewetting tests and used a rigorous statistical procedure to generate appropriate prediction values for k_w' and n_w based on the all the independent variables used for each test. They determined that n_w was merely a function of the relative humidity of the drying air ($n = 2.1867 - 1.67 rh$), but that k_w' was dependent on air temperature and grain moisture in the following manner:

$$k_w' = \exp(-8.5122 + 1.2178 \ln(1.8T + 32) + 0.0864 M_g) \quad (2.50)$$

An early work by del Guidice (1959) developed the following thin-layer equation to describe moisture absorption for shelled corn:

$$MR = \exp(-0.0625 P_s^{0.466 rh^3} t) \quad (2.51)$$

The EMC selected for this equation was determined by the Henderson (two parameter) model over a moderate temperature and humidity range with an initial moisture content of 6.95 % db. An equation of this form was tested as a candidate model by Osborn et al. (1991) by generating new

product-dependent parameters for rewetting soybeans, but prediction errors for this model were between 1.2 and 6.4 times higher than those observed by Page's modified equation (2.23) and the cellular diffusion model (2.16).

Rugumayo (1979) also investigated the rewetting behavior of shelled corn. He employed the de Boer equation to select EMC values and developed a relationship to describe the moisture uptake over a low temperature and relative humidity range as follows:

$$MR = \exp[(162.12 - 488 M_{t-1} + 118.6 \log(M_{t-1}) + 0.6966T_t (M_{t-1}^2) \exp(rh_2)) t] \quad (2.52)$$

Krueger and Bunn (1985) tested the equations developed by del Guidice (1959), Rugumayo (1979), and Misra and Brooker (1980) for predicting the final moisture of shelled corn after 11 hours of exposure at two environmental conditions. They incorporated both the de Boer and modified Henderson equations to predict EMC values in their analysis but discovered that the test equations over-estimated the rate of moisture uptake and did not adequately describe the rate of absorption in relatively short exposure times even though their environmental conditions were within the limits under which these models were developed.

Casada (1994) tested five models to describe his wetting and drying data of barley and hard red winter wheat. Thin-layer test conditions included two temperatures (15 and 30° C) and five humidity levels (46 to 80%) with a constant airflow rate (0.4 m/s). EMC values were determined by regression for each test condition but were not reported or compared to published values. He concluded that absorption rates were slower than desorption rates and that the modified Page equation (2.23) and the cellular diffusion equation (2.16) out performed the other equations when describing this mode of transport. The values for k_w generally increased with temperature and humidity with a range of 0.0129 to 0.0792 and 0.042 to 0.224 for barley and wheat, respectively. The values for n_w generally increased with humidity and ranged from 0.588 to 0.710 and 0.688 to 0.977 for barley and wheat, respectively. Earlier investigations on the moisture absorption behavior of wheat were reported by Becker (1960) and Bloome et al. (1982).

Banaszek and Sibenmorgan (1990) used the Page equation (2.22) to represent their absorption data for rough rice and revealed that the k_w' value could be represented as a function of temperature and initial moisture as follows with a mean square error (MSE) of 0.0068:

$$k_w' = a M_o' + b T + c \quad (2.53)$$

where, a , b , and c were 0.003818, 0.008185, -0.03892 , respectively. The n_w value was not influenced by any of the experimental variations and was found to be a constant 0.6792. The majority of the moisture absorption was within the first 24 hours of exposure for all test conditions and sorption rates increased with increases in temperature and humidity and decreases in the initial moisture level. Also, the EMC values varied significantly with the initial moisture. Their empirical equation was:

$$EMC = d M_o' + e rh + f T + g \quad (2.54)$$

with $d = 0.1267$, $e = 20.633$, $f = -0.298$, and $g = -2.589$.

Kunze (1991) emphasized the importance of understanding the moisture absorption characteristics of grain because of its strong influence on post-drying stress crack development, storability and grain quality in general. He cited the effects of the drying, cooling, and rewetting rates on milling quality of corn, rice, and wheat.

Other related studies of interest have reported the rate of liquid water uptake by soaking (adsorption) dry soybeans ($M_o \approx 14\%$) in distilled water over a range of constant temperatures to determine the time required for the seed to germinate. Fukuoka et al. (1994) employed a pulsed field gradient nuclear magnetic resonance technique over extremely short time intervals (18.5 to 113 ms) to graphically measure the liquid diffusion coefficient, which was found to be $4.3 \times 10^{-10} \text{ m}^2/\text{s}$. This value was approximately 10 times greater than the value determined by weighing samples directly during 10⁺ hour tests (Hsu, 1983; Phillips, 1968) who measured liquid diffusivities graphically as $6.3 \times 10^{-11} \text{ m}^2/\text{s}$ and $3.2 \times 10^{-11} \text{ m}^2/\text{s}$, respectively. The temperature range was between 25 to 28° C. Fukuoka et al. (1994) suggested that their large values might be attributed to the fact that water is highly mobile within the seed, particularly at the junction of the two cotyledons where oil may exist.

2.5. DELAYED HARVEST/FIELD WEATHERING STUDIES:

Physiological maturity (PM) occurs when the individual seed gains its maximum amount of dry matter and the seed and pod are completely yellow. Visual indicators have been identified to help producers determine this stage of development within a field. TeKrony et al. (1981) determined that PM occurs when a normal pod on the main stem reaches its mature color (yellow) which coincides with the R7 growth stage. Gbikpi and Crookston (1981) found that loss of green color in all pods is the best indicator of PM which occurs slightly later than the growth stage depicted by TeKrony et al. (1981). This slight difference between these two descriptions and large differences in weather conditions partially explain the wide variation in seed moisture content that have been reported at PM, namely 40 to 60% (wb).

Harvest maturity (HM) is generally considered to occur when the seeds first attain a storable moisture ($\leq 14\%$ wb) while still in the field (TeKrony et al., 1987). Field drying is preferred by most producers to offset artificial drying costs and usually requires only a few weeks of favorable weather after PM. This may not a viable option, however, during seasons when extended periods of wet weather prevail. Seed quality usually deteriorates rapidly when soybeans are left in the field and excessive rains occur between PM and HM. Deterioration from exposure to excessive sunshine, rainfall, or heavy dew is commonly referred to as 'field weathering' (TeKrony et al., 1987). Such deterioration is not always observed for seed quality factors however (Krul, 1978), and logically may or may not actually occur for other quality factors such as test weight, protein and oil yield, and other chemical components of the seed (Sidhu, 1992; Overhults, 1975).

2.5.1. Potential Problems Associated with Weather Exposure:

Exposure to rainfall or heavy dew can remoisten the seed above a level that is safe for storage which requires that the crop be re-dried either in the field or artificially. Repeated wetting and drying cycles can alter the moisture transfer rates from the material (Sokhannsanj et al., 1984). Wilcox et al. (1974) reported that, when harvest was delayed by as much as 8 to 10 weeks, seed

quality deterioration was more pronounced for early maturing varieties than late season varieties. TeKrony et al. (1980) found that seed germination can deteriorate to unacceptable levels (< 80%) during seasons when undesirable weather patterns prevail by the time harvest maturity is reached.

Calero et al. (1981) observed that the mechanisms that restrict water uptake for soybeans during germination were thought to be seed size and seed coat characteristics. They measured the rate of water absorption in a 100% RH environment and used a scanning electron microscope (SEM) to observe seed coat structure after an eight day exposure period at 25° C. These were compared with seeds that were subjected to a standard germination test (8 and 24 h on moist paper). Vast differences in the amount of water uptake between the two methods were reported as well as differences between the 12 cultivars that were included in the study. Seed coat weight and seed size showed a slight correlation in some cases.

Sidhu (1992) measured the protein, oil, and carbohydrate content of soybean seeds during a harvest period that extended 16 weeks past PM. Three varieties were included in the investigation which was conducted over a two year period. All chemical constituents were found to correlate closely with seed moisture at harvest. A visual inspection of the seed coat was recorded for the same samples throughout harvest to evaluate its structural integrity. This was a companion study to the current investigation and will be more fully discussed in Chapter VI to test possible correlations between wetting and drying parameters and chemical constituents.

The above reports highlight some of the differences that have been observed between soybean varieties in their ability to resist deterioration from extended weather exposure. Genotype differences include seed size, seed coat thickness, susceptibility to fungal attack, and differences in permeability of the seed, seed coat, and pod. Many studies that have focused on seed damage due to weathering have not reported weather data or given complete descriptions of the chemical and physical characteristics of the seed. This compounds data interpretation and prevents meaningful comparisons of different studies. Ideally a standard procedure for studies in this area should be devised for future use.

2.5.2. Field Moisture Studies and Predictive Models:

Typically, soybeans will dry from an average of 50% (wb) moisture to about 15% (wb) within a short period if weather conditions are favorable. Low humidity during sunshine hours aids the drying process to the extent that there is a daily net loss of moisture by the seeds and pods as the crop progresses from PM to HM. However during extended periods of heavy rainfall, extended cloud cover or cool temperature, little drying occurs which prolongs the harvest season.

Krul (1978) reported that mature soybean seeds remained dry in the field even after the pods had been thoroughly wetted by rain. He conducted limited imbibition tests with intact pods and seeds without pods and concluded that water uptake was reduced for seeds in the pod as compared with seeds alone. He concluded that pods deter the rate of water uptake by the seed and speculated that this might vary among different varieties. This result prompted a study by Yaklich and Cregan (1981) who reported significant differences between varieties in water uptake by pods and seeds. However, Yaklich and Cregan (1987) later found a significant differences between pods but not for seeds.

Yaklich and Cregan (1981) conducted extensive experiments to measure the rate of moisture uptake into mature soybean seed pods for 46 varieties over a two seasons, including intact pods that contained seeds. Exposure times varied from 1 to 24 hours to permit absorption by the pod-seed system and the increase in the moisture content of each material was measured. They found that early maturing varieties (Groups II through IV) absorbed more water than late maturing varieties (Groups V and VI). The average increase in seed moisture content after 1, 6, and 24 hours of exposure was 0.8, 10, and 41% (d.b.), respectively. Initial moisture levels were between 5.2 and 7.3%. Other interesting observations from this study were that differences across maturity groups were attributed to both genetic and environmental factors and that varietal differences were observed within and across all maturity groups. No model was presented to predict the rate of sorption of either material.

Yaklich and Cregan (1987) presented extensive moisture data for soybean seeds and pods left in the field after HM to determine if varietal differences existed. Samples were collected at 8 am

and 1 pm daily during a 4 and 5 week period during the first and second year of study, respectively. On average, seeds and pods harvested at 8 am were higher in moisture than those harvested at 1 pm for the maturity group III varieties. Pod moisture varied more and was usually higher than seed moisture on a day to day basis and depended largely on weather conditions. No significant differences were observed for average seed moisture at harvest across varieties in either year of study.

A few models have been developed to predict seed moisture based on weather conditions. In a comprehensive soybean study by Chen et al. (1986) field moisture samples were collected at 10 am sporadically over a 52 day harvest after PM in the fall of 1985. They reported considerable variations in seed moisture throughout the period with a range from 13% to 78% (db) that was highly affected by rainfall. They also developed and tested two models to describe the moisture content of soybeans; an equilibrium model and an energy balance model. The EMC model assumed that the rate of mass transfer in the seed was proportional to the difference between the moisture at any given time and the EMC for the average hourly conditions. The exponential model (2.20) was applied to estimate different values for k based on whether the seed was undergoing a wetting or drying process. Drying and wetting constants were computed over a wide range of initial moisture content levels ($15 \leq M_0 \leq 45\%$). In addition to ambient temperature and relative humidity, the energy balance model required inputs for evaporation energy, rainfall, and cloud cover with empirical functions to estimate solar radiation and wind speed. Both models were able to predict the trend of seed moisture changes from day to day, but the energy balance model out performed the EMC model, especially during rainfall events. The main limitation to the EMC model was, perhaps, because of the selection of the empirical equations, and, though the EMC model was preferred because it required fewer inputs, its performance might be improved by selecting a different equation. Different models have been reported for predicting seed moisture of corn, wheat, and barley in the field by Bruns et al. (1975), Smith et al. (1981), and Atzma (1993), respectively.

Tyagi (1992) summarized the factors that cause field deterioration in soybean seeds after PM to be seed moisture, ambient temperature and relative humidity, rainfall, cultivar, and field fungi.

Moore (1971) found that the rate of alternate wetting and drying in the field resulted in damage to the cotyledon and seed coat. Mechanical damage by the combine, excessive temperatures in the dryer, poor handling equipment, and improper storage management can cause additional deterioration to the seed during harvest and post-harvest operations (Paulsen et al., 1981).

2.5.3. Predictive Models for Imbibition:

Except for tabular or graphical presentation of the data, none of the studies mentioned above have quantified the rate or degree of imbibition to a great extent. Peleg (1988) developed a straightforward purely empirical equation to describe the moisture sorption curves that are typical in food products as given by:

$$M(t) = M_0 + t/(k_1 + k_2 t) \quad (2.55)$$

where k_1 and k_2 are dependent on the product and environmental conditions. He verified this model with data collected by others for milk powder and rice.

Sopade and Obekpa (1990) tested the Peleg (1988) equation to predict the liquid sorption rate of soybeans from 2 to 40° C. Both chemical and physical properties were given for these products but no attempt was made to relate them to the equation parameters that were generated. However, they did show that k_1 was temperature dependent and developed a regression equation for this relationship. Although they did not report correlation coefficients, prediction errors for soybeans ranged from 0 to 15 percentage points of moisture which indicates that this model needs further refinement for this product.

Water absorption experiments were reported by Deshpande et al. (1994) for soybeans using three initial moisture levels at ambient temperature during short duration soaking tests (≤ 2 h). They observed that the rate of liquid transport was rapid initially but diminished to near zero as the grain reached saturation and concluded that the process was controlled by diffusion mechanisms. They developed the following empirical polynomial form by regression to describe the rate of imbibition ($R^2 = 0.96$):

$$dM/dt = 4.657 - 0.0662 M + 0.0002455 M^2 \quad (2.56)$$

They also determined that the maximum seed moisture content attainable at ambient temperature was 138% db when the initial moisture was 43.4% and reported that the liquid diffusion coefficient was $2.154 \times 10^{-5} \text{ cm}^2/\text{s}$.

Phillips (1968) determined that soybean seeds germinated in 20 hours in distilled water and between 30 and 95 hours in soil at moistures ranging from 20 to 4%, respectively. He also found that beans with the hilum covered with epoxy glue and soaked in distilled water for 20 hours absorbed 0.179 g/seed while uncovered beans absorbed 0.156 g/seed. He concluded that the absorption mechanisms do not favor the hilum region. Finally, he compared the liquid diffusivities of corn and cotton seeds to soybeans, discovered that they were approximately 4 and 18 times less, respectively, and concluded that the differences were attributed to physiological factors rather than the water permeability of the seed coat. The spherical diffusion model (2.13) adequately described the rate of water uptake by the soybeans in this study.

Factors that affect the extent of deterioration of soybeans during field exposure after PM have been investigated by many different researchers in different disciplines. Seed germination, viability, and vigor characteristics have received the most attention because of the obvious importance of these properties to the perpetuity of the industry.

CHAPTER III

PHYSICAL AND CHEMICAL DESCRIPTION OF SOYBEAN SEEDS

Seed researchers have identified some of the features that affect the absorption of liquid moisture by soybeans during imbibition. Food scientists have suggested that the chemical makeup of a product affects its water activity and EMC relationship. Engineers have quantified the rate of moisture uptake by various seed and food products but few have attempted to relate these parameters to either the physical or chemical characteristics of a particular product. This chapter will present a brief description of the physical and chemical properties of soybean seeds and how these properties will be considered in the mathematical model.

3.1. MORPHOLOGY OF SOYBEAN SEED COMPONENTS:

Soybean seeds are comprised of three distinct structural components namely the cotyledon, germ, and seed coat (see Figure 3.1). The relative weights of each component of a mature seed are 90 to 92, 1.5 to 2.0, and 6 to 8% by wet weight, respectively (Markley, 1950; Snyder and Kwon, 1987). Most commercially grown varieties are nearly spherical in shape with a slightly greater dimension in the direction parallel with the length of the hilum/cotyledon seam. Seed weights range from 0.131 to 0.198 g/seed (Mbuvi and Litchfield, 1988). They also reported an inverse, linear relationship between oil and protein content and concluded that seed size and composition are influenced by genetics and the environment, as have other authors (TeKrony et al., 1987; Tyagi, 1992). Moisture transport relationships were not investigated in their study.

The seed coat primarily consists of three well defined layers that are clearly viewed with the aid of a scanning electron microscope (SEM), namely, the epidermis, hypodermis, and parenchyma layers, as shown in Figure 3.2. The epidermis is covered by a thin, somewhat impermeable cuticle layer that appears to exist to control the rate of moisture transport into and out of the seed. Beneath the cuticle is a single layer of palisade cells that are 35 to 70 μm long and oriented with their long

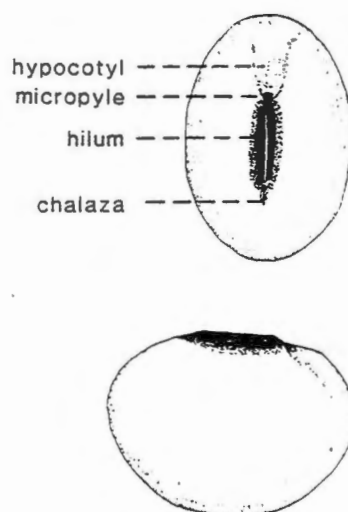


Figure 3.1. Morphological features of a typical soybean seed. Source: Wolf, W.J., and J.C. Cowan. 1975. Soybeans as a Food Source. CRC Press, Cleveland, OH.

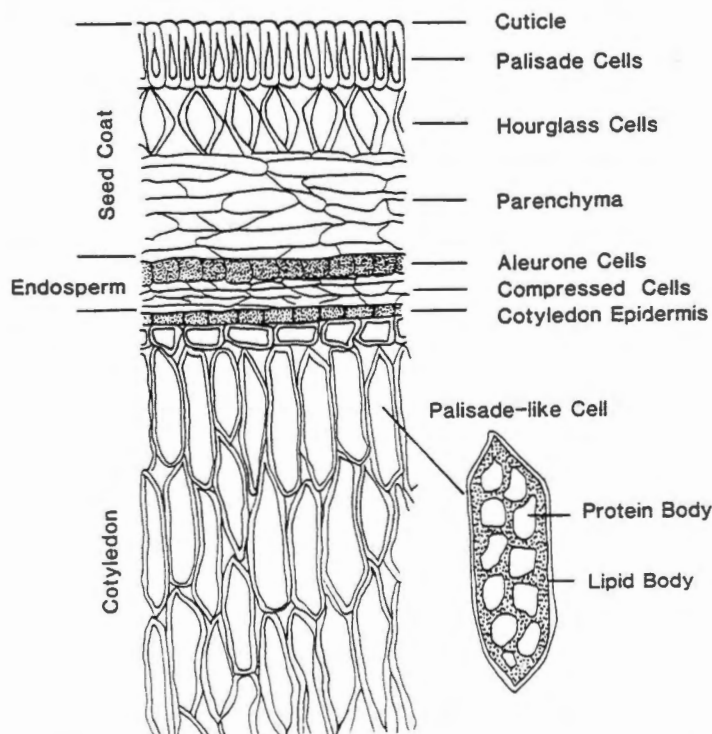


Figure 3.2. A sketch of the microscopic structure of the soybean seed coat and cotyledon. Source: Bair, C.W. 1979. Microscopy of soybean seeds: Cellular and subcellular structure during germination, development, and processing with emphasis on lipid bodies. PhD Dissertation. Iowa State University, Ames, IA.

dimension perpendicular to the surface (Carlson and Lersten, 1987). These cells have relatively thick walls and fewer void spaces between them than most others in the seed coat which suggest that they are arranged to retard moisture movement.

Just beneath the palisade cells is the unique feature of all legume seed coats that may play an important role in moisture transport more than any other structure, namely, the hourglass or column cells. These are the only cells in the hypodermis layer and are wider at the top and bottom points of attachment and tapered towards the center. These widely spaced cells are between 30 and 100 μm in length (Patel, 1976; Yaklich et al., 1995), connect the palisade cells to the parenchyma cells and are oriented with their longest dimension parallel to the radial direction of the seed. They act in concert with the palisade cells to give the seed coat its structural support (Carlson and Lersten, 1987). The numerous void spaces between the cells in this layer offer relatively little resistance to moisture transport and have been shown to facilitate moisture uptake by the seed during imbibition (Pereria and Andrews, 1985; McDonald et al., 1988a; Casini, 1990). They are thought to have a similar role for moisture vapor when conditioning the seed with air.

Adjacent to the hourglass cells is the parenchyma layer, which consists of parenchyma and aerenchyma cells. Parenchyma cells are 6 to 8 layers deep, oriented with their longest dimension perpendicular to the seed radius, have thin walls, and are somewhat cigar shaped with a long narrow profile and tapered ends (Carlson and Lersten, 1987). There is a sub-layer of aerenchyma cells within this region which are similar in structure and orientation to the parenchyma cells but have larger areas of intercellular spaces between them (Yaklich et al., 1995). The relative thickness of each layer of the seed coat mentioned above was estimated by scaling from a scanning electron microscope (SEM) image published by Yaklich et al. (1992) to be 0.6, 18.0, 23.0, 43.8, and 14.6 % of the total seed coat thickness for the cuticle and palisade, hour glass, parenchyma, and aerenchyma cells, respectively.

The hilum or seed scar is located on the seed coat where the bean was formerly attached to the pod. For most yellow seed varieties (including the cultivars selected in this study), it is a dark-

brown/black oval structure that typically covers only a small area of the seed coat. The hilum consists of dense cellular tissue with a double layer of palisade cells beneath the surface (Andrews, 1996). A micropyle (tiny hole) and raphe (small groove) are located at opposite ends of the hilum (Carlson and Lersten, 1987). The embryonic/hypocotyl-radicle axis (germ) is shaped like a two pronged pitchfork, is usually visible just beneath the seed coat and is located adjacent to the micropyle (Figure 3.1).

The cellular tissue within each layer of the seed coat was formerly considered by many researchers to be essentially uniform except in the region of the hilum, which is only a small portion of the entire surface (~10%). This supposition was partially based on the report given by Carlson and Lersten (1987) who noted that the hilum contains a fissure in the center which is connected to the micropyle and parenchyma cells which are, in turn, directly connected to the relatively large area of intercellular space in the hypodermis layer (i.e., the hourglass cells). Since the palisade cells are covered with a waxy cuticle, they projected that the epidermis layer is relatively impermeable to gases leaving the primary pathway for water vapor exchange between the cotyledon and the environment through the hilum. Dzikowski (1936) speculated that the structure of the hilum probably had an effect on the moisture content of the inner seed. This assumption was refuted by Phillips (1966) and by McDonald et al. (1988a) who found no preferential pathway through the hilum during imbibition tests. Wolf et al. (1981) and Calero et al. (1981) determined that it is not uncommon for soybean seed coats to have deep pores that extend past the palisade cells even to the hourglass cells which, if present, could create a shunt for moisture exchange with the environment. Nevertheless, an experiment was conducted as part of this study to investigate the possible role of the hilum when soybeans exchange moisture with the atmosphere. The implications of this outcome on moisture transfer theory are presented in Chapter IV.

Figure 3.2 shows two types of cells that remain from the endosperm as the bean reaches maturity. These lie in a thin layer to the interior of the seed coat. The outer region is made up of a single layer of cube-shaped aleurone cells which are filled with protein in the mature bean seed

(Carlson and Lersten, 1987; Yaklich et al., 1995). Adjacent to the aleurone cells are several layers of compressed cells which are oriented similar to the parenchyma cells with their thinnest dimension perpendicular to the radius.

The embryo consists of two relatively large hemispherical cotyledon sections that are bounded by an epidermis of cube shaped (aleurone-like) cells that are one layer thick (Carlson and Lersten, 1987). Adjacent to these are numerous palisade-like cells which contain the oil and protein bodies that are bounded by the cell walls. These cells comprise the remaining seed volume and are approximately 15 to 20 μm in diameter and 70 to 80 μm in length (Snyder and Kwon, 1987). Small calcium oxalate crystals are distributed throughout the intercellular voids of the cotyledon (Carlson and Lersten, 1987). Considering that the cotyledons are approximately 3mm thick, one might think that the distance a water molecule must travel to reach the outer regions of a soybean dictates that this region offers the greatest restriction to moisture transport, especially when compared to the more porous structure of the seed coat. The relative magnitudes of the resistance of each component will be fully developed in the mathematical analysis of Chapter IV.

The embryonic or hypocotyl-radicle axis (germ) is approximately 5 mm in length and is slightly flattened on the outer and inner surfaces which is connected to the seed coat and cotyledon, respectively (Carlson and Lersten, 1987). When soybeans are cracked prior to oil extraction, the germ may adhere to either seed component (Snyder and Kwon, 1987).

3.2. CHEMICAL COMPOSITION:

The proximate analysis of typical soybean seeds and their components has been reported by Markley (1950), and are summarized in Table 3.1. The cotyledon and germ are both high in protein but the germ contains only about half as much oil. Comparatively, the seed coat is low in protein and has virtually no oil but is highest in carbohydrates, comprised mostly of cellulose, pentosans, and lignin (Smith and Circle, 1978). This data set also indicates that moisture and ash in the cotyledon, germ, and seed coat are fairly uniform in distribution relative to the other seed components. Recall

that the rate of moisture transfer was shown to be quite different between the cotyledon and seed coat (Mensah et al., 1979). Additionally, the moisture holding capacity of the germ has been shown to be significantly higher than the other components (McDonald et al., 1988a). These differences could be due to the physical or chemical composition of each material but neither have been clearly distinguished among the numerous studies that have been reported on the liquid sorption/imbibition properties of soybeans (Casini, 1990). Specific proteins, fatty acids, carbohydrates, sugars, and mineral components of soybeans are given in several references previously listed (Smith and Circle, 1978; Snyder and Kwon, 1987; Tang, et al., 1993; Liu and Brown, 1995).

Table 3.1. Composition of the component parts of soybean seeds (Markley, 1950).

Constituent	Composition, %		
	Cotyledons	Seed Coat	Germ
Protein	41.3	7.0	36.9
Carbohydrates	14.6	21.0	17.3
Oil	20.7	0.6	10.4
Moisture	10.6	12.5	12.0
Ash	4.4	3.8	4.1
Total seed weight	90.0	8.0	2.0

Tang et al. (1993) measured the spatial distribution of selected protein compounds within thinly sliced cross-sections of soybean cotyledons (cultivar Amsoy 71) at various stages of maturity, including physiological maturity (PM). They found location differences between the storage proteins (glycinin and β -conglycinin) but not the trypsin inhibitors and concluded that the relative protein composition within each half of the cotyledon was not vastly different.

Liu and Brown (1995) measured the composition of five fatty acids for each structural component of soybean seeds using gas chromatography. The axis, seed coat, and both sections of the cotyledon were sampled from six cultivars during the one year study. They found that the seed coat and axis had a higher percentage of saturated and polyunsaturated fatty acids, respectively.

While the relative percentages of fatty acids varied considerably between components they were homogeneous within both cotyledons.

3.3. INFLUENCE OF STRUCTURE AND COMPOSITION ON EMC AND CONDITIONING PROPERTIES:

Most agronomic/germination/seed quality studies have been conducted by soaking the material in distilled water for a few hours to emulate germination and expedite the uptake of moisture by the seed. Calero et al. (1981) observed that the mechanisms that restrict water uptake for soybeans during germination were thought to be seed size and seed coat characteristics. They measured the rate of water absorption in a 100% RH, 25° C environment and used a scanning electron microscope (SEM) to observe seed coat structure after an 8-day exposure period. These were compared with seeds that were subjected to a standard germination test (8 and 24 h on moist germination paper). Vast differences in the amount of water uptake between the two methods were reported as well as differences between the 12 cultivars that were included in the study. Average increases in seed weight were nearly twice as high for the 8-day high RH condition than for the 8-h germination test (79 versus 40 g). Seed coat weight and seed size showed a slight correlation.

Pereira and Andrews (1985) reported that the thickness of hourglass cells decreased gradually at a rate proportional to the distance from the hilum and they disappeared entirely in the area opposite the hilum. Degago and Longer (1989) found that the seed coat near the hilum was between 1.5 to 1.7-mm thick and 0.2 and 0.35-mm thick in the area opposite the hilum. Casini (1990) found similar results and showed that the thinnest area of the seed coat extended to the ends of the seed in a direction that was parallel with the cotyledon seam.

Other investigators have provided very descriptive details of the seed coat surface by employing a scanning electron microscope (SEM) at various magnification levels (Wolf et al., 1981; Yaklich et al., 1984; Yaklich et al., 1986; Vaughn et al., 1987; McDonald et al., 1988a; and Casini, 1990). These studies reveal that some commercial varieties have a smooth seed coat while others have a pitted surface of various densities. Still other cultivars have shallow crater-like features

uniformly across the surface. Also, natural cracks can form as the seed matures under certain environmental conditions, some of which can penetrate beyond the palisade cells to the hourglass cells (Wolf et al., 1981).

McDonald et al. (1988b) investigated the sequence of water absorption by liquid and vapor in different components of soybean seeds by excising seeds at various stages of exposure. They found that while the seed coat was the first component to imbibe water, particularly in the area most distant from the hilum. However, the embryonic axis gained more moisture by both mechanisms than any other component, followed by the cotyledon, seed coat, and intact seed. They also found a difference in water holding capacity of the axis between aged seeds and 'fresh' seeds.

McDonald et al. (1988a) used a SEM to determine how the absorption of liquid water affected seed coat morphology in soybeans. They reported that the seed coat facilitates the movement of water around the seed so that both cotyledons imbibe moisture evenly. Pereira and Andrews (1985) suggested that the hourglass cells act as a reservoir, and Casini (1990) suggested that the hourglass cells provide an active mechanism of water diffusion even in the thinner areas where they are absent because the compositional nature of the seed coat permits rapid water penetration there.

Casini (1990) found no correlation between seed coat structure and permeability and that seed size did not affect imbibition. Although the most predominant area for absorption was 180 degrees from the hilum, an exclusive pathway of initial water uptake was not found. Seeds absorbed water from all locations measured and was aided greatly by the hourglass cells. Although no determination was made regarding the chemical make up of these materials his review of previous studies indicated that researchers had not clearly identified sufficient justification for such an extensive effort. He proposed a new concept to describe the rate of imbibition by soybean seeds that includes the interaction between structural features of the seed coat and weather conditions, which disregards the hilum as a preferential pathway to moisture uptake.

Several investigators have suggested that the EMC properties of grain and food products are based on the chemical composition of its component parts, but relatively few have presented detailed

data in this area. Salwin and Slawson (1959) investigated the moisture transport between two or more dehydrated foods in moisture proof packages with relatively large pieces in the mixture (ground beef+diced onions+dried potatoes). Prediction errors for the final moisture content of each component in the mixture ranged from 0 to 7.3 percentage points. Labuza (1968) later suggested that this area of study merits more extensive investigation for manufactured and unaltered foods but pointed out some of the anticipated difficulties in this area of research, namely that sugars are highly active and can change phase quickly even at room temperature.

Iglesias et al. (1980) reviewed the works of others in this area and applied the method to insoluble food mixtures of various protein and carbohydrate products. Their results were highly variable, giving good agreement for a few products but large discrepancies for most others. The differences between the observed and predicted values were attributed to the interactions between compounds and mixing techniques but no attempt was made to quantify these variables. They recognized the arduous task of delineating such terms and suggested that processing techniques possibly could play a role in the magnitude of these values for some manufactured products.

Kaminski and Al-Bezweni (1994) proposed that the EMC values for multi-component protein mixtures could be calculated if the mass fraction and moisture sorption isotherm of each component were known in addition to the interactions of water active components. Their approach was based on an improvement to the work reported by Salwin and Slawson (1959) and Labuza (1968) by including interaction terms in their model, even though they clearly recognized these variables could introduce a significant source of error when predicting EMC. The following equation was evaluated with data for a variety of protein concentrations (such as bakers' yeast and blood plasma) that were mixed with carbohydrate sources (starch and cellulose, respectively):

$$EMC = \sum_{i=1}^n DM_i \xi_i M_{ei} \quad (3.1)$$

where DM_i = dry matter component of the i th component
 ξ_i = interaction coefficient/function between the i th component and mixture
 M_{ei} = equilibrium moisture content for the i th component

The interaction terms were selected to account for any differences that may result when materials are adjacent to one another as opposed to their moisture sorption behavior when isolated, and were termed the activity coefficients. EMC vs ERH plots were generated for each mixture which resulted in very good agreement between the observed and predicted values ($0.984 \leq R^2 \leq 0.998$) with a maximum relative error of 3.2%. These authors pointed out that interaction coefficients were approximately equal for binary mixtures and that in cases where there was no interaction, the coefficient was equal to unity.

Ng et al. (1995) investigated the effects of variety and mechanical damage on the ERH of shelled yellow corn over a range of ambient temperatures ($5 \leq T \leq 45^\circ \text{C}$) and typical harvest moisture contents for natural air/low heat drying systems ($13 \leq M_o \leq 22\%$). ERH differences were found between hybrids, which were related to their compositional makeup by modifying their equations to predict the EMC of shelled corn based on the equilibrium properties and weight fractions of each major component (fiber, minerals, oil, protein, and starch). This was an application to the model that was proposed by Chung et al. (1972), applied by Crapiste and Rotstein (1982) and further refined by Chen (1988) and Ng (1993) for corn. Interaction terms were not mentioned in the report by Ng et al. (1995), hence they were implied to be equal to one. The EMC-ERH model was also not given but was assumed to be one suggested by Chen and Morey (1989). Nevertheless, they reported that their equations predicted the ERH of all three cultivars to within a 2% error at 25°C in the 15 to 28 % moisture range, based on their chemical composition. Although confined to limited data, they concluded that the chemical composition could be used to predict ERH and thereby storability for shelled corn. This study suggests that similar models need to be evaluated for other grains.

Such a relationship could be developed for oilseeds provided that sufficient information is available regarding the major components within the seed. Development of such an equation would require extensive data to quantify the dry matter fractions, the respective EMC properties of each component and whether the interaction terms are significant, and should be carried out over a wide

temperature and relative humidity range to test the extent of these effects on all equation variables. Additionally, microscopic techniques such as those developed by Yaklich et al. (1994) might be needed to determine the relative position of each component within the material and the distance between them to delineate the activation coefficients. Finally, the influence of variety and age or condition of the product should be included to determine if these effects are significant.

Xiong et al. (1991) reported the influence of composition on the effective mass diffusivity for extruded food products, including different mixtures of gluten and starch. Desorption isotherms were determined by experiment in a narrow temperature range of 25 to 40° C over an ERH/AW range of 10 to 90% but no attempt was made to relate EMC to the composition of these products. Their results showed that mixtures high in starch possessed higher EMC values whereas the products that were high in protein had lower corresponding EMC values. Values for products with equal amounts of each component were bounded by the other two curves on the EMC plot. They naturally concluded that the starch components are more active than their protein counterparts and would therefore gain more water under the same conditions. Recall that for the 'average lot' of soybeans, the ratio of starch to protein is approximately 1 to 1.1.

Xiong et al. (1991) also conducted drying experiments with the same mixtures of protein and starch products and used a truncated form of the cylindrical diffusion equation to estimate the effective mass diffusivity from the drying data. An empirical equation was derived to correlate the effective mass diffusivity with air temperature and a product dependent equilibrium 'constant.' However, this equation gave a poor fit to the values for the effective diffusivity estimates that were determined by regression from the diffusion equation.

Several researchers have observed that equilibrium moisture properties are generally lower for high oil products when compared to no/low oil grains at the same environmental conditions (Brooker et al., 1992). When compared on an oil-free basis these differences are diminished. Mensah et al. (1979) found that the EMC for the soybean cotyledon was about 10% lower than the EMC for the seed coat at the same temperature and relative humidity. This would be expected since

the cotyledon has much more oil than the seed coat. Further investigation is required to determine whether these or other components might affect the rate of moisture transfer. This remains an interesting research area but requires considerable effort to perform enough tests to gather the vast amount of data required to correlate this information. Moisture transport models that are based on the physiological features of the particular biological material are exceedingly more useful to the research community than empirical models because they establish a strong fundamental basis for similar materials. Many empirical models that are widely used successfully may have a stronger link to the physical or chemical constituents of a particular material than is recognized and, thus, may be significant on a physiological level. Hence, a moisture transport model that is based on these physical variables should be quite useful since the conditioning rate could be accounted for by characteristics that are easily measured rather than by developing an empirical model that may have to be recalibrated for soybeans of different variety, size or chemical composition.

CHAPTER IV

MATHEMATICAL ANALYSIS

Moisture sorption models that have been developed for biological materials can be grouped into three broad categories; namely, analytical, empirical, and numerical. This approach is analytical, based on the diffusion theory that has been widely used to describe the moisture conditioning behavior of cereal grains (Becker and Sallans, 1955; Brooker et al., 1992; Chittenden and Hustrulid, 1966; Steffe and Singh, 1982; and Walton et al., 1988) and oilseeds (Tang and Sokhansanj, 1993; Osborn et al., 1991; Young and Whitaker, 1971b). A model for the soybean was developed by the following steps:

- 1) identify the resistances to moisture diffusion by structural components of the seed,
- 2) apply the principle of homogeneity to determine the basic units of the system to be modeled geometrically,
- 3) determine the appropriate geometric model to represent the shape of each unit,
- 4) state the assumptions necessary to achieve a practical solution,
- 5) identify appropriate partial differential equations (PDE),
- 6) describe appropriate boundary conditions, and
- 7) derive the solution to the PDE.

4.1. PARTITION OF DIFFUSION RESISTANCES:

Major components of the soybean seed were presented in Chapter III to reveal that the cotyledon tissue contains the bulk of the moisture that will be added/removed during wetting/drying since it comprises 89% of the fresh weight. This tissue provides the first level of resistance to moisture transport/diffusion during drying. In this case, the moisture leaves the surface of the outer cotyledon cells as a vapor and diffuses through the pore space to the epidermis where it encounters the resistance offered by the various layers of cells in the seed coat. Final resistance to moisture transport is through the thin layer of air (boundary layer) that surrounds the outer surface of the seed coat. Hence, the resistance to moisture diffusion is divided into three parts: resistance of the

cotyledon tissue, resistance of the seed coat and resistance of the boundary layer of the air surrounding the soybean.

4.2. PRINCIPLE OF HOMOGENEITY:

A basic assumption for this analysis was that each of the two main structural seed components (cotyledon and seed coat) were considered to be a homogeneous unit. Cotyledons appear to be the best candidate for modeling as a homogeneous porous solid since they are made up of tightly packed palisade-like cells which have few void spaces. The soybean seed has two hemispherical cotyledons that are joined together at the flat surface to form a sphere. Hence, the two combined cotyledons were geometrically modeled as a single sphere and internal resistance was that of the cotyledon tissue. Resistance to moisture transport external to the geometric model was the sum of the resistances of the seed coat and of the boundary layer.

4.3 ASSUMPTIONS:

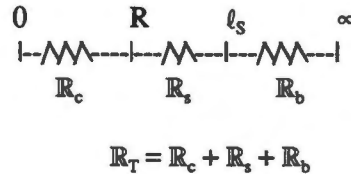
Assumptions made in this analysis were:

- 1) geometric models for each structural component were homogeneous,
- 2) mass diffusivities of the soybean seed was constant throughout wetting/ drying,
- 3) shrinkage of the materials was negligible,
- 4) there were no capillary effects,
- 5) changes in the void space were neglected,
- 6) solid and vapor reached moisture equilibrium instantaneously,
- 7) transport was isothermal, and
- 8) mass diffusion resistance of the seed was not affected by moisture changes.

The discussion in Chapter III led to the conclusion that soybean seeds are assumed to be non-homogeneous bodies comprised of three distinct components, namely the cotyledon, embryonic axis, and seed coat. Each component is made up of several layers of cells, some of which are different in orientation, wall thickness, composition, and structure (Bair, 1979; Carlson and Lersten, 1987; Snyder and Kwon, 1987; Stroshine and Hamann, 1994). As a molecule of moisture is transferred to or from the inner portion of a seed to the surrounding atmosphere, it must overcome all the

resistances encountered by the arrangement of the cells and the affinity for moisture in each component. When these resistances are grouped by a sub-level of local homogeneity, a better understanding is developed regarding the forces encountered that impede moisture transport. Such resistances will be discussed in this section to determine which structural components of the seed are most important when describing moisture transport. A few researchers have recognized that many seeds should not be modeled as if they were homogeneous, specifically for drying corn, lintels, rice, and tobacco (Aguerre and Suarez, 1992; Walton et al., 1988; Tang and Sokhansanj, 1993; Sharma and Kunze, 1982; Walton and Casada, 1986), yet, no one has fully developed a resistance model for soybeans.

The following schematic illustrates the expected resistance terms that are deemed significant when a water molecule enters or exits a soybean seed:



where

R = radius of the cotyledon, cm

ℓ_s = thickness of the seed coat, cm

∞ = thickness of the air film on the bean surface

R_c = the resistance to moisture transfer through the cotyledon

R_s = resistance of the seed coat

R_b = resistance of the boundary layer

R_T = the total resistance to moisture transfer across the domain

Total resistance to moisture transport is, thus, considered to be the sum of these individual resistance terms. Note that resistance offered by the seed coat is expressed as a single term which is in contrast to an analogous parallel circuit which would account for the resistances offered by the outer seed coat skin and hilum if it were deemed significant to transport.

Relative resistances to moisture transport by the two major seed components have been reported by Mensah et al. (1979), who prepared 45 and 56 mm² plate-shaped pieces from the seed

coat and cotyledon, respectively. They estimated the diffusivities of each material by regressing their data with a mass diffusion model for an infinite plate and found that the seed coat offered roughly six times more resistance to moisture transport than the inner tissue. The thickness of each material was reported to be 0.1 and 1.0 mm for the seed coat and cotyledon, respectively.

Early efforts at applying diffusion theory to drying and wetting of cereal grains and oilseeds assumed that resistance to moisture movement was uniform throughout the kernel or seed, i.e. the tissue was homogeneous. By assuming the corn kernel to be homogeneous and using negligible boundary layer resistance, Chittenden and Hustrulid (1966) found that the resulting diffusion model provided an adequate fit in the early and late portions of the drying test but did not fit the data across the entire curve satisfactorily. In light of the previous discussion, this observation is fairly obvious because the assumption of homogeneity was in error.

The soybean may be examined physiologically to determine which interior tissue can reasonably be considered homogeneous, determine the geometric model that best describes the homogeneous material, and apply the diffusion theory to derive a mathematical model for drying and rewetting of the soybean. This process results in a partitioning of the resistances shown above into internal and external terms for the geometric model. Thus, the resistances external to the geometric model may include resistances of certain cell layers in addition to the boundary layer resistance. These resistance terms will be quantified in the following analysis.

4.4. GOVERNING EQUATION, BOUNDARY CONDITIONS, AND SOLUTION:

The following equation governs the rate of moisture transfer from porous hygroscopic materials (Chinnan and Young, 1977a):

$$f_v \frac{\partial \rho_v}{\partial t} + \rho_m \frac{\partial M}{\partial t} = D \nabla^2 \rho_v \quad (4.0)$$

where f_v = void fraction, decimal

t = time, h

M = moisture content of the material, dry basis percent

D = mass diffusivity based on water vapor concentration, cm^2/h

ρ_m = bulk density of dry material, g_{DM}/cm^3
 ρ_v = water vapor concentration, g/cm^3

Moisture content M and the water vapor concentration are related through equilibrium moisture isotherms which have been represented by the empirical relationship (Henry, 1939):

$$M = \sigma + \rho_v \beta - \omega T \quad (4.1)$$

where σ, ω = product dependent constants
 β = slope of the moisture isotherm when expressed in terms of the EMC, specific humidity, H , and specific volume of the air, v , cm^3/g
 T = air temperature, C

For isothermal conditions this equation becomes:

$$M = \sigma_T + \rho_v \beta \quad (4.1a)$$

Substituting equation (4.1a) into (4.0) provides a relationship which is expressed in terms of the moisture content of the material:

$$\frac{f_v}{\beta} \frac{\partial M}{\partial t} + \rho_m \frac{\partial M}{\partial t} = \frac{D}{\beta} \nabla^2 M \quad (4.2)$$

which can be rewritten as:

$$\left(\frac{f_v}{\beta} + \rho_m \right) \frac{\partial M}{\partial t} = \frac{D}{\beta} \nabla^2 M \quad (4.2a)$$

or simplified to:

$$\frac{\partial M}{\partial t} = \frac{D}{(f_v + \rho_m \beta)} \nabla^2 M \quad (4.2b)$$

It will be shown that for soybeans the $\rho_m \beta$ term is $\gg 1$ which renders f_v insignificant since it is less than unity by definition. The above equation can be reduced to:

$$\frac{\partial M}{\partial t} = \frac{D}{\rho_m \beta} \nabla^2 M \quad (4.2c)$$

which may be simplified to the familiar form of:

$$\frac{\partial M(r,t)}{\partial t} = D' \nabla^2 M(r,t) \quad (4.2d)$$

where D' = mass diffusivity based on the moisture content, $cm^2/h = D / \rho_m \beta$

Equation (4.2.d) is written in spherical coordinates (for example, see Brooker et al., 1992):

$$\frac{1}{D'} \frac{\partial M(r,t)}{\partial t} = \frac{\partial^2 M}{\partial r^2} + \frac{2}{r} \frac{\partial M}{\partial r} \quad (4.3)$$

$$= \frac{1}{r^2} \left(r^2 \frac{\partial^2 M}{\partial r^2} + 2r \frac{\partial M}{\partial r} \right) \quad (4.3a)$$

$$= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial M(r,t)}{\partial r} \right) \quad (4.3b)$$

The initial condition ($t = 0$) assumes that moisture is uniformly distributed throughout the body, or:

$$M(r,0) = M_0 \quad (4.4)$$

At the center boundary of the body ($r = 0$) there is no moisture gradient:

$$\frac{\partial M(0,t)}{\partial r} = 0 \quad (4.5)$$

At the surface of the cotyledon ($r = R$), the boundary condition may be written by equating the moisture flux toward the cotyledon surface to the flux away from the cotyledon surface which involves a series of resistances to mass transfer (due to the seed coat and boundary layer resistances as previously defined):

$$-D \frac{\partial \rho_v(R,t)}{\partial r} = \frac{\rho_v(R,t) - \rho_{va}}{R_s + R_b} \quad (4.6)$$

where R_s = resistance of the seed coat = ℓ_s/D_s , h/cm
 ℓ_s = thickness of seed coat, cm
 D_s = mass diffusivity of the seed coat based on the concentration gradient cm^2/h
 $= [D' \rho \beta]_s$ (as previously defined)
 R_b = resistance of the boundary layer = $1/h_m$, h/cm
 h_m = convective mass transfer at the seed surface, cm/h
 ρ_{va} = water vapor pressure concentration of ambient air, g/cm^3

The sum of resistance terms in the denominator in (4.6) can also be represented by a combined term for convenience as $R_{ext} = R_s + R_b$ and that (4.1a) describes the relationship between

ρ_v and the moisture content and similarly between ρ_{va} and the equilibrium moisture content for isothermal conditions.

Substituting equation (4.1a) into (4.6) gives the boundary condition at the cotyledon surface in terms of the moisture content, which is the desired form:

$$D \frac{\partial M(R, t)}{\partial r} = \frac{M(R, t) - M_e}{R_s + R_b} \quad (4.6a)$$

where M_e = equilibrium moisture content of the cotyledon at ambient temperature and relative humidity, decimal

$$D = D' \rho_m \beta$$

This boundary condition is in contrast to the often used case of zero resistance [$R_b = 0$] which implies that the surface reaches moisture equilibrium instantaneously (i.e., $M(R, t) = M_e$) thus:

$$\frac{\partial M}{\partial r}(R, t) = 0 \quad (4.7)$$

To solve equation (4.3b) using the initial condition (4.4) and boundary conditions (4.5) and (4.6a) the dimensionless moisture ratio, $\Theta(r, t)$ is defined as:

$$\Theta(r, t) = \frac{M(r, t) - M_e}{M_0 - M_e} \quad (4.8)$$

Inserting equation (4.8) into (4.3b) and rewriting the initial and boundary conditions in terms of the variable Θ yields:

$$\frac{1}{D'} \frac{\partial \Theta(r, t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Theta(r, t)}{\partial r} \right) \quad (4.9)$$

With initial condition (4.4) and definition (4.8):

$$\Theta(r, 0) = \frac{M_0 - M_e}{M_0 - M_e} = 1 \quad (4.10)$$

The center boundary condition (at $r = 0$) becomes:

$$\frac{\partial \Theta(0, t)}{\partial r} = 0 \quad (4.11)$$

and the boundary condition at the surface ($r = R$) becomes:

$$-D \frac{\partial \Theta(R, t)}{\partial r} = \frac{\Theta(R, t)}{R_{ext}} \quad (4.12)$$

An intermediate step for the solution of the Θ function is obtained by applying the following transformation, as suggested by Arpaci (1966) and Crank (1975):

$$\Theta(r, t) = \frac{1}{r} \Psi(r, t) \quad (4.13)$$

Then equation (4.8) is written as:

$$\frac{1}{D'} \frac{\partial}{\partial t} \left(\frac{1}{r} \Psi(r, t) \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \left(\frac{1}{r} \Psi(r, t) \right) \right) \quad (4.14)$$

$$\frac{1}{D'} \frac{1}{r} \frac{\partial}{\partial t} (\Psi(r, t)) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \left(-\frac{1}{r^2} \Psi + \frac{1}{r} \frac{\partial \Psi}{\partial r} \right) \right) \quad (4.14a)$$

$$= \frac{1}{r^2} \frac{\partial}{\partial r} \left(-\Psi + r \frac{\partial \Psi}{\partial r} \right) \quad (4.14b)$$

$$= \frac{1}{r^2} \left(-\frac{\partial \Psi}{\partial r} + r \frac{\partial^2 \Psi}{\partial r^2} + \frac{\partial \Psi}{\partial r} \right) \quad (4.14c)$$

$$= \frac{1}{r} \frac{\partial^2 \Psi}{\partial r^2} \quad (4.14d)$$

$$\frac{1}{D'} \frac{\partial \Psi(r, t)}{\partial t} = \frac{\partial^2 \Psi}{\partial r^2} \quad (4.14e)$$

with the initial condition:

$$\Psi(r, 0) = r \quad \Theta(r, 0) = r \quad 1 = r. \quad (4.15)$$

At the center of the material ($r = 0$) the boundary condition is:

$$M(0, t) = \text{finite} \Rightarrow \Theta(0, t) = \text{finite} \Rightarrow \Psi(0, t) = r^{\neq 0} \text{ finite} = 0 \quad (4.16)$$

Before writing the boundary condition at the cotyledon surface an expression must first be derived

in $\Psi(r, t)$. Substituting into equation (4.12):

$$-D \frac{\partial}{\partial r} \left(\frac{\Psi(r, t)}{r} \right) = \frac{\Psi(r, t)}{r R_{ext}} \quad (4.17)$$

$$-D \left(\frac{1}{r} \frac{\partial \Psi(r, t)}{\partial r} - \frac{\Psi(r, t)}{r^2} \right) = \frac{\Psi(r, t)}{r R_{ext}} \quad (4.17a)$$

$$\frac{\partial \Psi(r, t)}{\partial r} = \frac{\Psi(R, t)}{r} - \frac{\Psi(r, t)}{D R_{ext}} \quad (4.17b)$$

$$\frac{\partial \Psi(r,t)}{\partial r} = \left(\frac{1}{r} - \frac{1}{D R_{ext}} \right) \Psi(r,t) \quad (4.17c)$$

At the cotyledon surface ($r = R$):

$$\frac{\partial \Psi(R,t)}{\partial r} = \left(\frac{1}{R} - \frac{1}{D R_{ext}} \right) \Psi(R,t) \quad (4.18)$$

Assume a product solution is attainable by the method of separation of variables, i.e.:

$$\Psi(r,t) = \Phi(r) \Gamma(t) \quad (4.19)$$

A solution to equation (4.9) is obtained by inserting (4.19) into (4.14.e), combining common functions and equating to a separation constant $-\lambda^2$:

$$\frac{1}{D'} \frac{\partial}{\partial t} [\Phi(r) \Gamma(t)] = \frac{\partial^2}{\partial r^2} [\Phi(r) \Gamma(t)] \quad (4.20)$$

$$\frac{1}{D'} \Phi(r) \frac{\partial \Gamma(t)}{\partial t} = \frac{\partial}{\partial r} [\Gamma(t) \frac{\partial \Phi(r)}{\partial r}] \quad (4.20a)$$

$$= \Gamma(t) \frac{\partial^2 \Phi(r)}{\partial r^2} \quad (4.20b)$$

$$\frac{1}{D' \Gamma(t)} \frac{\partial \Gamma(t)}{\partial t} = \frac{1}{\Phi(r)} \frac{\partial^2 \Phi(r)}{\partial r^2} = -\lambda^2 \quad (4.20c)$$

The left side of equation (4.20c) contains the temporal term which is solved directly by combining like terms and integrating:

$$\int \frac{d\Gamma}{\Gamma} = -D' \lambda^2 \Gamma \int dt \quad (4.21)$$

$$\ln \Gamma = -D' \lambda^2 t + C \quad (4.22)$$

Apply the initial condition (4.10) to find the constant of integration which is at $t = 0$, $\Theta = 1$.

Therefore, $\Gamma = 1$, thus $\ln(1) = 0 = -D' \lambda^2 (0) + C$ and $C = 0$ to obtain:

$$\boxed{\Gamma(t) = e^{-D' \lambda^2 t}} \quad (4.23)$$

Note that the diffusion term remains with the temporal portion of the solution which will be inserted into equation (4.19) after a solution is obtained for the spatial function Φ .

The right side of equation (4.20c) contains the spatial function, Φ which can now be expressed as an ordinary derivative:

$$\frac{d^2 \Phi}{dr^2} + \lambda^2 \Phi = 0 \quad (4.24)$$

The boundary condition at $r = 0$ is given by equation (4.11) so $\Phi(0) = 0$ (4.25)

The surface boundary condition at $r = R$ is given by equation (4.12) as:

$$\frac{d\Phi(R)}{dr} + \left(\frac{1}{D R_{ext}} - \frac{1}{R} \right) \Phi(R) = 0 \quad (4.26)$$

The general solution of equation (4.24) with boundary conditions (4.25) and (4.26) is given by the following series:

$$\Phi(r) = \sum A \sin \lambda r + B \cos \lambda r \quad (4.27)$$

Applying the first boundary condition at $r = 0$:

$$\Phi(0) = A \sin 0 + B \cos 0 = 0 \quad (4.28)$$

Thus, $B = 0$ and

$$\Phi(r) = \sum A_n \sin \lambda_n r \quad (4.29)$$

with A_n a characteristic/eigen function with λ_n eigenvalues (roots/solutions).

Applying the second boundary condition ($r = R$) to reduce the second term ($\sin \lambda_n r$):

$$\frac{d}{dr} \sin \lambda_n r \Big|_{r=R} + \left(\frac{1}{D R_{ext}} - \frac{1}{R} \right) \sin \lambda_n R = 0 \quad (4.30)$$

$$\lambda_n \cos \lambda_n R + \left(\frac{1}{D R_{ext}} - \frac{1}{R} \right) \sin \lambda_n R = 0 \quad (4.30a)$$

$$\lambda_n R \cos \lambda_n R + \left(\frac{R}{D R_{ext}} - 1 \right) \sin \lambda_n R = 0 \quad (4.30b)$$

$$\text{or,} \quad \lambda_n R \cos \lambda_n R = (1 - Bi_m) \sin \lambda_n R \quad (4.30c)$$

where Bi_m is the Biot number for mass transfer, which is defined as the ratio of the internal resistance

to the external resistance. For orthogonal functions, the following expansion provides a solution to the coefficient in equation (4.29) (see Arpaci, 1966):

$$A_n = \frac{\int_0^R r \sin \lambda_n r dr}{\int_0^R \sin^2 \lambda_n r dr} \quad (4.31)$$

The solution is obtained by integrating the numerator by parts while the denominator can be evaluated by using two trigonometric identities, which results in the following form:

$$A_n = \frac{2 \left(\sin \lambda_n R - \lambda_n R \cos \lambda_n R \right)}{\lambda_n \left(\lambda_n R - \sin \lambda_n R \cos \lambda_n R \right)} \quad (4.32)$$

The solution to the characteristic spatial function (4.29) may be combined with the solution to the temporal function (4.23), inserted into equation (4.19) and applied to equation (4.13) to solve for $\Theta(r,t)$.

$$\Theta(r,t) = \frac{\Psi(r,t)}{r} = \frac{\Phi(r) \Gamma(t)}{r} \quad (4.33)$$

yielding the closed form solution

$$\Theta(r,t) = 2 \sum_{n=1}^{\infty} \frac{\left(\sin \lambda_n R - \lambda_n R \cos \lambda_n R \right)}{\lambda_n \left(\lambda_n R - \sin \lambda_n R \cos \lambda_n R \right)} * \frac{\sin \lambda_n r}{r} e^{-D' \lambda_n^2 t} \quad (4.34)$$

This equation may be solved directly for the moisture ratio at any position within a spherical body at any time. However, given the difficulty of actually measuring the local moisture content inside a soybean seed or cereal grain, a solution for the average moisture content is more desirable. Such a solution is obtained by integrating over the domain and dividing by the total volume. Mathematically this is written as:

$$MR(t) = \bar{\Theta}(r,t) = \frac{\int_v \Theta(r,t) dv}{V} \quad (4.35)$$

with
$$V = \frac{4}{3} \pi R^3 \quad (4.36)$$

and
$$\int_v \Theta(r,t) dv = \int_0^R \Theta(r,t) 4 \pi r^2 dr = 4 \pi \int_0^R r^2 \Theta(r,t) dr \quad (4.37)$$

Combining this equation with (4.35) and integrating by parts as described previously yields,

$$MR(t) = \frac{K}{V} \int_0^R r \sin \lambda_n r dr = \frac{K}{V} \frac{1}{\lambda_n^2} (\sin \lambda_n R - \lambda_n R \cos \lambda_n R) \quad (4.38)$$

where

$$\frac{K}{V} = \frac{(3)(8)\pi}{4\pi R^3} \sum_{n=1}^{\infty} \frac{(\sin \lambda_n R - \lambda_n R \cos \lambda_n R)}{\lambda_n (\lambda_n R - \sin \lambda_n R \cos \lambda_n R)} e^{-D' \lambda_n^2 t} \quad (4.39)$$

Combining equations (4.38) and (4.39) yields the final solution for the average moisture content of a spherical body with a finite resistance to mass transfer at the surface:

$$MR(t) = 6 \sum_{n=1}^{\infty} \frac{(\sin \lambda_n R - \lambda_n R \cos \lambda_n R)^2}{(\lambda_n R)^3 (\lambda_n R - \sin \lambda_n R \cos \lambda_n R)} e^{-\frac{D'}{R^2} (\lambda_n R)^2 t} \quad (4.40)$$

where λ_n values are the eigenvalues (roots) of the surface boundary condition which can be expressed as:

$$\frac{\lambda_n R}{(1 - Bi_m)} = \tan \lambda_n R \quad (4.41)$$

where the Biot number may be expressed as:

$$Bi_m = \frac{\text{Internal Resistance}}{\text{External Resistance}} \equiv \frac{R/D}{R_{ext}} = \frac{R/D' \rho_m \beta}{R_s + R_b} \quad (4.42)$$

4.5. APPLICATION OF THE ANALYTICAL SOLUTION:

Resistance to mass transfer at the interface of the cotyledon, seed coat, and air stream can be incorporated into the R_{ext} term which is the sum of each component, as shown previously as $R_{ext} = R_s + R_b$. Each term of equation (4.42) will be presented to reveal the association of these variables with the theoretical model. The sequence follows the list of variables as shown above. The resistance to moisture transport for the hourglass cells, R_b , is estimated to determine its portion of the total resistance for the seed coat. The hourglass cell region was assumed to be comprised primarily of air with negligible solid volume. Geankoplis (1978) gives the diffusion coefficient of

water vapor in still air (D_a) at 20° C of 884 cm²/h. Casini (1990) and Carlson & Lersten (1987) reported the range in thickness of hourglass cells (l_h) between 0 and 100 μm. Taking an average thickness of 50 μm, the average resistance across the hourglass cells is:

$$R_h = \frac{l_h}{D_a} = \frac{50 \mu m \times 10^{-4} \text{ cm}/\mu m}{884 \text{ cm}^2/\text{h}} = 5.66 \times 10^{-6} \text{ h/cm} \quad (4.43)$$

Mbuvi and Litchfield (1988) measured various physical properties of six soybean varieties over two years, specifically seed volume and seed mass at a harvest moisture of 13% moisture. The averages were:

$$M_{\text{wet}} = 0.1656 \text{ g}; \quad V = 0.1345 \text{ cm}^3; \quad \rho = M_{\text{wet}} / V = 1.23 \text{ g/cm}^3.$$

Assuming no shrink, the average mass of dry matter for each seed was:

$$M_{\text{DM}} = M_{\text{wet}} (1 - M/100) = 0.144 \text{ g}_{\text{DM}} / \text{seed}$$

Stroshine and Hamann (1994) stated that the cotyledon and seed coat comprised 89.5 and 9.0% of the seed's dry weight, respectively. Assuming an average radius (R) for the cotyledon of 0.318 cm, the average volume of the intact seed, cotyledon, and seed coat is estimated to be 0.1345, 0.1224, and 0.0121 cm³, respectively. These values were used to calculate an estimate for the dry matter density of each seed component and are shown in Table 4.1.

Mensah et al. (1979) used thin slices of the cotyledon and seed coat with an approximate width to thickness ratio of 1:7. Consequently, they used an analytical model based on an assumed slab geometry configuration. The effective diffusion coefficient for the cotyledon and seed coat were determined by regression to be expressed in terms of the ambient temperature and relative humidity as:

$$\text{Cotyledon:} \quad D_c' = 10300 \exp \left(- \frac{7962}{T_K} + 46.2 \text{ rh} - 0.141 T_K \text{ rh} \right) \quad (4.44)$$

$$\text{Seed coat:} \quad D_s' = 4.46 \times 10^{12} \exp \left(- \frac{14673}{T_K} + 44.6 \text{ rh} - 0.139 T_K \text{ rh} \right) \quad (4.45)$$

These equations were used to estimate the effective diffusivity for each material at different relative humidity values at 20° C and are shown in Table 4.1.

Table 4.1. Physical and diffusive properties of soybean seed components at 20° C.

	Dry Matter per seed g	Volume cm ³	Dry Matter density g/cm ³	D' cm ² /h		Eqn no.
				RH 20	RH 90	
Cotyledon	0.129	0.1224	1.054	0.0001556	0.004763	(4.44)
Seed coat	0.013	0.0121	1.074	6.214E-06	9.346E-05	(4.45)
Equilibrium Moisture Content, % db						
	RH 10	RH 20	RH 90	RH 95		Eqn no.
Cotyledon	6.27	6.71	23.98	31.38		(4.46)
Seed coat	6.61	7.53	23.67	29.05		(4.47)
Beta values						
	RH 20	RH 90	Eqn no.	RH 20	RH 90	Eqn no.
Cotyledon	256000	8810000	(4.48)	41.98	44230	(4.49)
Seed coat	535000	6405000	(4.48)	3.57	299	(4.49)

Mensah et al. (1979) also developed empirical equations to describe the isotherms of each major structural component and found that they were dependent on temperature and relative humidity. Hence, they were selected for this study because the temperature range of their tests were within 5°C of the conditions used for these tests. Separate equations were given for each component as:

$$\text{Cotyledon: } EMC_c = 33.13 - 0.0927 T_K - 8.92 rh - 11.31 \ln(1 - rh) \quad (4.46)$$

$$\text{Seed coat: } EMC_s = 36.12 - 0.1035 T_K - 7.764 \ln(1 - rh) \quad (4.47)$$

Predicted values from these equations are shown in Table 4.2 for each component. β (beta) values are estimated by the local slope of the EMC versus ERH isotherm and are, thus, equation dependent.

The equations developed by Mensah et al. (1979) for each component of the soybean seed gave reasonable values and were chosen for this evaluation. Humidity ratio and specific volume values were computer generated (Gates, 1995), and are shown in Figure 4.1 and Table 4.2.

$$\beta_c^{RH_i} = \frac{EMC_C^{RH_i} - EMC_C^{RH_{i-1}}}{[H/v]_{RH_i} - [H/v]_{RH_{i-1}}} \equiv \frac{g_{H_{20}}/g_{DM}}{[g_{H_{20}}/g_{da}]/[g_{da}/cm^3]} = \frac{cm^3}{g_{DM}} \quad (4.48)$$

The D values for each material in both modes of moisture conditioning at 20° C were estimated (Table 4.1) by applying the definition stated previously, which is expressed in a general form as:

$$D_i^{RH} = [D' \rho \beta]_i^{RH} = cm^2/h \quad (4.49)$$

These values permit the resistance terms to be calculated for equation (4.42) after assuming an average seed coat thickness from the values reported by Degago and Longer (1987) of $\ell_s = 1.0$ mm.

$$\text{For 20\% RH} \quad R_s^{20} = \frac{\ell_s}{D_s^{20}} = \frac{0.1 \text{ cm}}{3.57 \text{ cm}^2/h} = 0.028 \text{ h/cm} \quad (4.50)$$

$$\text{For 90\% RH} \quad R_s^{90} = \frac{\ell_s}{D_s^{90}} = \frac{0.1 \text{ cm}}{299 \text{ cm}^2/h} = 3.34 \times 10^{-4} \text{ h/cm} \quad (4.50a)$$

The resistance of the boundary layer, R_b , may be estimated by considering the results of Brown and Otten (1992) with those of Miketinac et al. (1990) for soybeans at 40°C:

M	h_T	h_m	$R_b = 1/h_m$
%db	W/cm ² C	cm/s	h/cm
8.7	0.0132	10.85	2.56×10^{-5}
11.8	0.0125	10.28	2.70×10^{-5}
13.6	0.0124	10.20	2.72×10^{-5}

where $h_m = h_T/\rho_a c_p$ with $\rho_a = 1.21 \text{ kg/m}^3$ and $c_p = 1005 \text{ J/kgC}$.

Comparison of the resistance terms for the hourglass cells ($R_h \approx 10^{-6}$) with that of the boundary layer ($R_b \approx 10^{-5}$) and seed coat ($10^{-4} \leq R_s \leq 10^{-2}$) indicates that the seed coat resistance is the most significant term, that R_h contributes only a small portion of this resistance, and that R_b offers nearly an equal contribution during absorption but only a fraction of the total during desorption.

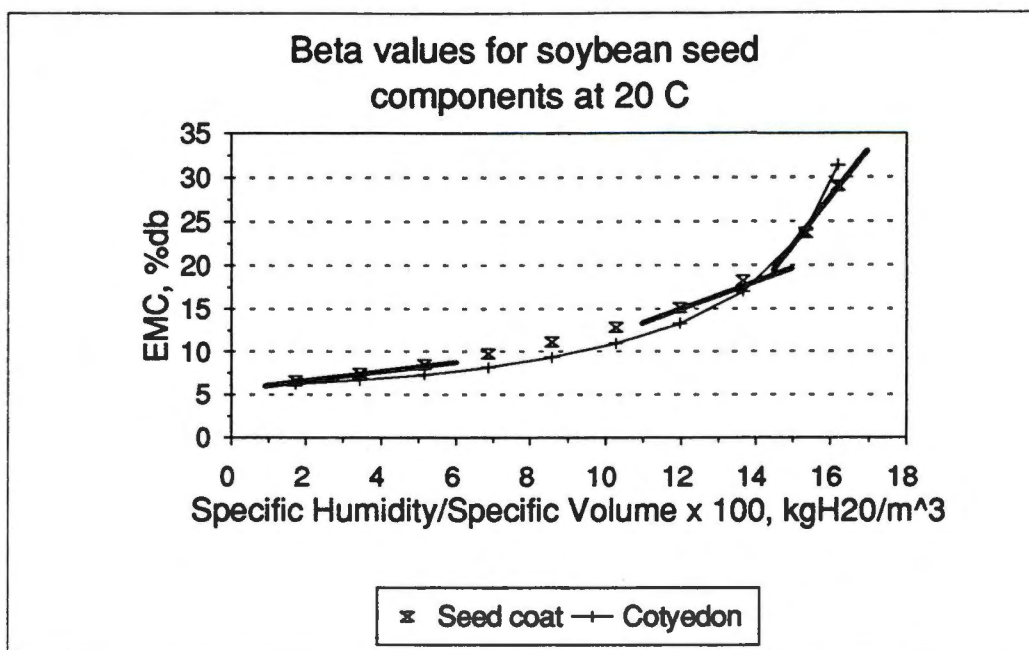


Figure B1. Beta values for soybean seed components at different moisture levels (represented by the slope of each bold line segment).

Table B1. Beta values for soybean seed components at different moisture content levels at 20 C.

* EMC, % db		ERH	H	v	H/v	Beta (slope)	
Seed coat	Cotyledon	%	gW/gda	cm ³ /g (x 10 ⁶)		Seed coat	Cotyledon
6.61	6.27	10	0.00144	831.8	1.726		
7.53	6.71	20	0.00287	833.8	3.447	531515	255813.9
8.56	7.33	30	0.00432	835.7	5.163	603995	360181.9
9.76	8.18	40	0.00576	837.6	6.876	698974	497263.1
11.18	9.35	50	0.00720	839.6	8.580	830388	686379.4
12.91	10.98	60	0.00865	841.6	10.278	1020451	961118.3
15.14	13.34	70	0.01010	843.5	11.979	1313383	1388721
18.29	17.04	80	0.01156	845.5	13.672	1858646	2180882
23.67	23.98	90	0.01301	847.5	15.351	3205908	4138741
29.05	31.38	95	0.01374	848.5	16.193	6389547	8778268
		100	0.01447	849.5	17.034		

* from Mensah et al. (1979) for soybean cotyledon and seed coat materials.

Theoretical Biot numbers for each mode of moisture conditioning were estimated by equation (4.42):

$$Bi_m = \frac{h_s R}{D_c} = \frac{R}{R_s D_c} = \frac{D_s R}{l_s D_c} \quad (4.51)$$

For the drying and wetting condition, respectively:

RH = 20%

$$Bi_m^{20} = \frac{3.57 \text{ cm}^2/\text{h} * 0.318 \text{ cm}}{0.1 \text{ cm} * 41.98 \text{ cm}^2/\text{h}} = 0.27 \quad (4.51a)$$

RH = 90%

$$Bi_m^{90} = \frac{0.318}{3.57E-04 * 44,230} = 0.020 \quad (4.51b)$$

The estimated value for absorption was lower than the value found from regression by Osborn et al. (1991). Differences between the diffusivity values for wetting and drying were primarily due to the (local) slope of the isotherm (β value) in each humidity region (Figure 4.1) which may actually be due to the different internal forces involved in the moisture holding capacity of the product for these vapor pressure gradients. Also consider that the diffusivity, which describes the rate of mass flux or the dynamic condition, was related to the EMC which essentially describes the static condition. For each materia the following relationship was observed:

$$D_c^{90} \approx 1050 D_c^{20} \quad \text{and} \quad D_s^{90} \approx 80 D_s^{20} .$$

4.6. MODEL FOR HOMOGENEOUS MATERIALS:

Thin hygroscopic agricultural products such as tobacco leaves, peanut pods, and soybean pods have much faster absorption and desorption characteristics than intact grain kernels or seeds. These materials are considered to have an insignificant moisture gradient across the body during mass transport processes and consequently are assumed to have a much lower resistance to moisture flux. A mass balance equation can be used to describe the rate of water gain or loss in a wetting or drying condition for such homogeneous materials as:

$$\beta \rho_s V dM = h A (M(t) - M_e) dt \quad (4.52)$$

Combining common terms and integrating yields a solution in a similar manner as shown previously by assuming a uniform moisture distribution throughout the material initially:

$$\int_{M_o}^{M_e} \frac{dM}{M(t) - M_e} = - \frac{h A}{V \rho_s \beta} \int_0^t dt \quad (4.53)$$

$$\ln(M(t) - M_e) \Big|_{M_o}^{M_e} = \frac{-h A}{\rho_s \beta V} t \Big|_0^t \quad (4.53a)$$

$$\text{or,} \quad \frac{M(t) - M_e}{M_o - M_e} = e^{-\left(\frac{h \delta}{\rho_s \beta} \right) t} \quad (4.53bc)$$

where $\delta = A/V$ and the physical properties that influence the 'drying constant' (k'') in the exponential model (2.20) can be clearly identified for homogeneous materials.

4.7. DEVELOPMENT OF A NEW COMPONENT MODEL:

One basic assumption in the development of equation (4.40) was that the moisture diffusivity was not dependent on temperature, moisture, or any other property of the product or environment. This was necessary to facilitate the solution to the second order partial differential equation. Actually, the mass diffusive properties for a given product are influenced by a shape factor and a combination of the moisture diffusivity of each unit or sub-component within the material, and possibly the interaction of two or more sub-components within the product. Yet the mass diffusivity has been more often expressed as an Arrhenius-type equation (2.36) in terms of the environmental conditions. In this evaluation, an ancillary data set that contains the chemical composition for the same soybean varieties and field treatments used in this study will be matched with the estimates that describe the diffusive properties for these materials to test possible correlations between predictive parameters.

Previous research has revealed that, for homogeneous materials, the average moisture ratio is given by the semi-theoretical equation (2.20) which is rewritten here for convenience:

$$MR_{HO}(t) = \exp(-kt). \quad (4.54)$$

This exponential model has been enhanced by Page (1949) to improve the fit of his experimental data for drying corn (a heterogeneous material) to yield the empirical form:

$$MR_{HE}(t) = \exp(-kt^n). \quad (4.55)$$

Overhults (1975) and Osborn (1986) modified the above equation merely to simplify the units of the time coefficient, k as:

$$MR_{HE}(t) = \exp(-(k' t)^n). \quad (4.56)$$

These mathematically straightforward models can be rearranged to gain further insight into the relationship between homogeneous and heterogeneous materials by considering the following relationship:

$$MR_{HE}(t) = \exp(-(kt)^n) = [\exp(-k t)]^{(kt)^{n-1}} = [MR_{HO}(t)]^{(kt)^m} \quad (4.57)$$

where $m = n - 1$. Note that for homogeneous materials $n = 1$ which renders $MR_{HE} = MR_{HO}$ or $m = 0$. Thus, the collective power term $(kt)^m$ may possibly be used to differentiate between these two classes of products which implies that the smaller the value of m , the more homogeneous the material behaves during moisture sorption. This equation can be compared to the analytical solution which has been shown to produce good agreement with absorption data for soybeans (Osborn et al., 1991) and desorption data for corn (Walton et al., 1988).

The following functional form of the analytical solution (equation 4.40) can be written by inspection:

$$MR_{HE}(t) = f_1(A_n, D', \lambda_n) \quad (4.58)$$

A similar functional relationship can be written to represent the modified Page equation (4.56) in terms of the variables that have been shown to influence the k and n parameters for soybean desorption (White et al., 1981):

$$k = f_2(T, M_o, RH) \quad \text{and} \quad n = f_3(T, RH) \quad (4.59)$$

In contrast, Hutchinson and Otten (1982) reported that the k value was temperature dependent while the n value was reported to be a function of temperature and relative humidity (equations 2.38 and 2.39, respectively). Osborn et al. (1988) found n to be constant (0.8267) for soybean absorption, and

that k was also a function of temperature and relative humidity (equation 2.47). ASAE Standard S344 (ASAE, 1996) provides an estimate for the k value of soybeans based on the air temperature and air flow rate while the n value is a function of relative humidity and initial moisture.

It seems reasonable to project that properties that affect the EMC also affect the rate of diffusion (absorption or desorption) of a material, which would in turn also affect the equation parameters mentioned in the previous models (i.e., D' , k , and n). Although most of the previously mentioned studies dealt with mixtures of distinctly different food products (in terms of their water activity) these observations may extend to oilseeds in general and soybeans in particular because they are comprised of different amounts of protein, carbohydrates, oil, and minerals/ash, even though they are distributed somewhat uniformly within the cotyledons which are the major physical components of the seed.

Recall that the relationship developed in Chapter III led to equation (3.1) in an attempt to describe the EMC as a function of the activity coefficients in oilseed, grain, or other food products. These coefficients may be determined by regression if vast amounts of EMC-ERH data are available but this necessitates that experiments be conducted over a wide range of environmental conditions with materials of vastly different properties. In addition, the dry matter content and EMC of each component must be known. Activity coefficients may actually be functions of temperature, relative position or distance between each component within the material and age or level of damage of the material, which may be expressed as:

$$\xi_i = f_4(T, x_i, \delta_{ij}) \quad (4.60)$$

where T = local temperature,
 x_i = local position or distance between components, and
 δ_{ij} = material dependent parameter.

Since the EMC and the conditioning parameters D' , k , and n are all interrelated, a similar functional relationship could be written to relate these parameters:

$$\{D', k, n\} = f_5(T, M_o, RH, x, \delta, t) \quad (4.61)$$

This relationship suggests that the conditioning parameters could be described in terms of the

properties of the material, its composition, the temperature of the body and the time of exposure. Note the time term accounts for the fact that these parameters represent a dynamic system whereas the EMC parameter (ξ) represents a static condition.

One may consider the functional relationships that bind the analytical solution with the empirical model by inspecting the two proposed solutions for moisture conditioning and considering the potential influence of the chemical components and their position within the material on the EMC and perhaps D' , k , and n . Expressing equation (4.58) and its related terms in a concise functional form that includes only the dependent variables for each parameter we have:

$$\text{from (4.40):} \quad MR(t) \approx f_6 (\lambda_n, R, D') \quad (4.62)$$

$$\text{from (4.41):} \quad \lambda_n \approx f_7 (R, Bi_m) \quad (4.63)$$

$$\text{from (4.44) and (4.45):} \quad D_j' \approx f_8 (T, RH, M_o) \quad (4.64)$$

$$\text{from (4.51):} \quad Bi_m \approx f_9 (l_s, R, D_j) \quad (4.65)$$

$$\text{from (4.49):} \quad D_j \approx f_{10} (T, \rho, \beta, \delta_{ij}, x_{ij}, DM_{ij}) \quad (4.66)$$

$$\text{by definition:} \quad \rho_i \approx f_{11}(DM, V)_i \quad (4.67)$$

$$\text{from (4.48):} \quad \beta_i \approx f_{12} (T, DM_i, H, v) \quad (4.68)$$

$$\text{from the psychometric chart:} \quad (H, v) \approx f_{13} (T, RH) \quad (4.69)$$

$$\text{and finally:} \quad \delta_{ij} \approx f_{14} (T, \partial M / \partial t |_r) \quad (4.70)$$

where the only previously undefined terms are listed here:

i = an index for the chemical composition of the material

j = an index for the physical component of the material

D_j = mass diffusivity of the j th structural component, cm^2/h

x_{ij} = location of i th chemical component within the j th structural component

δ_{ij} = interaction term or function of i th chemical component within the j th structural component

The last expression stems from the logical assumption that the interaction of moisture attraction between adjacent chemical components may actually depend upon the local gradient within the particular sub-component. For example, a water molecule has stronger attraction to carbohydrate components than for protein or minerals and may be repulsed by the presence of oil or fat.

The average moisture ratio at any point in time within the body may be expressed by compiling these functional forms in terms of only the basic units. The functional form of the coefficient in the series expansion (4.40) is $A_n \approx g_1(\lambda_n, R)$ which may be rewritten by inspection as:

$$A_n \approx g_1(R, T, RH, M_o, V_i, x_{ij}, \delta_{ij}, DM_{ij}) \quad (4.71)$$

The functional form of the exponential term is based on the two terms λ_n and D' which may be combined in terms of the basic units as:

$$g_2(R, T, RH, M_o, V_i, x_{ij}, \delta_{ij}, DM_{ij}) \quad (4.72)$$

Merging equations (4.71) and (4.72) with (4.40) provides a new perspective on the coefficient and exponential parameters in the analytical solution in terms of the respective functional forms which is written by inspection as:

$$MR(t) \rightarrow \{g_1[R, T, RH, M_o, (V, \delta_i, x_i, DM_i)_j]\} \exp \{g_2[R, T, RH, M_o, (V, \delta_i, x_i, DM_i)_j]\} \quad (4.73)$$

For a given set of environmental conditions ($T = \text{constant}$, $RH = \text{constant}$) with heterogeneous material of uniform size and chemical composition ($R = \text{constant}$, $V = \text{constant}$, $DM_i = \text{constant}$), the only variables that could feasibly change with time during moisture conditioning are the interaction terms or functions (δ_{ij}) and possibly the effect of position of each chemical constituent, x_i . However, the likelihood that x_i will change with time when undergoing vapor exchange between the seed and its environment is slim unless the chemical constituents are partially mobile with liquid water molecules. This remains an interesting research question that bears further investigation as mentioned earlier in Chapter III. For the purposes of further discussion, this effect will be assumed to be negligible and our attention will focus on the interaction term, which possibly provides a link with the analytical solution and Page's modified equation, especially with respect to the exponent term. This discussion is presented in an attempt to further identify the functional form of the power term in equation (4.57) in general and the empirical parameter (n) in particular.

By inspecting equations (4.57) and (4.73) the pertinent empirical variables may be related to the two terms in the exponent, namely k^n and t^n . The first term may be considered to be affected by the chemical/physical components of the material which relate to the diffusion term (D') in the

analytical solution. In contrast, the interaction term (δ_{ij}) can be expected to be a function of time by recalling that this variable primarily describes the affinity of water molecules between the different chemical constituents during a conditioning phase. Moreover, by equating the functional form presented in equation (4.73) with the exponential term in (4.57) we have:

$$[\exp(-k t)]^{(kt)^m} \rightarrow \exp(-(kt)^n) \rightarrow \exp \{g_2[R, T, RH, M_o, (V, \delta_j, x_j, DM_i)_i]\} \quad (4.74)$$

which can be partitioned to segregate the terms that are time dependent as:

$$k^n t^n \rightarrow \{g_3[R, T, RH, M_o, (V, x_i, DM_i)_j], g_4(\delta_{ij})\} \quad (4.75)$$

This leads to the following relationship by association:

$$k^m t^m \rightarrow \{g_5[R, T, RH, M_o, (V, x_i, DM_i)_j], g_6(\delta_{ij})\} \quad (4.76)$$

and to the conclusion that k^m can be related to g_5 , since they are both independent of time and t^m can be similarly be related to g_6 . Recalling that for the isothermal case from equation (4.70) the interaction term can be expressed as a function of only the local change in moisture with time within the material:

$$t^m \rightarrow g_6(\delta_{ij}) \rightarrow f_{14}(T, \partial M / \partial t |_r) \quad (4.77)$$

and follows that

$$k^m \rightarrow g_5[R, T, RH, M_o, (V, x_i, DM_i)_j] \quad (4.78)$$

The Page (1949) equation (2.22) as modified (2.23) for soybean absorption and desorption by Osborn (1986) and Overhults (1975), respectively, will be used in this study to investigate this new relationship. Based on the previous discussion, the k value in Page's modified equation for any product contains a combination of the moisture diffusivity and a shape factor, which has most often been expressed in terms of the environmental conditions by most researchers. Similarly, the n value in Page's modified equation has gained acceptance because of its curve fitting ability but is generally regarded as a purely product dependent empirical parameter in most cases. However, both parameters may also be linked to the chemical properties of a product as well as the descriptive parameters k^n and k^m which combine the two regression parameters into one term. The potential influence of selected physical and chemical properties between soybean varieties and field treatments on the k , n , k^n , and k^m values will be evaluated in this study.

Further identification of the interaction term will require additional research. Particularly useful information would be the location of each chemical constituent within each structural sub-component of the material. Such an extensive study would probably require several preliminary tests before attempting a broad based experimental design.

CHAPTER V

EXPERIMENTAL PROCEDURES

Two basic studies were conducted in this experiment. Soybean seeds were subjected to a humid environment (RH = 90%) for 3 to 8 days to observe the rate and extent of moisture regain by the samples when held at a constant temperature and humidity. Immediately after the humid condition, the atmosphere was quickly switched to a low humidity (RH = 20%) for 3 to 4 days to observe the rate and extent of moisture loss. Tests were conducted with three different varieties that were harvested each week over a 16 week harvest period and repeated in a second year of study. Weather data from both years were recorded and collected by Logan (1991) from the UT Plant and Soil Science weather station that was located within 100 m of the field plots for this experiment.

5.1. EXPERIMENTAL DESIGN:

The statistical design for the field experiment was a complete randomized split-plot layout with the following dependent variables: year, soybean variety, week of harvest, field replication, and conditioning mode, as shown in Table 5.1. The total number of experimental units that were analyzed was actually less than the maximum produced by the design (576) because several samples from the 1989 crop were damaged in storage while awaiting testing.

Table 5.1. Statistical design for field weathered soybean seed conditioning tests.

Variable	Items considered	Levels
Year	1989, 1990	2
Variety	Tn4-86, Essex, Leflore	3
Week of harvest	1 thru 16	16
Replication	1, 2, 3	3
Conditioning mode	Wetting, drying	2
Total (maximum experimental units)		576

5.2. MATERIAL PROCUREMENT, HANDLING, AND PROCESSING PROCEDURES:

Soybeans were grown on the University of Tennessee's Experiment Station Farm in Knoxville, Tennessee, adjacent to the Tennessee River in 1989 and 1990. The varieties selected for this study were TN4-86, Essex, and Leflore, which represent early, medium, and late maturity groups IV, V, and VI, respectively. The field was subdivided into three blocks, with three varieties grown in each block. Each block contained one replication of sixteen sub-plots for each variety, one for each week of harvest. Sub-blocks consisted of three 6.1 m rows (side by side) throughout the field, with a row spacing of 11.8 cm.

The planting dates for 1989 and 1990 were June 4 and June 1, respectively, and were not unduly delayed by weather either year. These dates are typically used in conventional tillage operations by soybean farmers in the central and eastern portions of the Tennessee growing area. The crop was fertilized, routinely scouted for weed, disease, and fungal infestations, and otherwise grown according to sound agronomic practices which are currently used in private and commercial production.

Harvest began for the each maturity group when the respective plot had reached physiological maturity, as judged by visual inspection that was designated by Fehr and Caviness (1980) and TeKrony et al. (1981) (i.e., at least half the leaves on the stalk were yellow and one pod on the main stalk was mature). It was noted, however that there was considerable color variation within the field for the same variety and that some sub-plots seemed to mature earlier than expected while others matured later than expected. In other words, the date of maturity varied somewhat throughout the field for all varieties. Nevertheless, harvest progressed in the sequence that was specified by the experimental design even though a few green seeds were harvested during the first week by adhering to this timetable. The actual day of harvest within each week varied slightly as weather, labor and holiday schedules permitted, and are shown in Tables A1 and A2.

Soybean pods were hand-harvested by removing the stalks from the field, transporting them to a laboratory and manually stripping the pods from the stalks to prevent any mechanical damage

to the seed or seed coat. Harvested stalks were tied in bundles and tagged to preserve their identity and to reduce shatter losses during gathering, handling, and transport. During wet weather, wet pods were air dried after stripping at low temperature ($T < 25^{\circ}\text{C}$) to a moisture content below 14% to prevent mold growth and preserve seed quality. The beans were sealed in plastic bags and held for testing at -20°C .

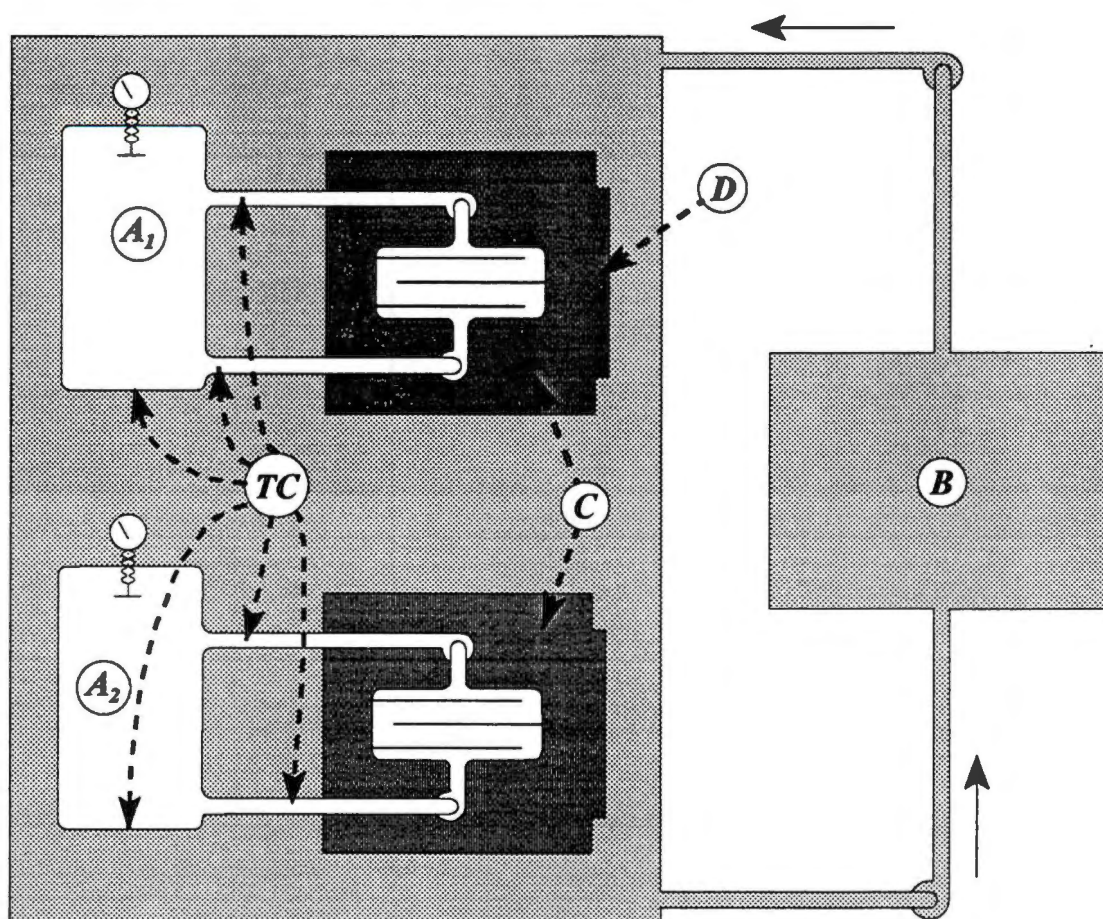
Three 100 g samples from each field plot were hand shelled for a moisture sample at the time of harvesting, which were dried in a forced-convection oven at 103°C for 72 hours (Association of Official Seed Analysis, 1981). This also permitted close inspection of the seeds and a preliminary evaluation of their physical integrity as harvest progressed throughout the 16 week test period.

Frozen samples were removed from cold storage in preparation for testing and held in their original plastic bag at room temperature overnight to permit temperature equilibration (approximately 16 hours). Approximately 6.0 g from each field replication were placed in separate mesh pouches. Samples were pre-conditioned by holding them in a sealed, insulated container with a saturated lithium chloride solution ($T = 20^{\circ}\text{C}$; $\text{RH} = 12\%$) for at least two weeks to establish a narrow range of initial moisture conditions prior to each test.

Pre-conditioning chambers consisted of 48L insulated containers which held a saturated solution of LiCl to control the relative humidity to near 12% (at room temperature). Wire screen trays were mounted above the saturated solution on which the mesh pouches with sample material were placed. A small fan (2.5 cm diameter) was used to circulate the air in the chambers. Individual chambers held 3 trays with 9 sample pouches on each tray for a total of 27 pouches. All chambers were held inside an insulated, walk-in type cold storage room held at 20°C .

5.3. THE ABSORPTION-DESORPTION SYSTEM:

The system for the sorption-desorption exposure tests consisted of two closed-loop sub-systems, one for temperature control and one for humidity control, as illustrated in Figure 5.1. The temperature control sub-system (chamber B in Figure 5.1) consisted of a refrigeration unit with a



Legend:

- $A_{1,2}$ Conditioning chamber for soybean samples.
- B Refrigeration unit for temperature control.
- C Humidity control chambers with trays.
- D Access doors for changing trays.
-  Load cell for weighing samples.
-  Fan.
- TC Location of thermocouples for monitoring dry and wet bulb temperatures.

Figure 5.1. Schematic diagram of the environmental control system used for moisture conditioning tests with field weathered soybeans.

recirculating duct network that encompassed the sample chamber (chambers A₁ and A₂ in Figure 5.1) and a humidity control chamber (chamber C in Figure 5.1). Access doors (item D in Figure 5.1) were mounted on both humidity control chambers to expedite loading and unloading of the trays.

Air from the temperature control chamber was continuously circulated around the outside walls of the sample chamber(s) and humidity control chamber to assure a constant temperature throughout all chambers in the system. The exterior of both chambers was insulated (R=11) and thick walled PVC tubing (3.65 cm, id) was used to transfer air between chambers. The system was able to continuously hold the desired temperature near the set point of 20° C for the duration of the absorption-desorption tests.

The humidity control chambers held six trays each (26 x 39 x 2 cm deep) that provided a total surface area of 0.6 m² and contained distilled water during the absorption phase or desiccant crystals during the desorption phase. The distilled water was quickly changed to the desiccant crystals at the end of the absorption phase to provide an immediate low humidity condition for the desorption phase. Although actual humidity values varied slightly between tests, the target levels were held to within $\pm 5\%$. Fluctuations were influenced by variations in temperature, air leaks in the system, calibration errors of the humidity probes or other erroneous measurements due to human oversight.

A small centrifugal fan (10 cm diameter) was used to continuously recirculate air from the humidity chamber into the sample chamber, through the samples and back across the trays. In the wetting mode, the soybean material, thus, acted as a desiccator to the supply air.

The dimensions of each sample chamber (chambers A₁ and A₂ in Figure 5.1) were 30 x 27 x 64 cm (depth x width x height). A 30 x 100 cm plexiglass sheet with a 10 cm diameter hole cut in the center was attached to the outside of each chamber to facilitate loading/unloading and access by the operator when weighing samples. The access port was sealed between weight data collection with a large rubber stopper.

Two Copper-Constantan thermocouples were used to continuously measure the dry bulb and wet bulb temperatures inside the conditioning chamber(s) during each test. A Vascila relative humidity (RH) probe was also mounted inside each chamber(s) during these tests and used to record this value directly. The manufacturers reported precision was $\pm 2\%$ from 0 to 80% RH and $\pm 3\%$ from 80 to 95% RH.

A 10 g electronic load cell was mounted above and outside each sample chamber with a thin wire hook extending through the wall to allow samples to be weighed during the test without removing them from the conditioning air. The sensitivity of each load cell was 1 mg.

5.4. THE ABSORPTION - DESORPTION TESTS:

The test chambers were brought to a steady state before each test ($T = 20^\circ \text{C}$; $\text{RH} = 90\%$). The pre-conditioned pouch samples were weighed on an electronic balance before being placed in the chamber, then on the load cell after being placed in the chamber. Initial sample weight was approximately 6.0 g for the shelled soybeans. Pouches were suspended in the airstream between weighings. Changes in the weight of each sample were recorded electronically.

Following several hours (90 to 140 h) of humid conditioning to near the equilibrium point, the relative humidity was quickly altered to near 20% at the same temperature to subject the samples to a drying environment. Weight loss was recorded periodically until all samples were near the moisture equilibrium. Following this wetting-drying cycle, all samples of each material (approximately 6 g) were dried completely to determine the final moisture and dry matter content using the same oven method as described previously ($T = 103^\circ \text{C}$ for 72 h).

5.5. DATA COLLECTION:

Collected data included weight changes with time throughout the sorption and desorption cycle as well as dry and wet bulb temperature and relative humidity using the two separate systems. One system recorded wet and dry bulb temperatures directly by averaging data over 1 minute

intervals that were scanned once every second. The second system used an A/D voltage converter for the load cell and humidity probe. The resultant data were stored on a computer disk for subsequent analysis.

The load cell was calibrated by measuring a known calibration weight before and after each set of samples were weighed. Initial sample weights (to the nearest 1.0 mg) from an analytical balance were checked against an electronic load cell value. Weight changes over the period of each test were recorded periodically by hanging each pouch of material on the load cell and storing the weight directly coincident with the time of each weighing on the computer. Between weighings, sample pouches were suspended in the air stream without touching each other by hooks that were attached to wires strung across the width of the chamber.

The first step in data evaluation was to import all raw data (sample identification and weight, time, temperature, and relative humidity) into a spreadsheet, manually enter the dry matter data for the particular sample to calculate the change in moisture over time and generate a graph for a visual depiction of the change in moisture with time. This approach greatly enhanced the comparison of different materials within and across tests and allowed erroneous data to be quickly identified and corrected. Some tests were repeated in both years as a result of this initial review of data. Similar graphs were generated from temperature and relative humidity data to aid in the evaluation of system performance and to observe how well the target levels were reached for different tests.

5.6. CONDITIONING TESTS WITH WAX COVERED HILUM:

An additional experiment was designed to test the hypothesis of a preferential pathway for moisture vapor transport through the hilum (Figure 3.1). Two varieties of treated seeds (Tn4-86 and Tn6-90) were obtained from the UT Plant and Soil Science seed lab that were grown in 1995. Initial moisture as received was 8 to 9%. Six hundred soybeans from each variety were inspected for seed coat cracks and other surface or sub-surface defects and sub-divided into two lots, each with 3 replications. The statistical design for this conditioning test is shown in Table 5.2.

Table 5.2. Statistical design for wax covered soybean seed conditioning tests.

Variable	Items considered	Levels
Variety	Tn4-86, Tn6-90	2
Treatment	Wax covered hilum vs uncovered control	2
Replication	1, 2, 3	3
Conditioning mode	Wetting, drying	2
Total		24

Paraffin wax was melted in a shallow metal container on a hot plate using the minimum heat setting to obtain a depth of liquid that was approximately 1 mm. Soybeans were held by forceps while the hilum area of each bean was quickly dipped into the liquid paraffin and cooled by blowing air over the treated area. Approximately 10% of the bean surface area around the hilum area was covered with wax. The time required to inspect, treat, and cool 100 soybeans was approximately one hour. Untreated soybeans were held in sealed plastic bags while their counterparts were being treated. Additional seed samples were collected at the time of processing to ascertain the variation in the initial moisture of treated and untreated seeds between lots since it was considered that the wax covered samples could not be used to directly determine an accurate dry weight by the oven method. Wax treated samples were considered to be locally impermeable to moisture transport in the hilum region which would interfere with moisture gain and loss during exposure to sorption and desorption conditions. All samples were placed in mesh pouches to provide full exposure of the soybeans with the conditioning air. The samples were then subjected to an absorption and desorption atmosphere, as described below to determine the relative moisture movement through the hilum area.

A commercial environmental control unit ($\pm 0.1\%$ and $\pm 2\%$ RH) was used in these conditioning tests which was large enough to hold all samples. Air flow within the chamber was sufficiently turbulent to assure uniform exposure among the evenly spaced samples. The relative humidity set points for the wetting and drying tests were 90 and 65%, respectively, with a constant

temperature of 20° C. Temperature and relative humidity values were visually monitored when samples were weighed periodically during the wetting and drying cycles. Additionally, dry and wet bulb temperatures were monitored inside the control chamber using a copper-constantan thermocouple for each probe.

Weights were recorded initially and intermittently to the nearest 1.0 mg on an analytical balance during both conditioning tests. The same samples were used for each mode of conditioning which was conducted over a 100 and 216 hour period for the absorption and desorption tests, respectively. Final moisture and dry matter determinations were made for the untreated samples by the oven method described previously.

CHAPTER VI

RESULTS AND DISCUSSION

The results of this study are presented in the following order: harvest data for the field weathering study; comparative sorption through the hilum area; absorption and desorption tests with soybeans from the field weathering study; a comparison of the empirical model and the diffusion model with selected samples from the absorption and desorption tests; and the results of a statistical analysis that attempted to identify significant correlations with the sorption parameters from the modified Page equation with a companion set of chemical data that was collected by another researcher (Sidhu, 1992) with the same soybeans that were used in the field weathering study.

6.1. HARVEST DATA FOR THE FIELD WEATHERING STUDY:

Harvest dates during each week of study for Tn4-86, Essex, and Leflore soybean field plots are shown in Tables A1 and A2 for 1989 and 1990, respectively. Average field ambient temperature, relative humidity, and cumulative rainfall during the week that preceded harvest are shown throughout the harvest season for each year of study in Figures A1 and A2. A 20 week period is shown to match all harvest events. A similar pattern of mean air temperature and cumulative rainfall was observed in both years. The mean weekly temperature gradually fell from 18° C during the first week to below 0° C by the twelfth week. Mean weekly temperatures during the last eight weeks of the 1989 study were approximately 5° C higher than the same period in 1990. Rainfall was low during the first three weeks of harvest then increased in a near step wise fashion through the end of the study each year. Total rainfall during the harvest period was 56 and 50 cm in 1989 and 1990, respectively. Most rainfall in 1990 occurred in the last seven weeks, which could have affected the physical properties of the latest maturing variety (Leflore) more than the earlier maturing varieties.

Mean weekly relative humidity levels were highly variable during both years. However, the week-to-week variation in relative humidity in 1989 was much more erratic. A drying trend was

observed during the first 10 to 12 weeks of harvest. This was followed by rising humidity levels by week 15 or 16. After week 15 the mean weekly humidity varied by an average of 10% each week through the end of harvest in 1989. In 1990, humidity levels fell from 78% to 64% during the last four harvest weeks even though 7 cm of rain fell during this period.

Perhaps a more significant observation was moisture content of the seed at harvest, which is shown in Figures A3 and A4 for 1989 and 1990, respectively. The time scale (x-axis) matches the harvest date for each variety in these graphs. Similar graphs for harvest moisture levels are also shown in Figures A5 and A6 with the same data but the time scale is shifted to overlay the harvest week of each variety. All of the graphs that follow are shown with week of harvest overlaid in this manner, but the reader may refer to Figures A3 and A4 to compare the different lengths of time of field exposure between varieties.

High moisture content levels were expected when harvest began because the crop was near the physiological maturity stage. Moisture levels at the beginning of harvest were higher for Tn4-86 and Essex in 1989 than in 1990, but the opposite was observed for Leflore soybeans. As the crop progressed from physiological maturity to harvest maturity, seed moisture fell to near 20% or lower by the third week (field maturity). Seed moisture patterns were very erratic throughout the season in 1989 and seemed to reflect the highly variable relative humidity. Harvest moisture generally coincided with rainfall events or periods of high humidity in both years. On average, seed moisture levels were higher in 1989 except during a few weeks in the later part of harvest (week 9, 14, 15, 17, and 18). Additionally, the most stable seed moisture levels were observed during the most stable weather period during harvest week 7 through 12 in 1990. As expected, seed conditions deteriorated markedly as harvest progressed in both years, which required larger quantities to select an adequate sample for the conditioning tests and companion chemical analysis. Other implications of these weather patterns on the material used in this study will be discussed in each of the following sections in more detail.

6.2. COMPARATIVE SORPTION THROUGH THE HILUM AREA:

Wax was applied to the hilum area (approximately 10% of the bean surface, as shown in Figure 3.1) of two varieties of soybeans (Tn4-86 and Tn6-90) to determine if this treatment altered sorption rates. Treated and untreated beans were exposed to wetting and drying conditions as described in Chapter V. Mean values for the temperature and relative humidity were 19.3° C and 91% for the absorption test (Figure B1), and 19.5°C and 65% for the desorption test (Figure B2). Deviations from these mean values occurred when the chamber was opened to weigh samples but conditions stabilized shortly thereafter.

Data were analyzed by a non-linear regression with the Marquardt method to generate the predicted parameters equilibrium moisture content (EMCR), k , and n values from the modified Page equation (4.57). A summary of these values for each replication of the absorption and desorption condition are shown in Tables 6.1 and 6.2, respectively. The EMCR value for each replication was used to calculate the observed moisture ratio. Changes in the observed and predicted moisture ratio with time are shown for the absorption and desorption conditions in Figures B3 and B4, respectively.

An analysis of variance was conducted to test the influence of variety, wax treatment (partially covered or uncoated control), replication, the interaction of variety and treatment, and initial moisture content. Statistical differences were determined by the Tukey studentized range test with a 0.05 level of significance. Results of the analysis of variance for absorption are shown in Table 6.3. The mean value for the initial moisture content was 8.2% which was significantly influenced by variety, wax treatment, and the interaction of variety and wax treatment. The mean value for the regression equilibrium moisture content (EMCR) was 25.8% which was very near the level predicted by the modified Henderson equation (2.25) of 25.3%. EMCR was significantly affected by variety and wax treatment. The EMCR of the unwaxed control was 1.1 percentage points higher than the waxed and Tn6-90 was 1.2% percentage points higher than TN4-86. The overall mean k value was 0.0440 which was lower than the value (0.1078) found by the prediction equation (2.47) given by Osborn et al. (1991) for soybean absorption in a lower humidity range. The k value

Table 6.1. Experimental values and predicted variables under absorption conditions for Tn4-86 and Tn6-90 soybeans with a wax coated hilum and uncoated control.

Variety	Treatment	Rep	Mo	EMCR	k	n	k^n	k^m	pseudo
									r ^2
Tn4-86	Waxed	1	7.90	24.7	0.0406	0.902	0.0556	0.731	0.9997
		2	8.70	25.5	0.0486	0.863	0.0734	0.661	0.9999
		3	8.13	24.8	0.0416	0.882	0.0605	0.688	0.9999
	Control	1	8.75	25.7	0.0460	0.900	0.0625	0.736	0.9997
		2	8.75	25.2	0.0532	0.904	0.0705	0.755	0.9999
		3	8.77	25.5	0.0620	0.878	0.0870	0.713	0.9999
	Waxed	1	7.71	25.7	0.0392	0.906	0.0532	0.738	0.9997
		2	7.77	25.0	0.0496	0.905	0.0660	0.752	0.9995
		3	7.60	26.2	0.0405	0.846	0.0663	0.611	0.9999
Tn6-90	Control	1	8.28	28.0	0.0342	0.830	0.0607	0.564	0.9993
		2	8.07	26.9	0.0362	0.828	0.0641	0.564	0.9998
		3	8.00	27.0	0.0366	0.842	0.0618	0.592	0.9999
	Summary	Max	8.77	28.0	0.0620	0.906	0.0870	0.755	0.9999
		Min	7.60	24.7	0.0342	0.828	0.0532	0.564	0.9993
		Avg	8.20	25.8	0.0440	0.874	0.0651	0.676	0.9997
	Statistics	Std	0.42	0.95	0.0078	0.030	0.0085	0.071	

Table 6.2. Experimental values and predicted variables under desorption conditions for Tn4-86 and Tn6-90 soybeans with a wax coated hilum and uncoated control.

Variety	Treatment	Rep	Mo	EMCR	k	n	k^n	k^m	pseudo
									r ^2
Tn4-86	Waxed	1	24.0	8.88	0.0632	0.622	0.180	0.352	0.9995
		2	24.8	8.77	0.0616	0.628	0.174	0.355	0.9995
		3	24.1	8.99	0.0624	0.627	0.176	0.355	0.9996
	Control	1	25.0	9.13	0.0786	0.590	0.223	0.352	0.9996
		2	24.5	9.02	0.0749	0.594	0.214	0.349	0.9997
		3	24.6	9.03	0.0793	0.604	0.216	0.367	0.9997
	Waxed	1	24.7	8.91	0.0557	0.592	0.181	0.308	0.9997
		2	24.8	8.90	0.0546	0.601	0.174	0.313	0.9998
		3	25.0	8.90	0.0557	0.622	0.166	0.336	0.9998
Tn6-90	Control	1	26.1	9.15	0.0683	0.560	0.223	0.307	0.9995
		2	25.5	9.03	0.0674	0.574	0.213	0.317	0.9997
		3	25.5	8.98	0.0646	0.572	0.209	0.309	0.9998
	Summary	Max	26.1	9.15	0.0793	0.628	0.223	0.367	0.9998
		Min	24.0	8.77	0.0546	0.560	0.166	0.307	0.9995
		Avg	24.9	8.97	0.0655	0.599	0.196	0.335	0.9997
	Statistics	Std	0.57	0.10	0.0082	0.022	0.021	0.022	

was significantly affected by variety and the interaction of variety and wax treatment. Mean k values were 0.0487 and 0.0393 for Tn4-86 and Tn6-90, respectively. The overall mean n value was 0.8740 which was slightly higher than the value (0.8267) found by Osborn et al. (1991) and was significantly influenced only by the interaction of variety and wax treatment.

Table 6.3. Summary of analysis of variance for the initial moisture content and predicted variables from wax treated absorption tests with Tn4-86 and Tn6-90 soybeans.

Variable	Mean	Significant Terms			R² value
M₀	8.2	Wax	Variety	Variety*Wax	.961
EMCR	25.8	Variety	Wax		.847
k	0.0440	Variety	Variety*Wax		.821
n	0.8740	Variety*Wax			.756

The rate of moisture transport during absorption was affected by the interaction of variety and wax treatment (Figure B3). Untreated Tn4-86 soybeans had the most rapid transport, but the untreated Tn6-90 had the slowest. Wax treated Tn4-86 seeds gained moisture slower than their untreated counterparts, but this observation was reversed for Tn6-90. Thus, the parameters of the absorption equation (4.57) indicated that the variation in moisture uptake across varieties was greater than the variation across wax treatments. Differences could be due, in part, to the physical integrity of the microstructure of the seed coat that enabled moisture vapor to bypass the hilum area.

A summary of the analysis of variance for the desorption test is shown in Table 6.4. The mean value for the initial moisture content was 24.9% which was significantly influenced by the variety and wax treatment. The mean regression equilibrium moisture content (EMCR) was 9.0% which was lower than the value predicted by the modified Henderson equation of 12.8%. The only significant variable that influenced the EMCR was wax treatment. However uncovered control samples were only 0.18% percentage points of moisture higher than the partially covered soybeans. The mean k value was 0.0655 which was higher than the value found for absorption, which indicates a faster rate of moisture transfer, but was lower than the value given by Overhults et al. (1973) for

desorption at this temperature level (0.0820 from equation 2.34). The k value was significantly effected by variety and wax treatment. The mean n value was 0.5987 which was lower than the value found for absorption, but higher than the value (0.4441) predicted by the relationship (equation 2.34) given by Overhults et al. (1973). Significant variables that influenced the n value were variety, wax treatment, and replication. Lower n values correspond to more rapid transport during the initial portion of the drying or wetting curve (for $t < 1/k$) but a decline in the moisture transfer rate after that time.

Table 6.4. Summary of the analysis of variance for the initial moisture content and predicted variables from wax treated desorption tests with Tn4-86 and Tn6-90 soybeans.

Variable	Mean	Significant Terms			R ² value
M_0	24.9	Variety	Wax		.807
EMCR	9.0	Wax			.757
k	0.0655	Wax	Variety		.983
n	0.5987	Wax	Variety	Rep	.957

Differences in the rate of desorption are illustrated in Figure B4. As in the absorption test, untreated Tn4-86 soybeans exhibited the fastest transfer rate. Unlike the absorption test, untreated seeds were only slightly more responsive than seeds with a partially sealed seed coat for both varieties. Thus, the rate of moisture movement for these desorption conditions was affected by covering the hilum area with wax but the effect was no greater than the relative area covered. It was concluded that the hilum area did not provide a preferential path for moisture vapor transport. This result compares with the findings with wax coated lintels (Tang and Sokhansanj, 1993).

6.3. SORPTION TESTS WITH FIELD WEATHERED SOYBEANS:

Changes in moisture content with exposure showed that, within tests, small differences in moisture gain/loss were observed for the different varieties and treatments. Across tests however, greater differences were found between replicates of the same varieties and week of harvest, but these

differences were considered to be due, in part, to the biological differences among the material and environmental conditions that were observed between tests. For these reasons, the observed variables (initial moisture content, M_0 , air temperature, T , relative humidity, RH , and the equilibrium moisture content estimated by the modified Halsey equation, $EMCH$, were treated as covariates in the statistical analysis of estimated parameters (Table 6.5). The discussion and statistical analysis that follows treats each field treatment (replication of variety and harvest week) as an experimental unit. Tukey's studentized range test was used to determine significance at the 0.05 level, as in the wax treated tests.

Table 6.5. Classification of variables used in the statistical analysis for each year of study.

Year	Category	Variable
1989	Main Effects	Variety Week Replication Test
	Observed-sorption	M_0 T RH $EMCH$
	Observed-chemical	Protein Oil FFA HM_0 Size CRain
	Predicted	$EMCR$ k n k^n k^m
1990	Main Effects	Variety Week Replication Test Chamber
	Observed-sorption	M_0 T RH $EMCH$
	Observed-chemical	Protein Oil FFA Ash Carbo HM_0 Size CRain
	Predicted	$EMCR$ k n k^n k^m

An ancillary set of chemical data from the same field treatments was matched with sorption parameters that were found by regression to determine whether the variables of oil, protein, free fatty acid (FFA), carbohydrate, seed size, and harvest moisture could help to explain the differences that were observed between and within treatments. The moisture content at harvest was found by a previous researcher (Sidhu, 1992) to correlate well with some of these chemical variables and was included in this analysis for that reason. This will be discussed in Section 6.4.

An initial non-linear regression analysis was performed using the modified Page equation (4.57) for both absorption and desorption data to estimate three parameters; the equilibrium moisture content ($EMCR$), k , and n values. Because some of the $EMCR$ values were so high/low for absorption /desorption, a rejection criteria was established to discard experimental units whenever the standard error of the estimate exceeded the mean standard error by a factor of four and the

estimated value was outside the bounds of other estimates (Saxton, 1996). The standard error of each estimate for the EMCR, k , and n values was extracted from the non-linear regression output file and inserted into a spreadsheet to compute the sum and mean of each standard error term. This procedure produced reasonable values for equilibrium moisture content in most cases, however much of the data in one particular test conducted during 1989 was rejected, consequently all the data from that one test were omitted from subsequent analysis. The remaining data set for 1989 and 1990 contained, respectively, 87 and 131 experimental units for subsequent evaluation.

The mean air temperature and relative humidity of each replication were used to determine the EMCH with parameter values suggested by Chen and Morey (1994) for the data collected by Pixton and Warburton (1971). The EMCH was included because it combines the effect of temperature and relative humidity into one term that is separate from the effect of each individual parameter. A poor correlation of the EMCH values was found with initial estimates that were generated by non-linear regression for each experimental unit. Consequently, the EMCH value was used only as a covariate in the statistical model building phase of the analyses.

The n value was bounded in this analysis as ≤ 1.0 which is the theoretical value for homogeneous materials. Two descriptive parameters (k^n and k^m) were added to the set of estimated variables to test possible correlations with the observed variables. Each of these parameters combine the effect of k and n values into a single term and were considered to have the potential to identify possible component interaction effects.

6.3.1. Absorption Tests:

The variations that were found between years for the high relative humidity absorption tests exceeded the variability among treatments. Consequently, observed and predicted results were evaluated independently for each year to identify the contribution(s) by each main effect (Table 6.5).

Representative plots of the observed and predicted moisture ratio against exposure time for absorption conditions in 1989 are shown in Figures C1 through C4 for Tn4-86, Essex, and Leflore

soybeans during selected weeks in the early, mid, and late harvest season (weeks 2 or 3, 6, 11, and 16). 1990 plots are shown in Figures C5 through C8 for the same varieties and weeks. The y-axis in the graphs for absorption conditions are plotted as $1 - MR(t)$ to enable the reader to quickly distinguish them from the desorption graphs, which are plotted with $MR(t)$ on the y-axis.

Time of exposure varied among tests to expedite the time required to conduct all experiments (Table 6.6). At least one sample from each treatment was included in tests that were conducted over an extended period of time to establish a reasonable estimate for the moisture equilibrium value. This approach was taken because of the absence of data and valid EMC models for weathered materials in the literature. Initially thought to be a useful parameter, the modified Halsey value (EMCH) predicted large changes in the equilibrium moisture content with small changes in relative humidity in the high humidity range ($\geq 90\%$). Conversely, the modified Henderson and Chung-Pfost equations gave estimated values that were lower than expected for absorption. For these reasons, and since EMCH combines the effect of temperature and relative humidity in one term, it was included as an observed variable (Tables 6.5 and 6.7) and treated as a covariate in the statistical analysis.

Table 6.6. Hours of exposure for absorption conditioning tests during 1989 and 1990.

Test	1	2	3	4	5	6	7	8	9	10	11	12	13
1989	97	94	96	94	97	95	95		165	146	94	93	96
1990			94	92		188	145	95	187	113	168		

6.3.1.1. Initial moisture content:

Initial moisture content (M_0) for absorption was determined after pre-conditioning soybeans in a controlled environment, which was similar to a quasi-equilibrium value for a drying condition. Observed values for each experimental unit in 1989 are shown in Tables C1, C2, and C3 for Tn4-86, Essex, and Leflore, respectively. 1990 values are shown in Tables C4, C5, and C6 for the same varieties. The mean value for all tests in 1989 and 1990 was 9.2 and 8.2% with a range between 5.4

Table 6.7. Summary of observed and predicted parameters for each variety with 1989 and 1990 soybean absorption data. Values in a given line may not be from the same replication.

1989	Observed variables				Predicted variables				
Tn4-86	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	12.2	20.6	98.3	100.8	63.3	0.05305	1	0.2037	3.839
Min	5.4	18.9	92.9	37.9	29.6	0.02335	0.5419	0.0243	1
Avg	9.0	19.7	96.4	66.1	45.4	0.03041	0.8790	0.0548	1.683
Std	1.54	0.52	1.61	18.04	8.56	0.00724	0.1382	0.0423	0.880
n	29								
Essex	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	16.7	21	98.4	104.4	76.3	0.08093	1	0.1930	6.804
Min	6.4	18.9	93	38.3	27.5	0.01067	0.5746	0.0182	1
Avg	9.7	19.7	96.8	70.5	48.4	0.02939	0.8842	0.0491	1.800
Std	1.87	0.53	1.41	16.74	9.80	0.01272	0.1349	0.0345	1.263
n	29								
Leflore	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	13.3	20.5	98.3	98	70.8	0.04006	1	0.1922	5.217
Min	6.4	18.8	93.2	39	34	0.01313	0.4996	0.0181	1
Avg	9.0	19.8	96.4	64.7	50.3	0.02430	0.8836	0.0438	1.821
Std	1.69	0.50	1.45	15.49	8.80	0.00632	0.1405	0.0343	1.215
n	29								
1990	Observed variables				Predicted variables				
Tn4-86	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	11.0	23.2	98.9	129.0	42.9	0.04955	1	0.1964	7.866
Min	5.5	18.2	93.1	38.8	22.8	0.01224	0.4411	0.0122	1
Avg	8.1	19.2	95.7	63.6	30.3	0.02832	0.9469	0.0379	1.345
Stdev	1.1	1.0	1.9	28.9	5.3	0.00842	0.0980	0.0275	1.039
n	45								
Essex	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	12.6	23.2	98.8	122.9	45.1	0.05234	1	0.1283	2.523
Min	5.6	18.3	91.4	33.4	23.2	0.01670	0.6894	0.0205	1
Avg	8.4	19.3	95.4	60.9	30.7	0.03551	0.9583	0.0423	1.194
Stdev	1.29	1.12	1.98	27.3	5.61	0.00892	0.0746	0.0195	0.379
n	44								
Leflore	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	10.5	23.2	98.8	126.8	44.1	0.06319	1	0.0902	4.610
Min	5.6	18.3	91.2	33.0	23.0	0.01523	0.6337	0.0000	1
Avg	8.2	19.2	95.5	61.9	31.0	0.03394	0.9526	0.0397	1.263
Stdev	1.2	1.0	2.0	28.2	5.4	0.00970	0.0792	0.0152	0.601
n	43								

to 16.7% and 5.5 to 12.6, respectively (Table 6.7). Mean values for each variety and week of harvest in 1989 were 9.0, 9.7, and 8.9% for Tn4-86, Essex, and Leflore, respectively. Corresponding values in 1990 were 8.1, 8.4, and 8.2 for Tn4-86, Essex, and Leflore, respectively (Table 6.7).

Initial moisture content was significantly related only to test in both years (Tables 6.8, 6.9, 6.10, and 6.11). Mean values for each test and year are shown in Figures A7 and A8. Differences among tests could be due to differences in air temperature, relative humidity, and length of exposure time in the pre-conditioning chambers before the material was introduced into the sorption chambers.

6.3.1.2. Chamber conditions:

Values for each replication of T, RH, EMCH are shown in Tables C1 through C6. Mean values by variety and year are given in Table 6.7. Mean temperature and relative humidity were consistent at $20 \pm 0.5^{\circ}\text{C}$ and $95 \pm 3\%$ (Figures A7 and A8) for both years and showed significant variation with test and week in 1989 and test, week, chamber, and test by chamber in 1990 (Tables 6.9 and 6.11). The mean EMCH values in 1989 and 1990 were 67 and 62%, respectively, but were highly variable across tests, as shown in Figures A7 and A8. Since the modified Halsey model is highly dependent on relative humidity and only slightly dependent on temperature, this result was expected (Table 6.7).

EMCH in 1989 was significantly related to week and test, as were T and RH, (Table 6.9) even though the minimum significant differences between all T and RH values were less than the accuracy of the instruments used in these experiments ($< 0.4^{\circ}\text{C}$ and $< 0.3\%$). Test means for each variable are shown in Figure A7.

Differences in T, RH, and EMCH in 1990 were significant across week, test, chamber, and the interaction of test and chamber (Table 6.11). However, mean T values varied only by 1°C across all weeks and the mean RH varied by only 2.2 percentage points, which was within the expected variation. Differences for all three variables across tests are shown in Figure A8 and between chambers for each test in Figures A9 and A10.

Table 6.8. Analysis of variance model statements used to test correlations among the observed and predicted variables for absorption and desorption tests in 1989.

Variable	Model No.	GLM Model Statement
M_o T RH EMCH	1	Variable = Var Week Rep Test Var*Week
EMCR	2	Variable = Var Week Rep Test Var*Week
k	3	Variable = Var Week Rep Test Var*Week M _o
n	4	Variable = Var Week Rep Test Var*Week M _o T EMCH
k^a	5	Variable = Var Week Rep Test Var*Week M _o T RH EMCH
k^m	6	Variable = Var Week Rep Test Var*Week Protein Oil FFA HM _o Size CRain
	7	Variable = Var Week Rep Test Var*Week Size
	8	Variable = Var Week Rep Test Var*Week HM _o FFA

Table 6.9. Summary of the analysis of variance results for observed and predicted variables for the absorption experiment in 1989. Model numbers refer to those listed in Table 6.8.

Variable	Model No.	Significant Terms	R ² value
M_o	1	Test	.715
T	1	Test Week	.953
RH	1	Test Week	.997
EMCH	1	Test Week	.990
EMCR	2	Test Var Var*Week Week	.954
	4	Var Var*Week Week M _o Test T EMCH Rep	.967
k	1	Test Var	.812
	4	Test EMCH Var M _o	.870
n	1	Test Var*Week	.929
k^a	1	Test Variety	.966
	3	Test Var M _o	.971
k^m	1	Test	.818

Table 6.10. Analysis of variance model statements used to test correlations among the observed and predicted variables for absorption and desorption tests in 1990.

Variable	Model No.	GLM Model Statement
M_o T RH EMCH	9	Variable = Var Week Rep Test Chamber Var*Week Test*Chamber
EMCR	10	Variable = Var Week Rep Test Chamber Var*Week Test*Chamber
k	11	Variable = Var Week Rep Test Chamber Var*Week Test*Chamber M_o
n	12	Variable = Var Week Rep Test Chamber Var*Week Test*Chamber M_o T RH EMCH
k^*	13	Variable = Var Week Rep Test Chamber Var*Week Test*Chamber Protein Oil FFA Ash Carbo HM _o Size CRain
k^{**}	14	Variable = Var Week Rep Test Chamber Var*Week Test*Chamber Oil

Table 6.11. Summary of the analysis variance results for observed and predicted variables for the absorption experiment in 1990. Model numbers refer to those listed in Table 6.10.

Variable	Model No.	Significant Terms	R ² value
M_o	9	Test	.860
T	9	Test*Cmb Test Cmb Week	.998
RH	9	Test*Cmb Test Week Cmb	.957
EMCH	9	Test*Cmb Test Week	.962
EMCR	10	Test Week Cmb Test*Cmb Rep Var	.963
	11	Test Week Var*Wek Cmb Test*Cmb Rep M_o	.971
k	10	Var Week Test Var*Week	.906
n	10	Test*Cmb	.617
k^*	11	M_o Test	.681
k^{**}	11	M_o	.525

6.3.1.3. Predicted parameters:

Exposure time for absorption tests ranged from 92 to 188 hours (Table 6.6). It was, therefore, necessary to establish a correct equilibrium moisture content for the short duration tests relative to an extended exposure. Estimates of the equilibrium moisture content were determined from the modified Page equation for each treatment replication by non-linear regression. Values from the seven tests that exceeded 100 h (Table 6.6) were used to establish estimates for companion tests (same year, variety, and adjacent week of harvest) that were conducted for shorter time periods. For each long run test, a ratio was calculated by dividing the regression equilibrium moisture content (EMCR) by the predicted moisture content value at 90 hours of exposure. This ratio was multiplied by the moisture content value at 90 hours of exposure that was predicted by the first regression estimate for the short duration tests to derive a more reasonable EMCRC value for these tests. These new EMCRC values were then used in a second non-linear regression to generate new parameters for the modified Page equation (k and n values) for the short run tests. Obviously, the EMCRC, k , and n values for the long run tests were unchanged. The results of these calculations were used in the final analysis and are listed in Tables C1 through C6 for the absorption tests in both years. A pseudo- R^2 value was computed from the non-linear regression output data ($1 - \text{the ratio of the residual and corrected total sum of squares}$) and is also shown for each replication in these tables.

A comparison of EMCRC and Halsey values (EMCH) for each year is shown in Figures C18a and C18b. The mean EMCRC value in 1989 was 48% which was much lower than the mean EMCH value of 67%. Significant components of variation were variety, week, test, replication, the interaction of variety and harvest week, initial moisture, mean temperature, and EMCH (Table 6.9). Tn4-86 had the lowest mean EMCRC value and was different from the others (Table 6.7). Average values for all replications within each treatment ranged from a minimum of 35% to a maximum of 65% (Figure C18a). Two values in harvest week five were outside this range but these were not replicated because samples were lost during storage. Across tests, EMCRC values were lower than EMCH values in most cases (Figures A7 through A14).

The overall mean EMCR value in 1990 was 31% with a range in values of 25 to 43% when all treatment replications were combined. Mean values across varieties were not different from one another but were considerably lower than the values predicted in 1989 (Table 6.7). Surprisingly, these values were also lower (by nearly 30 percentage points of moisture) than the corresponding values predicted by the Halsey equation (EMCH) (Figure C17b). The following were significant sources of variation for EMCR values: test, week, replication, chamber, initial moisture content, and the interactions between variety and week, and between test and chamber (Table 6.11). The pattern of EMCR values for each variety across harvest weeks was attributed primarily to the difference that existed between test chambers (Figure C18b), yet environmental differences were not found between them (Figures A9 and A10). The decline in EMCR values during the first 3 weeks of harvest matched the pattern observed for HM_0 , which was similar to the values found in 1989.

The mean k value for all 1989 tests was 0.028 which was approximately one-fourth the value estimated from the prediction equation from Osborn et al. (1991) for lower humidity conditions. The mean k value for each variety was 0.0304, 0.0294, and 0.0243 for Tn4-86, Essex, and Leflore, respectively, with Leflore being significantly lower than the others (Table 6.7). Variety, test, air temperature, EMCH, and M_0 along with other terms in the model accounted for 87% of the variation for this parameter (Table 6.9). No significant trend was identified for mean k values across harvest weeks for any variety in 1989 (Figure C19a). The two extreme values observed in week five were not replicated and were omitted from consideration.

The k values in 1990 were influenced primarily by variety, week, test, and variety by week interaction (Table 6.11). Figure C19b shows a general increase in k values as harvest progressed for all varieties. The mean k value was 0.0325, which was 16% higher than the value found in 1989 but 75% lower than the value predicted by Osborn et al. (1991) for the mean temperature and relative humidity from all tests. The range in replicated values in 1990 was between 0.013 and 0.051. Mean values for each variety were 0.0283, 0.0355, and 0.0339 for Tn4-86, Essex, and Leflore, respectively (Table 6.7), with Tn4-86 significantly lower than the other two varieties. Variations in the EMCR

values across harvest weeks for each variety in this year of study were not reflected in the k values. The fact that these k values were different than the value found by Osborn et al. (1991) for both years could be expected since this mean included values before harvest maturity and after beans were in a deteriorated state.

The mean n value for all combined treatments in 1989 was 0.882. Test and the interaction of variety and week significantly effected n and accounted for approximately 93% of the variation (Table 6.9). The maximum n value for each variety was 1.0, which was set by the logical bound of this variable and was selected by regression for 27 out of 87 total replicates. Replicated mean n values for each variety and week of harvest (Figure C20a) does not reveal a noticeable trend throughout the entire harvest period although a general decline in values is noted from harvest week one to week six and from week seven to week 11. Two sharp increases in n values occurred from week 5 to week 6 and again from week 13 to week 14.

The only significant source of variation for the n value in 1990 was the interaction of test and chamber (Table 6.11). The overall mean value was 0.953 which was higher than that found in 1989, with a range in replicated mean values between 0.72 and 1.0 (which was set as the logical bound for this parameter). The n value for all varieties was lower during the first and last portions of the harvest period in this study (Figure C20b). The period from harvest weeks four to ten indicated that all varieties behaved more as a homogeneous material since the n value was nearly equal to one. Conversely, this also implies that the beans were more heterogeneous before they reached harvest maturity and that the later field deterioration significantly effected this parameter, perhaps because of the changes that occurred in the chemical composition during this time. Values for the last week of harvest for each variety were near the mean for the entire harvest.

Mean n values for both years were higher than the value found by Osborn, et al. (1991) for moisture absorption tests in a lower relative humidity range ($75 \leq RH \leq 85\%$). A higher n value suggests that the moisture transport is slower during initial exposure but faster as the material approaches moisture equilibrium. This result was not expected since the higher humidity conditions

of this test produced a higher equilibrium moisture content. Higher n values (near 1.0) for week 4 and 7 in 1989 (Figure C20a) and from week 3 to 10 in 1990 (Figure C20b) indicate that during the optimum harvest period soybeans may behave as a homogeneous body but after continued weather exposure they are more heterogeneous, as indicated by lower n values in most cases after week 10.

The k^n parameter was generated to evaluate the combined effect of the semi-theoretical value of k with the empirical value of n . It is considered to be more directly comparable to the effective diffusion coefficient D' in the analytical solution (equation 4.40). Mean k^n values for each variety and week of harvest during the 1989 and 1990 season are shown in Figures C21a and C21b, respectively. A general increase in these values was observed for all varieties during the first eleven weeks in both years. For 1990, this trend continued through the end of harvest but in 1989 the values fluctuated between 0.025 and 0.10 for harvest week 13 and 14, respectively. Values for all varieties during the first week of harvest were approximately 0.03 for both years and increased to 0.05 and 0.04 by the end of harvest during 1989 and 1990, respectively. The mean value for all varieties across the entire harvest season was 0.049 and 0.040 for 1989 and 1990, respectively (Table 6.6).

The k^n value in 1989 was significantly effected by test, variety, and initial moisture content, which combined with the other variables in the base statistical model to explain 97% of the variation for this parameter (Table 6.9). In 1990, initial moisture content and test were the only significant variables in the model that accounted for 68% of the variations in this parameter (Table 6.11). Even though some week-to-week fluctuation was seen in the k^n value for both years (Figures C21a and C21b), it was relatively stable compared to weather, harvest moisture, EMCH, k , and n . Thus, the variability of k and n separately over the extended harvest period may be masked when their values are combined to form a diffusion like term. Also, note that k^n more nearly relates to the diffusion term ($D'\lambda_n^2$) in the exponent of the diffusion model (4.40). This may indicate that the diffusive properties of soybeans remain relatively stable for up to 16 weeks after physiological maturity in spite of the extreme variation observed in the separate values.

The mean value for k^m in 1989 was 1.77 with a range in mean values from 1.0 to 3.5 (Figure C22a). The only significant source of variation for this parameter was test (Table 6.9). A comparison of the k , n and k^m values during each week of harvest and each variety (Figures C19a, C20a, and C21a) revealed that the k^m values were closely correlated to the inverse of the n values, as expected since $m = n - 1$.

The overall mean value for k^m in 1990 was 1.27 which was lower than the value found in 1989 with a range of 1.0 and 3.3 (Figure C22b). The only variable that was found to be significant was the initial moisture content, but only 52% of the variation in this parameter was accounted for (Table 6.11). The highest values were confined to the initial and final weeks of harvest and also correlated well with the inverse of the n values.

6.3.1.4. Comparison of the modified Page equation with the diffusion equation:

The above analysis involved only the modified Page equation (4.57) because it was reported by Osborn et al. (1991) to give a slightly superior fit to their absorption data than the cellular diffusion equation (4.40). Because of the interest among researchers in diffusion theory, Biot number, eigenvalues, and D'/R^2 term for the diffusion equation were generated to compare the solution with the modified Page equation for a selected data set in this study. Data were chosen for all three varieties from harvest week six for both years after considerations were given to the weather patterns during harvest and the range of values found for the parameters in the modified Page model.

A computer program was written (Appendix E) to find a satisfactory number of eigenvalues that satisfied the initial condition ($MR(0) \geq 0.999$) after an estimate for the Biot number was given. The D'/R^2 term was then estimated to generate a solution for the moisture ratio with equation (4.40) for each observed time value. Residual sum of squares were then computed between the observed and estimated values for each time value and totaled to provide criteria for selecting values that gave the best fit with the data. The final solution was found by an iterative process and results produced equation estimates that gave very good agreement with the data. In order to provide a comparison

between the two solutions, the k and n values from the non-linear regression analysis of the modified Page equation were used to generate estimates of the moisture ratio and residual sum of squares for the same time values. Results are shown in Table 6.12 where the Biot number, D'/R^2 term, k , and n values are listed in addition to the residual sum of squares values of the moisture ratio and moisture content for both models. Figures D1 and D2 show virtually no difference between the two solutions, even though the residual sum of squares were slightly higher for the diffusion equation in most cases.

The D' value for each replication was estimated by assuming an average outside radius for these materials of 0.32 cm which produced a range of 0.00023 to 0.00108 for 1989 and 0.00057 to 0.00122 for 1990. The mean value for all six observations was 0.00692 which compared with an estimate of 0.00476 given by Mensah et al. (1979) for cotyledons (equation 4.44). The Biot numbers ranged from 1.1 to 157 with a mean of 29.4 which was near the value found by regression by Osborn et al. (1991) for soybean absorption in a lower humidity range but much higher than the extrapolated estimate given for absorption of 0.022 by equation 4.51.

The most notable result of this analysis was that the Biot numbers and the n values had a similar effect on the ability of each model to fit the absorption data. Figure D5 shows a plot of these two parameters to more clearly illustrate the interesting relationship between them. Large Biot numbers behave as small n values in that they create more curvature in the early portion of the moisture ratio versus time curves which describe a faster rate of mass transfer during initial exposure and a decrease in the mass transfer rate as the material approaches moisture equilibrium. This finding deserves more work in this area to further delineate the relationship between these two parameters. There is a possibility that each variable takes into account the interactivity of chemical components with water molecules that other researchers have found to be significant for equilibrium studies with food products. However, this relationship might be more easily accounted for by the Biot number and D'/R^2 terms because they have the ability to involve more of the physical or chemical material properties in the model than the n value, which has until now been considered by most researchers to be a purely empirical product dependent parameter.

Table 6.12. Comparison of empirical and theoretical model parameters for selected absorption and desorption tests for harvest week 6 in 1989 and 1990.

Absorption Tests:			Residual Sum of Squares									
Yr	Variety	Rep	Empirical model		Theoretical model		Biot No.	D'/R^2	k	n	k^n	k^m
			MC	MR	MC	MR						
89	Tn4-86	3	0.1735	2.33 E-05	0.2104	2.83 E-04	2.7	0.00529	0.02841	0.9405	0.0351	1.236
89	Essex	3	0.9381	9.17 E-04	1.4826	1.45 E-03	157.0	0.00106	0.01902	0.6398	0.0793	4.167
89	Leflore	3	0.2739	4.72 E-04	0.3869	6.67 E-04	10.0	0.00224	0.02453	0.8112	0.0494	2.014
90	Tn4-86	1	0.4243	1.11 E-03	0.4680	1.22 E-03	2.8	0.00569	0.03128	0.9353	0.0391	1.251
90	Essex	1	0.4005	1.12 E-03	0.3621	1.01 E-03	2.9	0.00562	0.03160	0.9390	0.0390	1.235
90	Leflore	1	0.5274	1.35 E-03	0.5553	1.43 E-03	1.1	0.01203	0.03148	0.9778	0.0340	1.080

Desorption Tests:			Residual Sum of Squares									
Yr	Variety	Rep	Empirical model		Theoretical model		Biot No.	D'/R^2	k	n	k^n	k^m
			MC	MR	MC	MR						
89	Tn4-86	3	0.0461	5.82 E-04	0.2660	3.39 E-04	44.0	0.00451	0.07312	0.6926	0.1634	2.235
89	Essex	3	0.6534	7.53 E-04	0.8356	9.63 E-04	42.2	0.00462	0.07446	0.6952	0.1643	2.207
89	Leflore	3	0.1170	1.89 E-04	0.3648	5.91 E-04	175.0	0.00293	0.05302	0.6431	0.1512	2.853
90	Tn4-86	1	0.1121	3.23 E-04	0.2162	6.24 E-04	2.5	0.00800	0.03921	1.00	0.0392	1.000
90	Essex	1	0.1620	4.96 E-04	0.1632	4.99 E-04	0.2	0.07010	0.04039	1.00	0.0404	1.000
90	Leflore	1	0.2141	5.47 E-04	0.2163	5.52 E-04	0.2	0.06240	0.03600	1.00	0.0360	1.000

6.3.2. Desorption Tests:

The drying sequence was conducted immediately after the absorption experiments for all tests in both years. The material was exposed to nearly the same temperature and low humidity environment for different durations during each test, as shown in Table 6.13. The time for each test was extended until the mass lost between weighings did not change appreciably, which was assumed to be near the moisture equilibrium.

Moisture ratio graphs for the desorption tests in 1989 and 1990 are shown in Figures C9 through C12 and Figures C13 through C16, respectively. For the test conditions used in these experiments soybeans lost moisture faster than they gained moisture. However, as in the absorption experiments, significant differences were found between the years of study, thus, observed and predicted results were evaluated by year of study in an attempt to identify the significant variables in the tests. Observed and predicted variables for each treatment replication, week of harvest, variety, and year are given in Tables C7 through C12. The maximum, minimum, mean, and standard deviation for each variable are also presented in Table 6.14 for both years.

Table 6.13. Hours of exposure for desorption conditioning tests during 1989 and 1990.

Test	1	2	3	4	5	6	7	8	9	10	11	12	13
1989	72	86	84	73	83	74	74		78	94	72	72	69
1990			72	72		98	89	54	54	72	72		

6.3.2.1. Initial moisture content:

The initial moisture content of each experimental unit was the final moisture value for the absorption test, which, in the case of the extended tests, was near the equilibrium value for the high humidity condition. The mean value for all treatments in 1989 was 43.7% and ranged between 27.4 and 62.8% (Tables C7, C8, and C9). The variation in initial moisture content was significantly related to variety, test, and field replication (Table 6.15). As in the absorption experiment, differences among tests were due in part by the design of the experiment because different materials

Table 6.14. Summary of observed and predicted parameters for each variety with 1989 and 1990 soybean desorption data. Values in a given line may not be from the same replication.

1989	Observed variables				Predicted variables				
Tn4-86	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	60	24.6	18.6	4.8	10.9	0.12991	1	0.2623	2.499
Min	27.4	18.6	13	4.2	4.5	0.05024	0.6377	0.0697	1
Avg	42.8	21.3	15.2	4.5	8.4	0.09341	0.8240	0.1463	1.578
Std	8.15	1.50	1.55	0.16	1.52	0.02110	0.1097	0.0488	0.425
n	29								
Essex	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	57.4	24.1	19.2	4.9	14.9	0.17161	1	0.3547	3.044
Min	27.4	18.4	13	4.2	4	0.05570	0.5465	0.0667	1
Avg	43.0	21.4	15.2	4.5	8.7	0.09882	0.8335	0.152	1.549
Std	7.88	1.41	1.69	0.18	2.21	0.02714	0.1299	0.061	0.505
n	29								
Leflore	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	62.8	24.8	18.7	4.9	11.4	0.14459	1	0.2773	3.976
Min	29.7	18.7	13.4	4.3	4	0.05177	0.5225	0.0638	1
Avg	45.1	21.6	15.1	4.5	8.1	0.09079	0.8081	0.1498	1.688
Std	7.50	1.63	1.44	0.15	1.88	0.02321	0.1249	0.0554	0.631
n	30								
1990	Observed variables				Predicted variables				
Tn4-86	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	37.2	22.0	21.8	5.2	10.2	0.09719	1	0.2702	4.340
Min	22.3	17.3	13.5	4.3	3.3	0.03804	0.5182	0.0392	1
Avg	28.7	20.3	16.3	4.6	7.0	0.06503	0.7658	0.1280	1.998
Stdev	4.06	1.52	2.17	0.22	1.56	0.01272	0.1054	0.0405	0.647
n	45								
Essex	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	42.5	22.0	28.5	5.9	12.3	0.10956	1	0.2618	4.795
Min	22.8	17.3	13.5	4.3	3.6	0.02607	0.5699	0.0404	1
Avg	30.0	20.2	16.6	4.7	7.0	0.06112	0.7591	0.1257	2.092
Stdev	4.58	1.57	2.95	0.31	1.77	0.01544	0.1159	0.0466	0.752
n	43								
Leflore	Mo	T	RH	EMCH	EMCR	k	n	k ⁿ	k ^m
Max	40.0	22.1	21.4	5.1	10.3	0.09840	1	0.2947	2.995
Min	22.0	17.3	13.5	4.3	4.2	0.03443	0.5269	0.0360	1
Avg	29.9	20.2	16.3	4.6	7.0	0.06228	0.7876	0.1172	1.851
Stdev	4.41	1.57	2.21	0.23	1.67	0.01458	0.0969	0.0450	0.442
n	43								

Table 6.15. Summary of the analysis of variance results for observed and predicted variables for the desorption experiment in 1989. Model numbers refer to those listed in Table 6.8.

Variable	Model No.	Significant Terms	R ² value
M_i	1	Test Var Rep	.951
T	1	Test Week	.997
RH	1	Test Week	.992
EMCH	1	Test	.993
EMCR	2	Test	.778
k	2	Test Var	.883
n	2	Test	.797
k^a	2	Test	.824
k^b	2	Test	.831

were selected for different tests, in addition to the slight differences between temperature and relative humidity that were observed. The mean values for each variety were 42.8, 43.0, and 45.1% for Tn4-86, Essex, and Leflore, respectively (Table 6.14), with the Leflore soybeans significantly higher than the other two varieties. Among tests the range of mean values was from 28 to 55% (Figure A11). For replications one, two, and three, the mean values were 41.7, 45.5, and 44.2%, respectively, with replication one significantly lower than the other two.

Desorption tests in 1990 were conducted in two separate chambers, as described in the absorption experiments. Mean initial moisture content was 29.5%, with a range between 22.0 and 42.5% (Tables C10 through C12). Initial moisture content showed significant differences with variety, week of harvest, field replication, test, chamber, and the interaction of test and chamber (Table 6.16). The mean value for each variety was 28.7, 30.0, and 29.9% for Tn4-86, Essex, and Leflore, respectively (Table 6.14), with a minimum significant difference of 0.7%. Across tests the mean values were from 26 to 33% with a minimum significant difference of 1.5% (Figure A12). Between chambers A and B mean values were 32 and 27%, respectively, with a minimum significant

Table 6.15. Summary of the analysis of variance results for observed and predicted variables for the desorption experiment in 1989. Model numbers refer to those listed in Table 6.8.

Variable	Model No.	Significant Terms	R ² value
M₀	1	Test Var Rep	.951
T	1	Test Week	.997
RH	1	Test Week	.992
EMCH	1	Test	.993
EMCR	2	Test	.778
k	2	Test Var	.883
n	2	Test	.797
k^a	2	Test	.824
k^{ab}	2	Test	.831

were selected for different tests, in addition to the slight differences between temperature and relative humidity that were observed. The mean values for each variety were 42.8, 43.0, and 45.1% for Tn4-86, Essex, and Leflore, respectively (Table 6.14), with the Leflore soybeans significantly higher than the other two varieties. Among tests the range of mean values was from 28 to 55% (Figure A11). For replications one, two, and three, the mean values were 41.7, 45.5, and 44.2%, respectively, with replication one significantly lower than the other two.

Desorption tests in 1990 were conducted in two separate chambers, as described in the absorption experiments. Mean initial moisture content was 29.5%, with a range between 22.0 and 42.5% (Tables C10 through C12). Initial moisture content showed significant differences with variety, week of harvest, field replication, test, chamber, and the interaction of test and chamber (Table 6.16). The mean value for each variety was 28.7, 30.0, and 29.9% for Tn4-86, Essex, and Leflore, respectively (Table 6.14), with a minimum significant difference of 0.7%. Across tests the mean values were from 26 to 33% with a minimum significant difference of 1.5% (Figure A12). Between chambers A and B mean values were 32 and 27%, respectively, with a minimum significant

difference of 0.5%, which was within the accuracy of the oven method used in this experiment (Figure A14).

Table 6.16. Summary of the analysis of variance results for observed and predicted variables for the desorption experiment in 1990. Model numbers refer to those listed in Table 6.10.

Variable	Model No.	Significant Terms	R ² value
M₀	9	Test Cmb Test*Cmb Var Week Rep	.950
T	9	Cmb Test*Cmb Test	.999
RH	9	Test Cmb Test*Cmb Week	.930
EMCH	9	Test Cmb Test*Cmb Week	.926
EMCR	10	Test	.798
k	10	Test Week Test*Cmb	.803
n	10	Test Test*Cmb	.696
k^a	10	Test Test*Cmb	.784
k^a	10	Test*Cmb	.607

6.3.2.2. Chamber conditions:

The mean temperature and relative humidity values among tests for both years were consistent at $22 \pm 3^\circ \text{C}$ and $17 \pm 3\%$, respectively, (Figures A11 and A12). EMCH values were computed by equation 2.31 for all replications, averaged across tests and shown in Figures A11 and A12 to illustrate that this parameter is not as sensitive to relative humidity in this range. Variations in the mean relative humidity across tests matched the variations observed for EMCH. Mean values of temperature, relative humidity, and EMCH for each variety and year are given in Table 6.14. Temperature and relative humidity were effected by test and week in 1989 (Table 6.15), as in the absorption experiment, even though the minimum significant difference for these variables was less than the accuracy of the instruments used in these experiments ($< 0.3^\circ \text{C}$ for the air temperature; and $< 0.05\%$ for the relative humidity). Test was the only variable that significantly related to EMCH

in 1989 (Table 6.15). Across tests the mean value for EMCH was 4.5%, with a range of 4.4 to 4.6%, although the minimum significant difference ($p < .05$) was only 0.05%.

The mean temperature for all treatments in 1990 was significantly related to test, chamber, and the interaction of test and chamber (Table 6.16). Variations in the mean relative humidity and EMCH were significantly related to test, chamber, interaction of test and chamber, and week of harvest (Table 6.16). The range in mean relative humidity values among tests was 15 to 19% (Figure A12); between chambers was 15 and 17% (Figure A13); and across harvest weeks was 15 to 19%. The mean EMCH was 4.6%, which was only 0.1 percentage point above the mean value for 1989. Values ranged from 4.2 to 4.9% during the first year of study and from 4.3 to 5.9% the second year. Between chambers, mean values were 4.72 and 4.65% for A and B, respectively (Figure A13).

6.3.2.3. Predicted parameters:

The best estimate for the equilibrium moisture content for drying (EMCR) was determined in a similar manner as previously described for the absorption tests. A non-linear regression analysis was performed with the modified Page equation to determine approximate values of EMC_R, k , and n . This preliminary analysis resulted in a few unreasonable values for the EMC_R (i.e., < 0). These values were reevaluated by adjusting the estimates produced for tests from other replicates within the same treatment, as previously described for the absorption experiment. For each long run test, a ratio was computed by dividing the EMC_R by the estimated moisture content at fifty hours of exposure. This ratio was multiplied by the estimated moisture content value of the treatment replications with unreasonable values to provide a reasonable EMC_R estimate. These new EMC_R values were used in a second non-linear regression to compute final values for k and n (Tables C7 through C12).

EMCR values were 1.5 to 6.9 percentage points higher than those estimated by the modified Halsey equation (Figures 23a and 23b) which indicated that it was not a good predictor for the equilibrium moisture content for these desorption tests in either year contrary to what was expected. This could be due in part to the fact that the parameters for the modified Halsey equation have not

been developed for partially deteriorated material. Further investigation is required to fully identify the cause for this observation.

The mean EMCR for all treatments in 1989 was 8.4%. Test contributed significantly to the variation in the EMCR (Table 6.15). A range of 5.3 to 10.2% was seen across tests (Figure A11) with a minimum significant difference of 2.6%, yet nine out of twelve tests were not significantly different. The mean values for each variety were 8.4, 8.7, and 8.1% for Tn4-86, Essex, and Leflore, respectively (Table 6.14). Differences for each variety and week of harvest are illustrated in Figure C24a, which shows a general erratic pattern across the harvest season for all varieties.

The mean EMCR for all test replications in 1990 was 7.0% with a range from 3.3 to 12.3% (Tables C10 through C12). Test was the only significant variable that contributed to the variation in EMCR (Table 6.16). The range in mean EMCR values across tests was from 5.1 to 9.2% (Figure A12) with a minimum significant difference of 1.1%. Interestingly, the mean value for each variety was 7.0% (Table 6.14). Mean EMCR values for each variety and harvest week for 1990 are shown in Figure C24b. When the harvest period was divided into three segments, the EMCR generally decreased between weeks one through four for all varieties, then increased for harvest week five only to gradually decline during the subsequent weeks until week ten when it increased again to week 13 before decreasing to week 16. This general pattern fit all varieties tested to varying degrees and could be attributed to field weathering.

The mean k value in 1989 was 0.0943 which was approximately 3.4 times larger than the mean value noted for the absorption tests. This value is in fair agreement with the value predicted for our test conditions by Overhults et al. (1973) of 0.0838, but lower than the value predicted by White et al. (1981) of 0.1631. Test and variety were found to contribute significantly to the variation in k values (Table 6.15). The k values across tests ranged from 0.066 and 0.133 while mean values for each variety were 0.093, 0.099, and 0.091 for Tn4-86, Essex, and Leflore, respectively (Table 6.14). The k values for each variety and week of harvest (Figure C25a) shown in, but no general trend was noted across all weeks. However, when this plot was compared to the EMCR graph

(Figure C24a), similar increases and decreases in these values were noted for the same week of harvest which indicates the strong correlation between these two parameters. Figure C29a shows the relationship between the k values for wetting with the corresponding k values for drying for each variety. All drying values were higher than their coincident counterpart for absorption (some by as much as five times) which reflected faster transport during drying. Essex exhibited more variation for both EMCR and k than the other two varieties.

The mean k value for all treatments in 1990 was 0.0627 which was approximately twice the mean value determined during the absorption phase of the experiment but lower than the value found in 1989 and predicted by Overhults et al. (1973) for these mean test conditions. The range in k values over all treatments was from 0.06 to 0.11. Test, week, and the interaction of test and chamber significantly contributed to the variation in the mean k value (Table 6.16). Across tests, mean values varied from 0.040 to 0.075 with a minimum significant difference of 0.01. Across varieties, mean values were 0.065, 0.061, and 0.062 for Tn4-86, Essex, and Leflore, respectively (Table 6.13). The mean k value generally increased from harvest week one to harvest week nine (Figure 25b), then decreased to near the initial level by harvest week sixteen. Figure C29b shows that k values for drying were greater than those for wetting for all varieties, which matches the relationship found for absorption and supports the observation that drying was more rapid for these tests.

The mean n value for 1989 tests was 0.8217 which was close to the value found for absorption but higher than the value predicted for our mean test conditions by Overhults et al. (1973) and White et al. (1981). Test was the only significant variable that contributed to the variation in this parameter (Table 6.15), which ranged from 0.632 to 0.947 across tests with a minimum significant difference of 0.157. The mean values for each variety were 0.824, 0.833, and 0.808 for Tn4-86, Essex, and Leflore, respectively (Table 6.14). The n values for each variety and harvest week were higher during the first half of the harvest season for all varieties (Figure C26a). Approximately one-half of the drying n values fall below the value found during absorption (Figure C30a). This compares with the average value predicted by White et al. (1981) and Overhults et al. (1973) of 0.433.

The overall mean n value for 1990 was 0.77 with a range in values for treatment means from 0.52 to 1.0. Test and chamber were the only significant variables that significantly contributed to the variation (Table 6.16). Mean n values across tests ranged from 0.65 to 0.87, while for each variety the mean values were 0.76, 0.76, and 0.79 for Tn4-6, Essex, and Leflore, respectively (Table 6.14 and Figure C26b). A comparison between the n values for absorption and desorption tests is shown in Figure C30b.

The mean k^n value for the entire harvest season in 1989 and 1990 was 0.1493 and 0.1237, respectively, the average of which is about half the value predicted for our mean test conditions by the equation given by Hutchinson and Otten (1983). Mean k^n values were influenced significantly by test in 1989, and by test and the interaction of test and chamber in 1990 (Tables 6.15 and 6.16). Values ranged between 0.075 and 0.23 in 1989 and between 0.075 and 0.2 in 1990. Across varieties, mean values were 0.146, 0.152, and 0.150 in 1989 and 0.128, 0.126, and 0.118 in 1990 for Tn4-86, Essex, and Leflore, respectively (Table 6.14 and Figures C27a and C27b). Essex exhibited the largest variation of this parameter during both years of study. These values were generally larger and more variable for all varieties than the corresponding values previously reported for the absorption tests. Although these values varied considerably for all varieties, no trend was observed over the entire harvest season and, in fact, the mean value for all varieties at the beginning of harvest were nearly equal to those at the end of harvest in both years. The k parameter did not exhibit the “dampening effect” that was noted for absorption perhaps because the k and n values were less variable for desorption. Figures C31a and C31b show the comparison between k^n values for absorption and desorption conditions in 1989 and 1990, respectively, and indicate that desorption values were higher in all but two observations.

The overall mean for the k^m value in 1989 was 1.61 which was significantly influenced by test (Table 6.15); the range across tests was between 1.14 and 2.65 with a minimum significant difference of 0.62; the mean for each variety was 1.58, 1.55, and 1.69 for Tn4-86, Essex, and Leflore, respectively (Table 6.14). Figure C28a shows a general increase for all varieties from the

first week of harvest until week 11 followed by a general decrease in values. Values were nearly equal for harvest weeks 2, 7, 12, and 15 for all varieties. A comparison between the k^m values for wetting and drying is shown in Figure C32a, and indicates an equal number of desorption values that were greater or less than absorption values.

The only significant variable that contributed to the variation in the k^m value in 1990 was the interaction of test and chamber but this accounted for only 61% of the variation (Table 6.16). Across tests, the mean k^m value ranged from 1.74 to 2.53 with a minimum significant difference of 0.59 and an overall mean of 1.986 which was higher than the value found in 1989. Mean k^m values for the first and last week of harvest are very close, which is similar to the results found in 1989 (Figure C28b). Figure C32b illustrates the relationship between these values for absorption and desorption and indicates that most desorption values are higher than absorption values.

6.3.2.4. Comparison of the modified Page equation with the diffusion equation:

The diffusion equation was tested against the modified Page equation in the manner previously described for absorption in 6.3.1.4 for the same data set selected for both years (harvest week six). The computer program shown in Appendix E was used to compare the two solutions of the modified Page equation with the cellular diffusion model, as previously discussed for absorption. The values for Biot numbers and D'/λ_n^2 are given in Table 6.12 for each replication that was evaluated. The residual sum of squares for both models were also computed by the program and shown for these data to illustrate the close agreement between them. Experimental values and those estimated by the two equations are shown in Figures D3 and D4 for 1989 and 1990, respectively.

The D' value for each desorption replication was estimated by assuming an average outside radius for these materials of 0.32 cm which produced a range of 0.0003 to 0.00047 for 1989 and 0.00081 to 0.0063 for 1990. The mean value for all six observations was 0.0254 which compared with an estimate of 0.00016 given by Mensah et al. (1979) for cotyledon slices (equation 4.44). The

Biot numbers ranged from 0.2 to 175 with a mean of 44.0 which is higher than the estimate given for desorption of 0.27 by equation 4.51, and 50% higher than the value found for absorption.

The relationship between the n values and the Biot numbers matches the interesting comparison made earlier for the absorption condition, as shown in Figure D5. Large Biot numbers correspond to low n values in a similar manner noted for absorption which indicates that the rate of mass transfer is faster upon initial exposure and slower as the material approaches equilibrium. Conversely, small Biot numbers correspond to n values near one, which indicates that the external and internal resistances to moisture transport are nearly equal and the material behaves as a homogeneous body. As noted in the case for absorption, this finding requires further investigation to determine the link between these theoretical and empirical parameters.

6.4. EFFECT OF CHEMICAL COMPONENTS:

Predicted variables from the moisture conditioning tests were combined with an ancillary set of chemical variables (protein, oil, free fatty acids, carbohydrate, seed size, and harvest moisture content) that was determined for the same materials during each year of this study by another investigator (Sidhu, 1992). An analysis of variance was used to identify correlations between the chemical and predicted variables (Table 6.5). The statistical analysis showed that the test variable was generally more closely related to the predicted variables than the chemical data for these experiments in most cases. The dependent parameters were variety, week of harvest, field replication, and test in 1989 with chamber added for 1990 (Table 6.5).

A summary of the analysis of variance for the predicted parameters in both years of study is also shown in Tables 6.8 through 6.12, 6.15, and 6.16 where the significant terms for each variable are listed with the model number (from Tables 6.8 and 6.10), and the correlation coefficient (R^2 value). Chemical variables were analyzed both individually and collectively in all possible combinations (Models 6 and 13 for 1989 and 1990, in Tables 6.8 and 6.10, respectively) to select the most appropriate model that described each predicted variable as completely as possible. Evaluation

criteria for this analysis included the correlation coefficient for the particular model and the p-value for each variable. Each term in the table is listed in order of its level of significance that was determined by the model.

6.4.1. Absorption Tests:

None of the covariates from the chemical analysis were able to explain the observed variations for any of the absorption parameters in either year. For most parameters, test emerged as a significant term in the model. This was anticipated to some degree because many factors influence the test parameter including those that were measured directly (including the chemical properties that were tested along with the environmental conditions in the ab/desorption chamber) and some that were not easily determined, such as the influence of the interactions of chemical properties with variety or age of material, errors of measurement, and human errors.

6.4.2. Desorption Tests:

A summary of the analysis of variance for the predicted variables from the desorption tests that were paired with the chemical data for 1989 and 1990 is shown in Table 6.17. The covariate models for EMCR produced two significant terms in 1989 to account for the variations in this parameter, namely test and seed size as measured by the mass of 100 seeds. This added variable helped to explain the variation in EMCR by an additional 3%.

The k value exhibited an interesting response during both years of study. In 1989, significant terms in the model included test, variety-week interaction, harvest moisture content, week, and level of free fatty acids in the product. This interesting result related to a small degree to the point made earlier in the mathematical analysis that chemical composition might play a role in the magnitude of the parameters that describe the rate of moisture transfer. Although this finding is somewhat surprising, it helps to link the field conditions to those observed in the lab. The amount of oil in the product was identified as the only significant covariate that contributed to the variations

observed in the k value in the 1990 tests. A correlation procedure (PROC CORR, SAS, 1996) was used to evaluate each parameter on an individual basis, but no correlation was found between oil and the k value either year. Since the k value primarily identifies the rate of moisture transport, these findings indicate that further investigation is needed to gain more knowledge of the basic relationships between the chemical composition of a product and its possible effect on the wetting or drying rate of agricultural products.

Table 6.17. Summary of the analysis of variance for selected variables and the significant terms from the 1989 and 1990 desorption experiments. Model numbers refer to those listed in Tables 6.8 and 6.10.

Variable	Model No.	Significant Terms	R ² value
1989			
EMCR	7	Test Size	.805
k	8	Test Var*Week HMO Week FFA	.941
1990			
k	14	Test*Cmb Week Oil	.814

In summary to this chapter, the modified Page equation was shown to adequately describe the absorption and desorption behavior of field weathered soybeans. The statistical analysis attempted to identify how each of the predicted parameters from this equation (EMCR, k, and n) and the two descriptive parameters (k^n and k^m) were influenced by field weathering, experimental conditions, and the chemical properties of the material. Values of these parameters are shown for each variety and week of harvest in Figures C19 through C24 and Figures C26 through C40 for absorption and desorption, respectively. A comparison by year and mode of sorption showed that some parameters had more variation than others, but when compared to the harvest moisture a few similarities were found. Specifically, for the absorption parameters, it appeared that the data might be divided into three distinct periods that paralleled weather conditions: (1) from physiological maturity (PM) to field maturity (two to three weeks after PM); (2) from field maturity to a time when

weather effects began to cause chemical changes, and (3) the time beyond 10 weeks when weather deterioration appeared to become more predominant.

The effect of field exposure, perhaps, may be seen most clearly by comparing the change of the predicted and descriptive parameters for 1990 absorption with changes in the chemical components. During the first three weeks the beans were changing as shown by the chemical analysis of Sidhu (1992) for the same material. The k and k^n values showed a general increasing trend after week three. However, the n value increased from physiological maturity to week three and remained close to one from week three to week nine (when harvest moisture was lowest) after which it began to decrease (Figure C20b). An inverse to this pattern was seen for the k^m value (Figure C22b). The observed changes over the harvest period for these two parameters may indicate that they are more sensitive to the changes occurring within the seed during increased field exposure. The k^m value seemed to be directly related to the harvest moisture and inversely related to relative carbohydrate content, as indicated by Sidhu (1992). The general pattern of variability of harvest moisture and k^m over the entire harvest period was reflected directly by protein, free fatty acid, and oil. These patterns were somewhat evident for the first half of the harvest for 1989 absorption but were not evident for desorption in either year. However, desorption k values were significantly related to free fatty acid in 1989 and oil in 1990.

While the overall value of k determines the fundamental shape of the moisture ratio curve and remained somewhat constant over the 16 week period with only a slight increase with field exposure, the n and k^m values more closely matched the trend seen from the chemical changes in the bean for absorption in 1990. This may be seen when Figures C20b and C22b are compared to Figure A6 and these are, in turn, compared with the data by Sidhu (1992).

It should be emphasized that the weather and relative humidity during the 1990 harvest (Figure A2) showed a more stable pattern from week four through week 10. During this period the bean had reached field maturity and after this time carbohydrate decline was noted (Sidhu, 1992). This implies that for the part of the harvest period where the bean had its highest quality, it appeared

to be a more homogeneous body. Before and after this time the bean was suspected of being less homogeneous as indicated by a decreasing n value. It has been identified in Chapters III and IV that the interaction of chemical components within the bean may have an impact on the diffusion coefficient (equation 4.61). Also, equation (4.76) identifies that the interaction may be associated with $(kt)^m$ where k^m was related to a spatial term that remains constant when dry matter (DM) remains constant. For a given sample, DM remains constant during a sorption test and k^m remains independent of time (equation 4.78) which leaves t^m as the only time dependent term (equation 4.77). However, as harvest progressed during this experiment, DM did not remain constant (Sidhu, 1992) and k^m would be expected to be different across weeks. Data in this experiment do not permit a full evaluation of k^m or t^m but indicate that the interaction of chemical components may exist during absorption and that further study is required to investigate this relationship more closely. It should be stressed that this observation was most evident in the 1990 absorption data. The fact that it was not evident in the 1989 absorption parameters or the desorption parameters of either year may be due to the variability caused by field weathering which was reflected in the parameter values to such an extent that the relationship was masked.

CHAPTER VII

SUMMARY AND CONCLUSIONS

Fundamental relationships were established which considered the physical and chemical characteristics of soybeans seeds. These relationships were applied to sorption data from seeds that were exposed to field weathering for normal and extended periods prior to harvest. Links between the physical and chemical properties were found for some cases.

An investigation of the morphological features of soybean seeds led to a sorption test with two varieties which included covering the hilum region (approximately 10% of the total surface area) with wax. It was determined that no preferential path to moisture vapor exchange with the atmosphere existed through this region for either absorption or desorption.

Absorption and desorption characteristics were determined for three varieties of soybean seeds that were harvested over 16 weeks in two crop years. Harvest began at physiological maturity and extended well beyond a normal harvest period. Desorption tests followed absorption tests in all cases under near constant temperature and air flow conditions. Experimental data for harvest weeks 3, 6, 11, and 16 are shown for both years with the predicted estimates.

The empirically based modified Page equation was used to estimate the moisture equilibrium value by non-linear regression and found to adequately describe both absorption and desorption behavior. Equation parameters k and n were used to generate two descriptive parameters, k^n and k^m , for each replication of variety and week of harvest to help identify the effects of field weathering. Some parameters were found to be more sensitive to harvest moisture conditions than others. For example, the absorption n and k^m values in 1990 closely followed the week-to-week pattern that was observed for harvest moisture for all varieties. A similar but less pronounced pattern was observed for the absorption k and k^n values after the first three weeks of harvest for that year. A close match of these parameters with the harvest moisture data was not found in 1989 perhaps because of the variability that was found in these materials for that year. For desorption, these parameters were

more variable for both years, which was somewhat surprising because the EMCR values were more variable for absorption, especially in 1990. The finding that n and k^m values were closely matched with harvest moisture requires more study to determine the extent of a physical or chemical link between these variables and other product properties.

The level of protein, oil, free fatty acids, harvest moisture, and seed size were merged with the variables found by regression from the modified Page equation that characterized the absorption and desorption response. The statistical model that accounted for most of the variation in k for 1989 contained the covariates of harvest moisture and free fatty acid, while the corresponding model in 1990 contained the covariate of oil. Also in 1989, the desorption EMCR value was correlated to seed size. These correlations were not too surprising when consideration is given to the structure and chemical composition of the seed and the interaction of these characteristics with moisture during transport.

The fact that chemical components affect the rate and extent of moisture transfer in soybean seeds suggests the need for further investigation. A non-destructive technique is suggested to facilitate measurements with the same sample during a moisture transfer cycle, which occurs every year in the field and in storage environments where seeds are fully exposed to a wide range of environmental conditions. The results of such an effort might enable engineers to improve existing designs of drying and storage equipment and controls and to maintain grain quality.

The cellular diffusion model was presented to develop reasonable estimates for the terms that describe the absorption and desorption characteristics of soybean seeds. The diffusion model was paired with a selected set of sorption data to determine estimates for the theoretical parameters (Biot number and diffusion term) by regression. Regression estimates from the data were an order of magnitude higher than the extrapolated estimates calculated from desorption data found in the literature (note that a different geometric shape was used). The diffusion model produced estimates for the moisture ratio that were in very good agreement with the data and were comparable to those produced by the modified Page equation in most cases. The most important result from this

comparison was that the Biot number had a similar effect on the relationship that describes the rate of moisture transport (for both absorption and desorption) as does the n value in the modified Page equation. Low Biot numbers produced a similar sorption curve response to n values near one, which is the case for homogeneous bodies. High Biot numbers generated a curve shape that resembled the same response as n values lower than one, which is the case for non-homogeneous materials.

Based on the findings of the experimental observations, the analytical and statistical evaluation of the results, and the associated investigation of the harvest moisture and chemical data with the same materials, the following conclusions were drawn:

- 1) There is no preferential path to moisture vapor transfer through the seed coat hilum.
- 2) The cellular diffusion equation adequately describes the absorption and desorption behavior of soybeans.
- 3) The modified Halsey equation needs further development in the high and low relative humidity range for weathered soybeans.
- 4) The modified Page's equation performed very satisfactorily when used to describe the absorption and desorption behavior of field weathered soybeans in this experiment.
- 5) Parameters generated from the modified Page equation should be investigated further to determine the potential link between the k , n , k^n , and k^m and product composition.
- 6) A potential link exists between the Biot number and diffusion term with product composition.
- 7) There is an association of the analytical Biot number with the empirical n value.
- 8) The rate of desorption as described by the k value was shown to be significantly affected in this experiment by moisture at harvest and free fatty acids in 1989 and oil content in 1990.
- 9) Future research in this important area should incorporate image analysis such as magnetic resonance imaging (MRI) or other similar non-destructive techniques to gain a more complete understanding of the mechanisms that affect internal moisture movement within seeds during moisture conditioning.

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APPENDICES

APPENDIX A

Harvest Data and Chamber Conditions for Field Weathered Soybeans

Table A1. Harvest dates during each week of study for soybean varieties Tn4-86, Essex, and Leflore during the 1989 season.

Week of Harvest	Date of Harvest for each variety		
	Tn4-86	Essex	Leflore
1	09-26-89	10-03-89	10-24-89
2	10-03-89	10-10-89	10-31-89
3	10-10-89	10-17-89	11-07-89
4	10-17-89	10-24-89	11-14-89
5	10-24-89	10-31-89	11-21-89
6	10-31-89	11-07-89	11-28-89
7	11-07-89	11-14-89	12-05-89
8	11-14-89	11-21-89	12-12-89
9	11-21-89	11-28-89	12-19-89
10	11-28-89	12-05-89	12-26-89
11	12-05-89	12-12-89	01-02-90
12	12-12-89	12-19-89	01-09-90
13	12-19-89	12-26-89	01-16-90
14	12-26-89	01-02-90	01-23-90
15	01-02-90	01-09-90	01-30-90
16	01-09-90	01-16-90	02-06-90

Table A2. Harvest dates during each week of study for soybean varieties Tn4-86, Essex, and Leflore during the 1990 season.

Week of Harvest	Date of Harvest for each variety		
	Tn4-86	Essex	Leflore
1	09-19-90	09-26-90	10-17-90
2	09-26-90	10-03-90	10-24-90
3	10-03-90	10-10-90	10-31-90
4	10-10-90	10-17-90	11-07-90
5	10-17-90	10-24-90	11-14-90
6	10-24-90	10-31-90	11-21-90
7	10-31-90	11-07-90	11-28-90
8	11-07-90	11-14-90	12-05-90
9	11-14-90	11-21-90	12-12-90
10	11-21-90	11-28-90	12-19-90
11	11-28-90	12-05-90	12-26-90
12	12-05-90	12-12-90	01-02-91
13	12-12-90	12-19-90	01-09-91
14	12-19-90	12-26-90	01-16-91
15	12-26-90	01-02-91	01-23-91
16	01-02-91	01-09-91	01-30-91

Weather Data for the 1989 Harvest

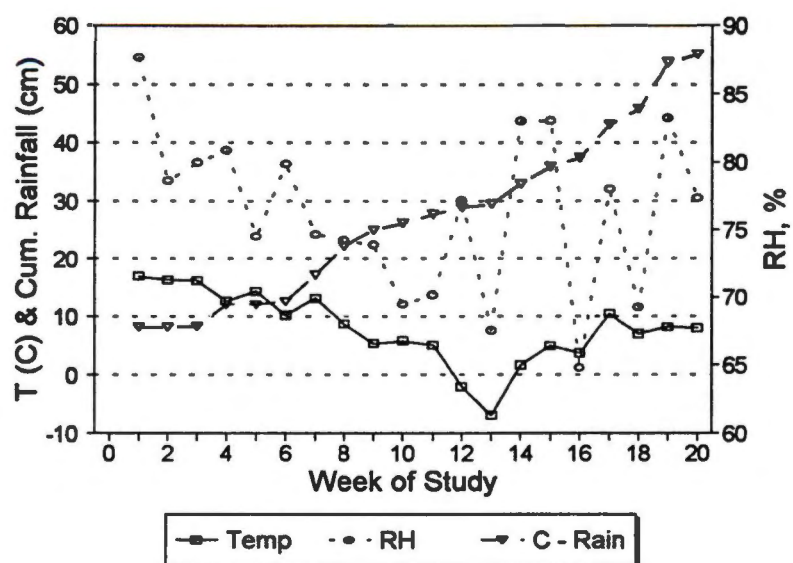


Figure A1. Cumulative rainfall and weekly mean temperature and relative humidity levels during the 1989 harvest season.

Weather Data for the 1990 Harvest

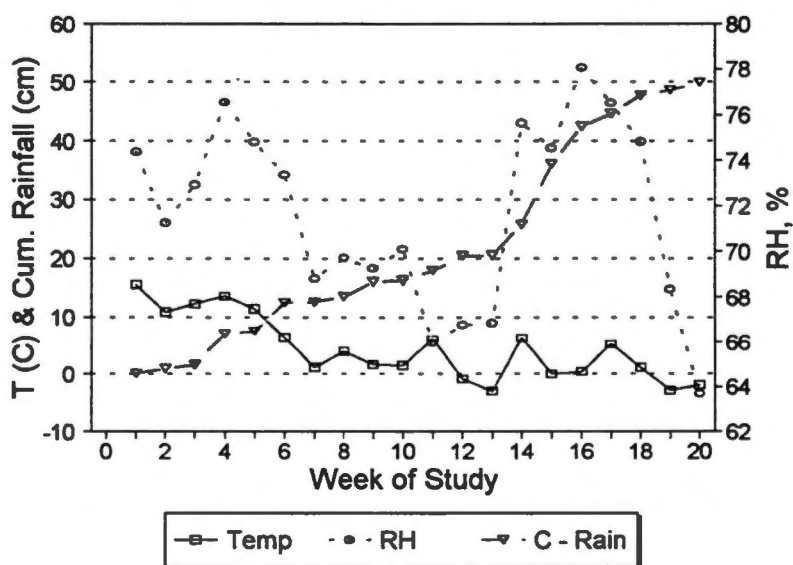


Figure A2. Cumulative rainfall and weekly mean temperature and relative humidity levels during the 1990 harvest season.

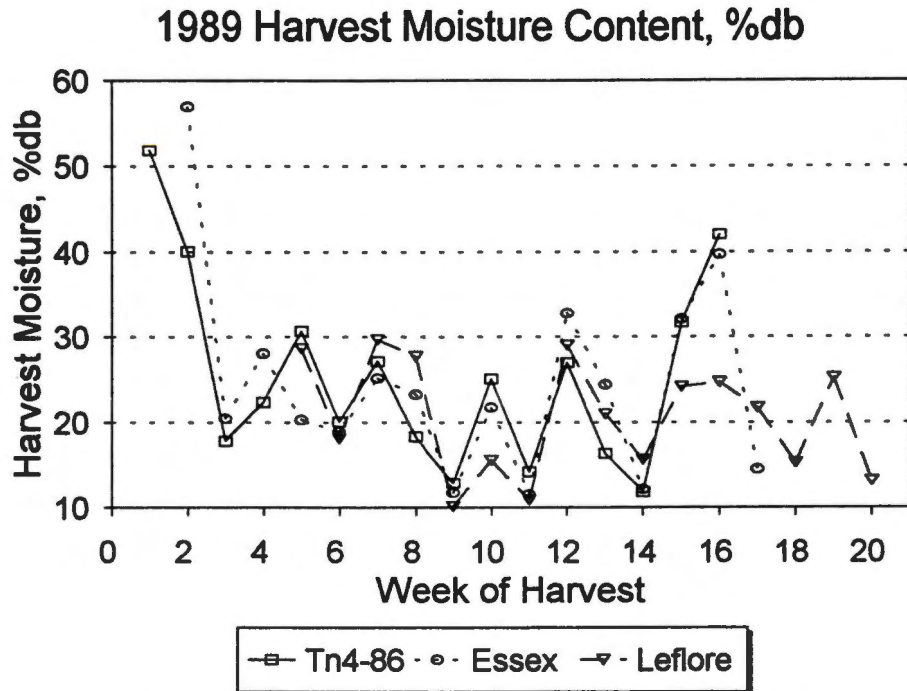


Figure A3. Moisture content for Tn4-86, Essex, and Leflore soybeans during the 1989 harvest season by calendar days.

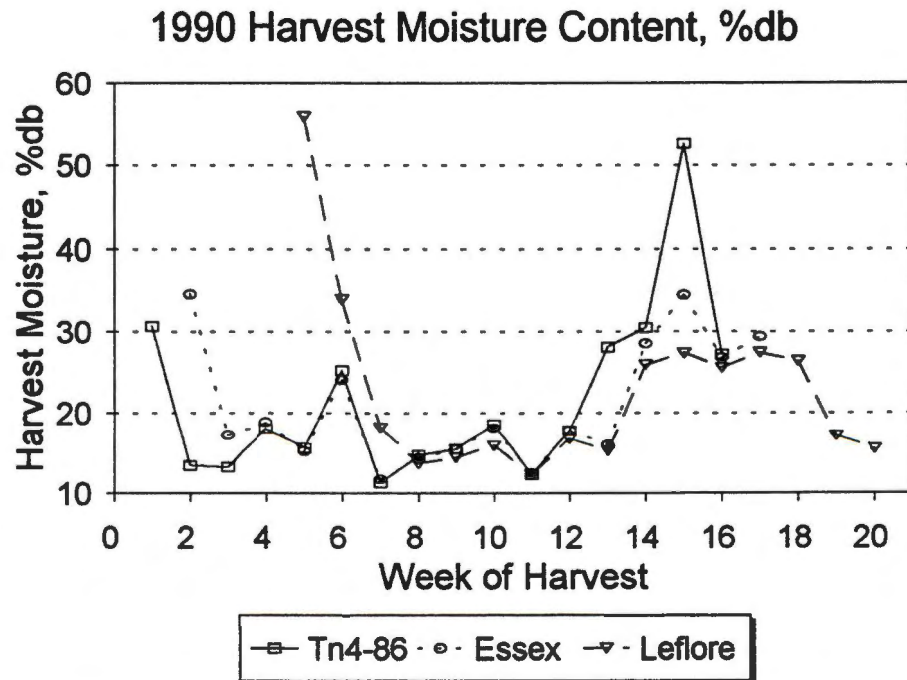


Figure A4. Moisture content for Tn4-86, Essex, and Leflore soybeans during the 1990 harvest season by calendar days.

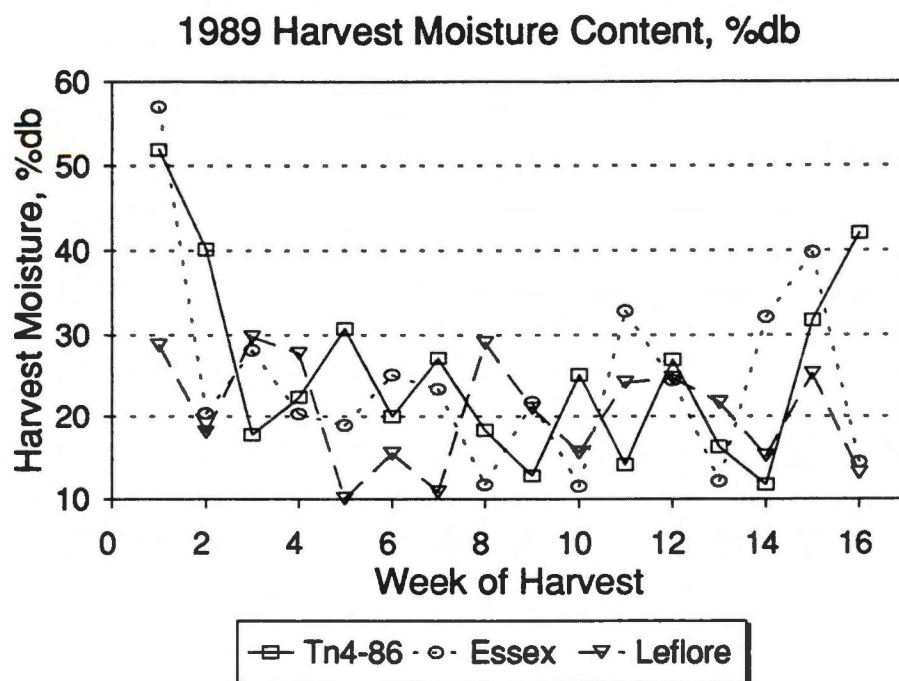


Figure A5. Moisture content for Tn4-86, Essex, and Leflore soybeans during the 1989 harvest season with weeks overlaid.

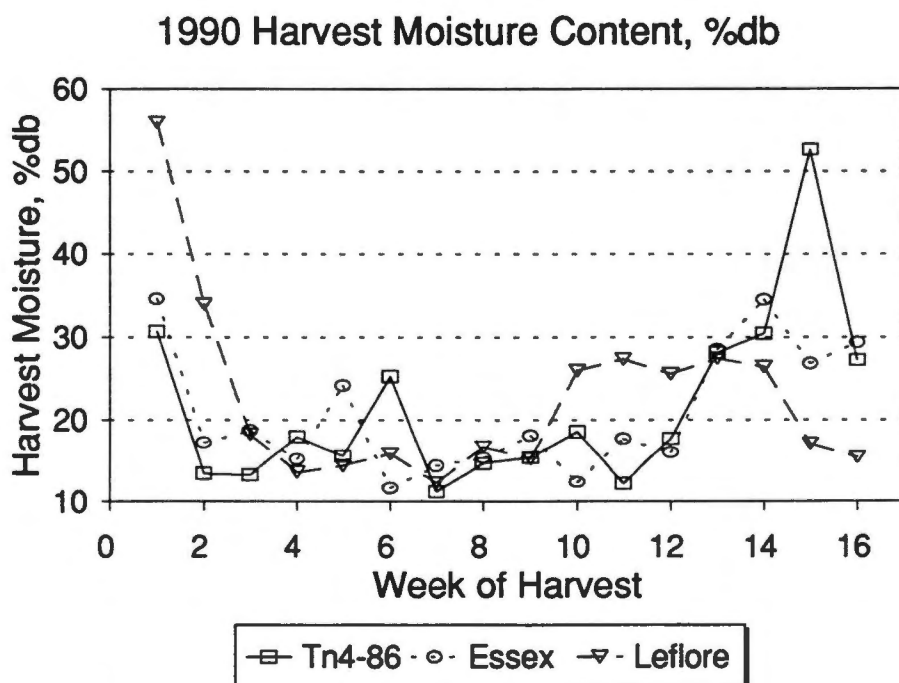


Figure A6. Moisture content for Tn4-86, Essex, and Leflore soybeans during the 1990 harvest season with weeks overlaid.

Absorption Conditions for 1989 Tests

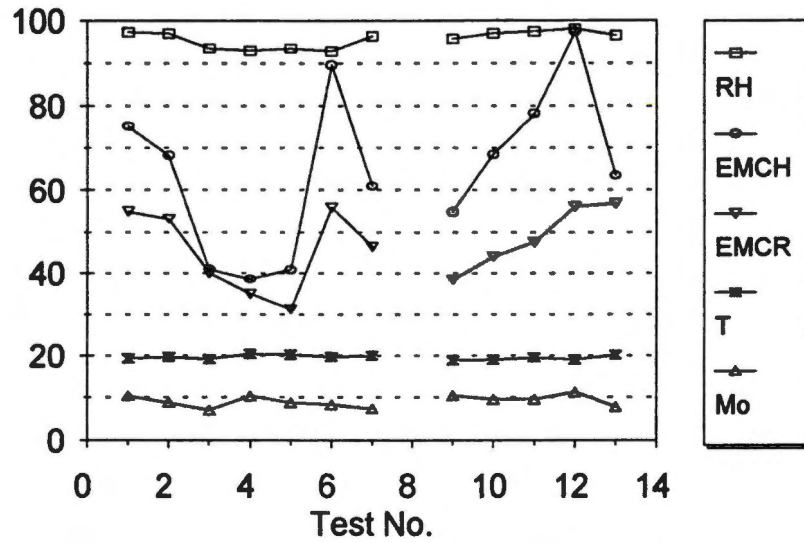


Figure A7. Mean relative humidity, temperature, initial moisture content, EMCH, and EMCR during the 1989 absorption tests.

Absorption Conditions for 1990 Tests

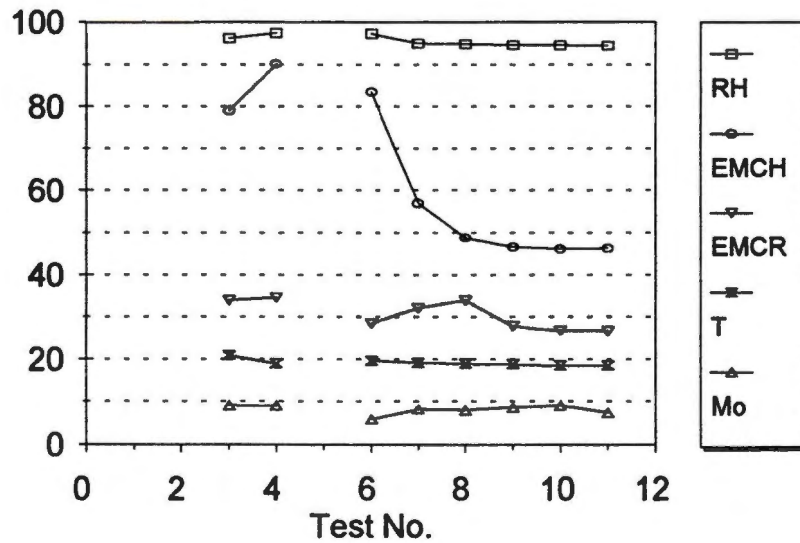


Figure A8. Mean relative humidity, temperature, initial moisture content, EMCH, and EMCR during the 1990 absorption tests.

RH and EMCH for 1990 Absorption Tests

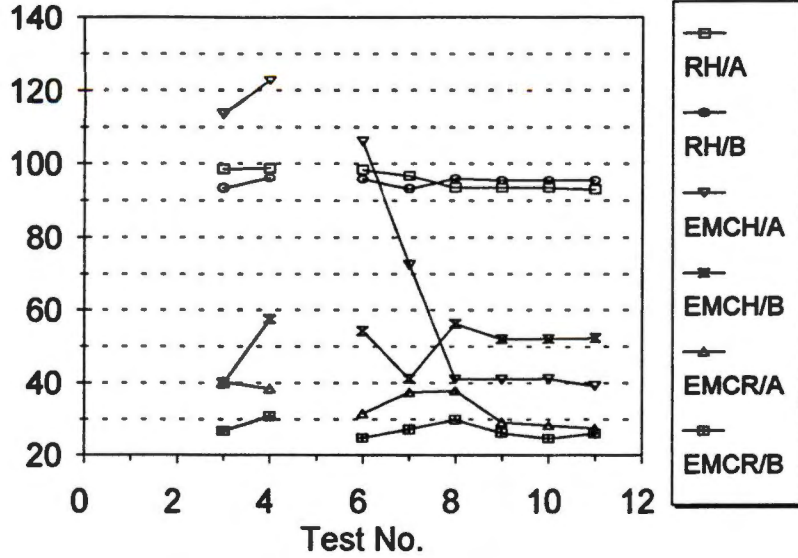


Figure A9. Mean relative humidity, EMCH, and EMCR for each chamber during the 1990 absorption tests.

Temp and Mo for 1990 Absorption Tests

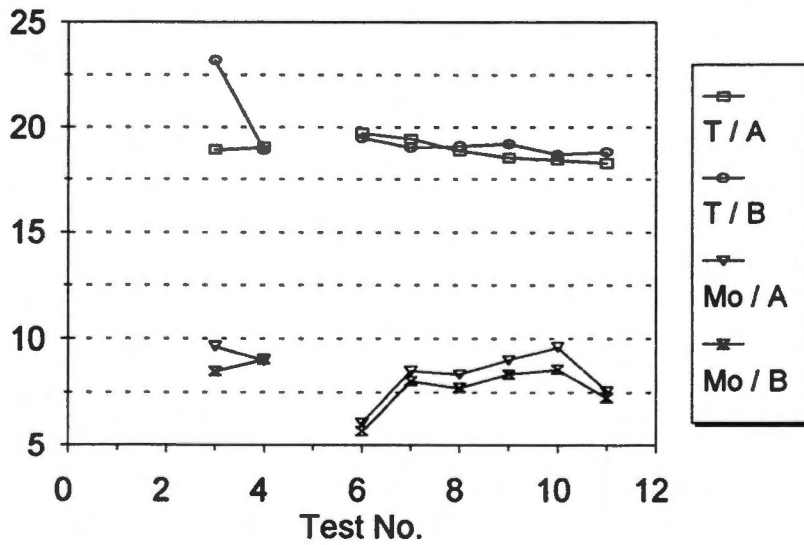


Figure A10. Mean temperature and initial moisture content for each chamber during the 1990 absorption tests.

Desorption Conditions for 1989 Tests

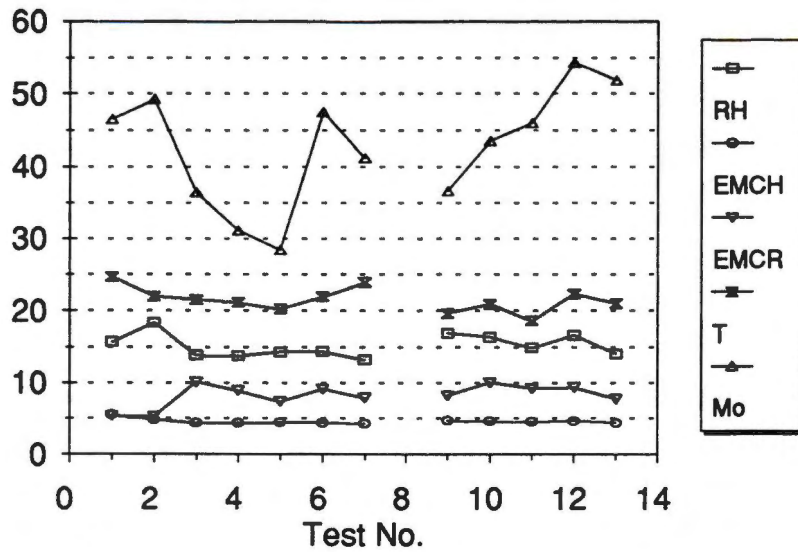


Figure A11. Mean relative humidity, temperature, initial moisture content, EMCH, and EMCR during the 1989 desorption tests.

Desorption Conditions for 1990 Tests

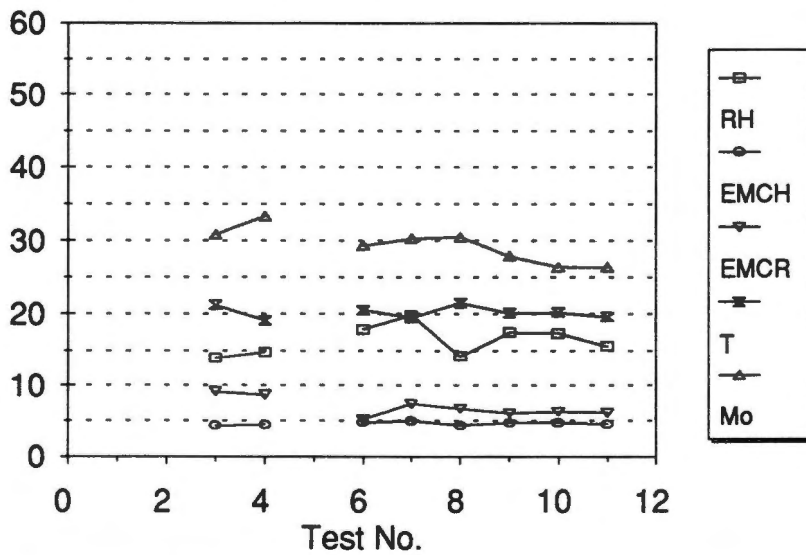


Figure A12. Mean relative humidity, temperature, initial moisture content, EMCH, and EMCR during the 1990 desorption tests.

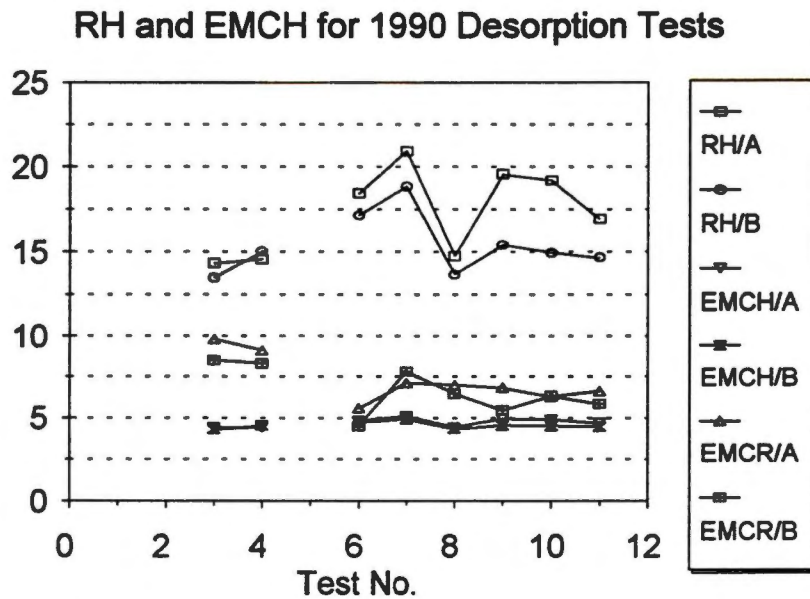


Figure A13. Mean relative humidity, EMCH, and EMCR for each chamber during the 1990 desorption tests.

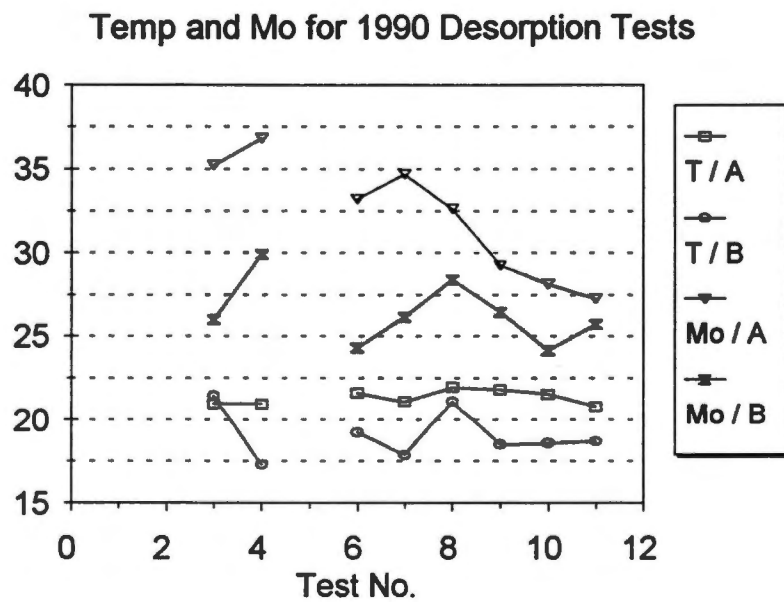


Figure A14. Mean temperature and initial moisture content for each chamber during the 1990 desorption tests.

APPENDIX B

**Chamber Conditions and Moisture Ratio Graphs
for Wax Treated Soybeans**

Chamber conditions during absorption tests with waxed and unwaxed soybeans

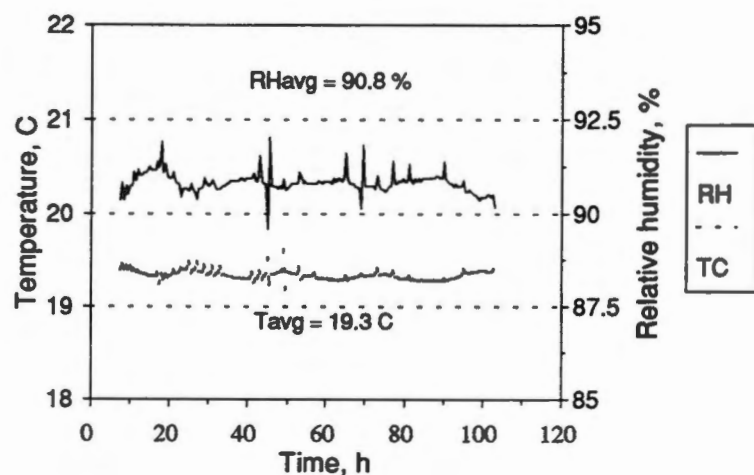


Figure B1. Mean temperature and relative humidity levels during the absorption tests with wax covered and uncovered control soybeans.

Chamber conditions during desorption tests with waxed and unwaxed soybeans

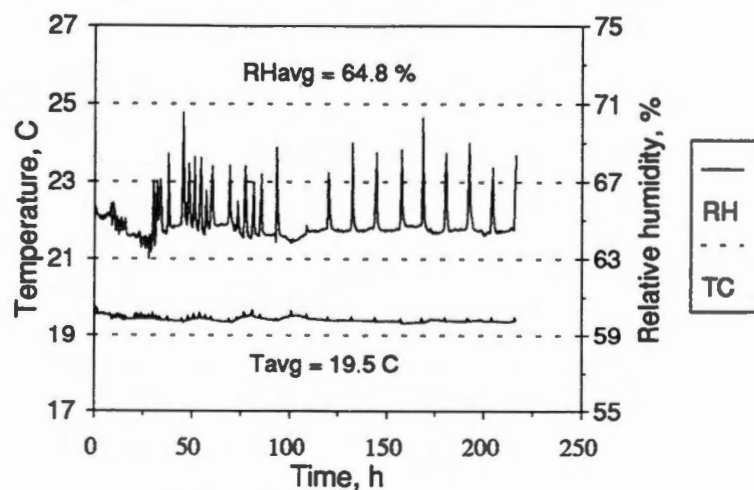


Figure B2. Mean temperature and relative humidity levels during the desorption tests with wax covered and uncovered control soybeans.

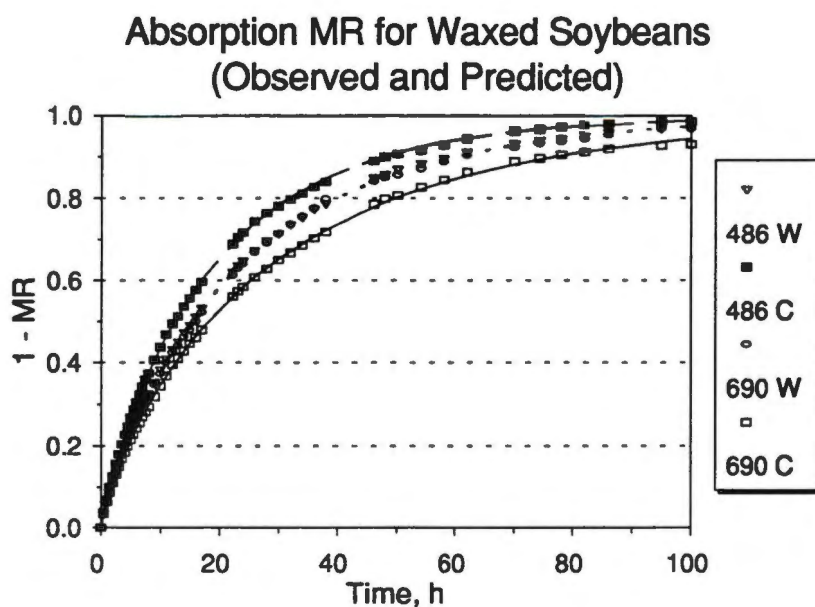


Figure B3. Observed and predicted absorption moisture ratios plotted against time for Tn4-86 and Tn6-90 soybeans with a wax covered hilum (W) and an uncovered control (C).

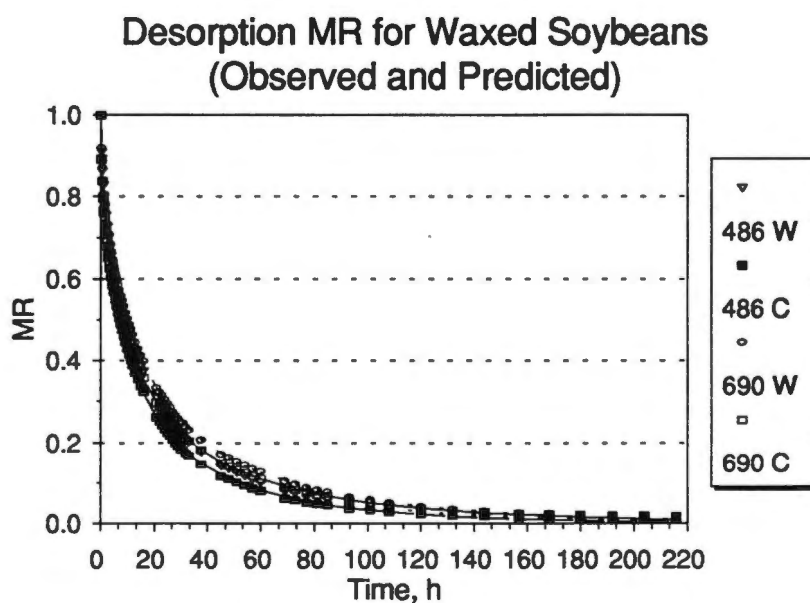


Figure B4. Observed and predicted desorption moisture ratios plotted against time for Tn4-86 and Tn6-90 soybeans with a wax covered hilum (W) and an uncovered control (C).

APPENDIX C

**Experimental Results and Predicted Parameters for Sorption Tests
with Weathered Soybeans**

Table C1. Summary of observed and predicted variables for Tn4-86 soybeans under absorption conditions in 1989.

YR	Vr	Wk	Rep	Exp	Mo	T	RH	EMCH	EMCR	k	n	k ^a	k ^m	pseudo R ²
89	T	1	1	10	10.0	19.0	97.3	73.5	44.4	0.0350	1.0000	0.0350	1.000	0.999
89	T	1	2	11	9.4	19.9	97.3	72.2	47.6	0.0350	0.9893	0.0362	1.036	0.999
89	T	1	3	6	7.8	19.8	98.2	95.6	53.6	0.0265	1.0000	0.0265	1.000	0.989
89	T	2	1	10	9.8	19.1	97.1	69.3	42.3	0.0365	0.9453	0.0437	1.199	0.995
89	T	3	1	7	8.7	19.5	96.8	65.1	43.3	0.0284	0.9318	0.0362	1.275	0.996
89	T	3	3	9	10.2	19.2	95.8	54.1	37.0	0.0332	0.7910	0.0676	2.038	0.999
89	T	4	2	11	9.5	19.6	97.7	80.6	49.8	0.0251	1.0000	0.0251	1.000	0.996
89	T	4	3	12	10.3	19.1	98.3	100.8	63.3	0.0243	1.0000	0.0243	1.000	0.996
89	T	5	2	5	8.6	20.4	93.8	41.4	31.4	0.0526	0.6382	0.1527	2.901	0.988
89	T	6	1	7	5.4	19.9	96.5	61.5	43.6	0.0278	1.0000	0.0278	1.000	0.972
89	T	6	3	9	9.5	18.9	95.9	55.3	36.8	0.0284	0.9405	0.0351	1.236	1.000
89	T	7	2	11	10.3	19.6	97.6	79.1	49.0	0.0313	0.9479	0.0374	1.198	0.999
89	T	7	3	12	10.5	19.1	98.3	99.7	59.6	0.0253	0.9763	0.0276	1.091	0.997
89	T	8	1	1	9.8	19.5	97.5	76.7	46.8	0.0234	0.8390	0.0428	1.831	0.990
89	T	8	2	2	8.1	19.8	97.1	69.8	49.1	0.0248	0.9062	0.0351	1.415	0.998
89	T	8	3	3	7.0	19.2	93.9	42.3	39.5	0.0286	0.7042	0.0819	2.861	0.989
89	T	9	1	4	8.3	20.6	93.2	39.0	29.6	0.0375	0.7053	0.0986	2.633	0.990
89	T	9	2	5	9.1	20.2	93.9	41.8	30.2	0.0531	0.5419	0.2037	3.839	0.991
89	T	9	3	6	8.8	19.4	98.0	88.5	47.0	0.0244	1.0000	0.0244	1.000	0.942
89	T	11	1	7	8.4	20.4	96.4	59.8	44.9	0.0268	0.9152	0.0364	1.359	0.990
89	T	11	3	9	12.2	19.0	95.9	54.9	39.1	0.0269	0.6744	0.0874	3.245	0.995
89	T	12	1	10	9.8	19.2	96.9	66.3	42.9	0.0320	1.0000	0.0320	1.000	0.998
89	T	12	3	12	11.5	19.2	98.1	92.1	52.4	0.0281	0.9516	0.0334	1.189	0.994
89	T	13	1	4	9.7	20.6	92.9	37.9	35.9	0.0321	0.6587	0.1038	3.234	0.972
89	T	14	1	13	7.5	20.2	96.9	65.8	54.7	0.0244	0.9630	0.0280	1.147	0.993
89	T	14	2	13	8.1	20.2	96.8	64.9	56.6	0.0252	0.9553	0.0297	1.179	0.995
89	T	14	3	13	7.3	20.3	96.6	62.7	56.2	0.0253	0.9618	0.0292	1.151	0.997
89	T	16	2	2	10.7	19.9	96.8	65.5	52.3	0.0280	0.9077	0.0390	1.391	0.999
89	T	16	3	3	5.5	19.3	93.4	39.9	38.7	0.0322	0.6463	0.1086	3.371	0.984
Summary Statistics (n = 29)				Max	12.2	20.6	98.3	100.8	63.3	0.0531	1	0.2037	3.839	1.000
				Min	5.4	18.9	92.9	37.9	29.6	0.0234	0.5419	0.0243	1	0.942
				Avg	9.0	19.7	96.4	66.1	45.4	0.0304	0.8790	0.0548	1.683	0.991
				Std	1.5	0.5	1.6	18.0	8.6	0.0072	0.1382	0.0423	0.880	

Table C2. Summary of observed and predicted variables for Essex soybeans under absorption conditions in 1989.

YR	Vr	Wk	Rep	Exp	Mo	T	RH	EMCH	EMCR	k	n	k ^a	k ^m	pseudo R ²	
89	E	2	1	1	12.5	19.3	97.6	79.6	61.2	0.0182	1.0000	0.0182	1.000	0.991	
89	E	2	2	2	12.1	19.7	97.2	70.4	57.6	0.0238	0.7627	0.0577	2.429	0.974	
89	E	3	1	7	8.8	20.1	96.5	61.3	46.1	0.0250	0.8619	0.0417	1.664	0.978	
89	E	4	1	10	9.4	19.1	97.2	70.7	41.8	0.0423	0.9928	0.0433	1.023	0.998	
89	E	4	2	11	10.0	19.5	97.8	82.6	44.7	0.0310	1.0000	0.0310	1.000	0.993	
89	E	4	3	12	11.0	19.2	98.4	104.4	56.7	0.0287	1.0000	0.0287	1.000	0.994	
89	E	5	3	6	8.5	20.0	98.2	93.6	76.3	0.0107	0.7370	0.0352	3.300	0.990	
89	E	6	1	7	8.2	20.2	96.5	60.7	48.1	0.0203	0.7644	0.0509	2.503	0.980	
89	E	6	3	9	10.9	18.9	96.0	55.7	42.9	0.0190	0.6398	0.0793	4.168	0.999	
89	E	7	1	10	9.7	19.2	97.0	67.6	44.7	0.0356	0.9135	0.0475	1.334	0.999	
89	E	7	2	11	9.2	19.7	97.4	75.3	46.9	0.0291	1.0000	0.0291	1.000	0.995	
89	E	7	3	12	9.6	19.2	98.2	96.4	50.0	0.0290	0.9431	0.0355	1.223	0.997	
89	E	8	1	1	11.2	19.5	97.4	75.2	59.4	0.0186	0.9765	0.0205	1.098	0.981	
89	E	8	2	2	7.8	19.8	97.0	68.4	53.3	0.0247	0.6898	0.0779	3.151	0.979	
89	E	9	1	4	8.8	20.1	93.0	38.3	27.5	0.0493	0.7910	0.0924	1.876	0.984	
89	E	9	3	6	11.1	19.1	98.2	95.5	50.7	0.0260	1.0000	0.0260	1.000	0.982	
89	E	11	1	7	8.7	20.3	96.4	59.6	42.4	0.0295	0.8977	0.0423	1.434	0.980	
89	E	11	3	9	9.5	19.1	95.8	54.2	33.5	0.0394	0.7625	0.0850	2.156	0.995	
89	E	12	1	10	9.5	19.2	96.9	66.9	44.1	0.0367	0.9812	0.0390	1.064	1.000	
89	E	12	2	11	9.2	19.5	97.9	85.2	46.6	0.0312	1.0000	0.0312	1.000	0.998	
89	E	12	3	12	16.7	19.2	98.2	94.4	58.5	0.0285	0.9936	0.0291	1.023	0.995	
89	E	13	1	4	10.7	21.0	93.0	38.4	39.1	0.0110	0.5746	0.0750	6.804	0.995	
89	E	13	2	5	8.8	20.4	93.4	40.0	29.0	0.0809	0.6544	0.1930	2.384	0.992	
89	E	13	3	6	8.1	20.4	97.7	80.2	47.5	0.0281	0.9623	0.0322	1.144	0.988	
89	E	15	1	13	9.0	20.3	96.7	62.9	47.8	0.0267	1.0000	0.0267	1.000	0.990	
89	E	15	2	13	9.1	20.4	96.7	63.8	54.5	0.0268	1.0000	0.0268	1.000	0.991	
89	E	15	3	13	7.7	20.3	96.7	62.9	44.7	0.0274	1.0000	0.0274	1.000	0.993	
89	E	16	1	1	10.5	19.6	97.3	72.8	57.7	0.0227	1.0000	0.0227	1.000	0.983	
89	E	16	2	2	6.4	19.9	96.9	66.7	51.2	0.0321	0.7418	0.0780	2.430	0.969	
Summary Statistics (n = 29)					Max	16.7	21	98.4	104.4	76.3	0.0809	1	0.1930	6.804	1.000
					Min	6.4	18.9	93	38.3	27.5	0.0107	0.5746	0.0182	1	0.969
					Avg	9.75	19.7	96.8	70.5	48.4	0.0294	0.8842	0.0491	1.800	0.989
					Std	1.87	0.53	1.41	16.74	9.80	0.0127	0.1349	0.0345	1.263	

Table C3. Summary of observed and predicted variables for Leflore soybeans under absorption conditions in 1989.

YR	Vr	Wk	Rep	Exp	Mo	T	RH	EMCH	EMCR	k	n	k ^a	k ^m	pseudo R ²	
89	L	2	1	1	10.4	19.4	97.6	78.5	51.6	0.0223	0.9732	0.0246	1.107	0.996	
89	L	2	2	2	10.8	19.7	97.1	70.0	56.1	0.0220	1.0000	0.0220	1.000	0.997	
89	L	3	1	7	6.5	20.3	96.5	60.8	47.1	0.0232	1.0000	0.0232	1.000	0.980	
89	L	3	3	9	11.6	19.2	95.8	54.0	40.2	0.0267	0.8279	0.0499	1.865	0.998	
89	L	6	1	7	6.4	20.3	96.4	60.4	47.1	0.0235	1.0000	0.0235	1.000	0.980	
89	L	6	3	9	9.9	18.8	96.0	56.2	34.0	0.0245	0.8112	0.0494	2.014	0.999	
89	L	7	1	10	9.2	19.2	97.0	67.8	46.7	0.0318	0.9730	0.0349	1.098	0.999	
89	L	7	2	11	9.2	19.7	97.5	77.0	48.2	0.0258	1.0000	0.0258	1.000	0.996	
89	L	7	3	12	10.2	19.2	98.3	98.0	59.8	0.0231	1.0000	0.0231	1.000	0.988	
89	L	8	1	1	8.9	19.6	97.4	74.2	51.1	0.0236	0.9733	0.0260	1.105	0.997	
89	L	8	2	2	7.1	19.8	97.0	67.4	53.0	0.0299	0.8782	0.0459	1.533	1.000	
89	L	8	3	3	8.1	19.3	93.7	41.4	39.1	0.0275	0.7482	0.0679	2.472	0.984	
89	L	9	1	4	13.3	20.5	93.5	40.0	40.5	0.0209	0.6146	0.0928	4.440	0.955	
89	L	9	3	6	7.8	20.1	98.0	89.4	61.8	0.0187	0.9720	0.0209	1.118	0.989	
89	L	11	1	7	7.0	20.3	96.4	60.3	55.9	0.0161	0.7724	0.0411	2.560	0.992	
89	L	11	3	9	10.5	19.1	95.8	54.6	44.9	0.0131	0.6286	0.0656	4.999	0.998	
89	L	12	1	10	9.4	19.2	96.9	67.1	46.2	0.0401	1.0000	0.0401	1.000	0.988	
89	L	12	2	11	9.8	19.8	97.4	74.3	47.9	0.0387	1.0000	0.0387	1.000	0.993	
89	L	12	3	12	10.3	19.2	98.2	94.4	48.5	0.0285	1.0000	0.0285	1.000	0.989	
89	L	13	1	4	11.6	20.3	93.2	39.0	38.5	0.0278	0.6961	0.0827	2.969	0.996	
89	L	13	2	5	9.0	20.4	93.6	40.6	34.9	0.0368	0.4996	0.1922	5.217	0.983	
89	L	13	3	6	6.7	20.1	97.9	85.3	54.0	0.0181	1.0000	0.0181	1.000	0.986	
89	L	14	1	13	7.4	20.3	96.6	62.5	58.9	0.0205	0.8991	0.0303	1.481	0.997	
89	L	14	2	13	7.7	20.3	96.6	62.7	70.8	0.0181	1.0000	0.0181	1.000	0.993	
89	L	15	1	13	8.0	20.3	96.6	62.7	59.0	0.0211	0.8946	0.0317	1.502	0.993	
89	L	15	2	13	7.6	20.3	96.6	62.7	59.7	0.0201	0.9444	0.0250	1.243	0.996	
89	L	15	3	13	7.6	20.2	96.8	64.9	61.8	0.0198	0.9301	0.0261	1.315	0.995	
89	L	16	1	1	9.7	19.9	97.2	70.3	56.6	0.0199	0.9016	0.0292	1.470	0.999	
89	L	16	3	3	7.9	19.4	93.6	40.7	43.6	0.0224	0.6853	0.0741	3.303	0.992	
Summary Statistics (n = 29)					Max	13.3	20.5	98.3	98	70.8	0.0401	1	0.1922	5.217	1.000
					Min	6.4	18.8	93.2	39	34	0.0131	0.4996	0.0181	1	0.955
					Avg	8.95	19.8	96.4	64.7	50.3	0.0243	0.8836	0.0438	1.821	0.991
					Std	1.69	0.50	1.45	15.49	8.80	0.0063	0.1405	0.0343	1.215	

Table C4. Summary of observed and predicted variables for Tn4-86 soybeans under absorption conditions in 1990.

YR	Vr	Wk	Rep	Exp	Cmb	Mo	T	RH	EMCH	EMCR	k	n	k ^a	k ^m	pseudo R ²	
90	T	1	1	7	A	8.1	19.3	98.9	129.0	38.7	0.0129	0.9442	0.0164	1.275	0.999	
90	T	1	2	8	A	8.7	18.8	93.8	41.7	42.9	0.0144	0.8515	0.0270	1.877	0.992	
90	T	1	3	3	A	10.0	18.8	98.7	116.3	40.8	0.0122	1.0000	0.0122	1.000	0.998	
90	T	2	1	7	B	8.6	19.0	95.6	53.0	27.9	0.0130	1.0000	0.0130	1.000	0.997	
90	T	2	2	8	B	8.4	19.0	96.2	58.2	32.1	0.0151	1.0000	0.0151	1.000	0.992	
90	T	3	1	4	A	8.5	19.0	98.8	126.8	39.5	0.0241	0.9629	0.0277	1.148	0.995	
90	T	3	2	9	A	8.8	18.5	93.8	41.6	27.0	0.0186	1.0000	0.0186	1.000	0.992	
90	T	3	3	6	A	7.2	19.7	98.6	109.9	32.1	0.0183	1.0000	0.0183	1.000	0.964	
90	T	4	1	4	B	8.5	19.0	96.2	57.7	28.5	0.0323	0.9575	0.0374	1.157	0.995	
90	T	4	2	9	B	8.5	19.2	95.7	53.1	24.3	0.0289	0.9875	0.0302	1.045	0.994	
90	T	4	3	6	B	5.7	19.5	95.9	55.0	23.6	0.0248	1.0000	0.0248	1.000	0.985	
90	T	5	1	7	A	8.7	19.4	96.8	65.1	34.9	0.0242	0.9219	0.0324	1.337	0.998	
90	T	5	2	8	A	8.3	18.9	93.7	41.4	34.3	0.0246	1.0000	0.0246	1.000	0.989	
90	T	5	3	3	A	8.7	18.9	98.6	112.8	35.4	0.0236	1.0000	0.0236	1.000	0.962	
90	T	6	1	7	B	7.0	19.0	93.8	41.6	26.6	0.0313	0.9353	0.0391	1.251	0.999	
90	T	6	2	8	B	6.8	19.1	96.1	57.0	28.1	0.0318	0.9339	0.0400	1.256	0.997	
90	T	6	3	3	B	8.5	23.2	93.5	40.0	23.4	0.0372	1.0000	0.0372	1.000	0.978	
90	T	7	1	4	A	8.7	19.1	98.8	122.0	36.4	0.0327	1.0000	0.0327	1.000	0.983	
90	T	7	2	9	A	8.8	18.5	93.6	41.0	27.2	0.0364	1.0000	0.0364	1.000	0.993	
90	T	7	3	6	A	6.0	19.7	98.5	106.5	29.4	0.0259	1.0000	0.0259	1.000	0.894	
90	T	8	1	4	B	8.4	19.0	96.2	58.0	26.2	0.0271	0.9934	0.0277	1.024	0.998	
90	T	8	2	9	B	8.5	19.2	95.6	52.3	26.7	0.0292	0.9079	0.0405	1.384	0.993	
90	T	8	3	6	B	5.5	19.5	95.8	54.2	25.7	0.0233	1.0000	0.0233	1.000	0.962	
90	T	9	1	4	A	8.6	19.1	98.7	120.1	38.4	0.0334	1.0000	0.0334	1.000	0.995	
90	T	9	2	9	A	9.5	18.6	93.5	40.6	32.7	0.0411	0.8902	0.0583	1.420	0.996	
90	T	9	3	6	A	5.7	19.8	98.4	103.8	32.8	0.0271	1.0000	0.0271	1.000	0.952	
90	T	10	1	4	B	8.7	18.8	96.1	57.1	29.1	0.0333	0.9870	0.0348	1.045	0.999	
90	T	10	2	9	B	8.0	19.2	95.5	51.7	26.5	0.0368	0.9521	0.0431	1.172	0.994	
90	T	10	3	6	B	6.1	19.5	95.7	53.3	24.4	0.0293	1.0000	0.0293	1.000	0.987	
90	T	11	1	7	A	9.0	19.7	95.3	50.6	36.2	0.0289	0.8610	0.0473	1.636	0.990	
90	T	11	2	8	A	8.1	19.0	93.6	40.7	37.9	0.0300	0.9385	0.0372	1.241	0.996	
90	T	11	3	3	A	8.3	18.9	98.6	111.5	38.4	0.0265	1.0000	0.0265	1.000	0.967	
90	T	12	2	8	B	7.7	19.1	95.9	55.3	28.6	0.0313	1.0000	0.0313	1.000	0.990	
90	T	12	3	3	B	8.7	23.2	93.4	39.6	30.7	0.0174	0.7599	0.0460	2.646	0.980	
90	T	13	1	10	A	8.4	18.4	93.7	41.5	27.3	0.0467	0.9425	0.0557	1.193	0.999	
90	T	13	2	10	B	7.7	18.7	95.6	52.6	22.8	0.0443	0.8036	0.0817	1.844	0.998	
90	T	13	3	11	A	7.4	18.2	93.3	39.7	28.9	0.0272	0.8080	0.0544	1.998	0.997	
90	T	14	1	10	A	11.0	18.5	93.7	41.4	30.4	0.0250	0.4411	0.1964	7.866	0.983	
90	T	14	2	10	B	7.9	18.7	95.6	52.5	23.7	0.0316	1.0000	0.0316	1.000	0.974	
90	T	14	3	11	A	7.3	18.3	93.2	39.2	25.9	0.0257	1.0000	0.0257	1.000	0.990	
90	T	15	1	10	A	9.2	18.5	93.6	41.0	28.9	0.0496	1.0000	0.0496	1.000	0.991	
90	T	15	3	11	A	7.9	18.3	93.1	38.8	29.5	0.0312	1.0000	0.0312	1.000	0.992	
90	T	16	1	11	B	7.2	18.8	95.7	53.4	24.0	0.0320	0.8591	0.0520	1.624	0.990	
90	T	16	2	11	B	7.8	18.8	95.6	52.7	25.1	0.0358	0.9699	0.0396	1.106	0.995	
90	T	16	3	11	B	7.5	18.8	95.5	51.8	27.9	0.0285	1.0000	0.0285	1.000	0.990	
Summary Statistics (n = 45)						Max	11.0	23.2	98.9	129.0	42.9	0.0496	1	0.1964	7.866	0.999
						Min	5.5	18.2	93.1	38.8	22.8	0.0122	0.4411	0.0122	1.000	0.894
						Avg	8.1	19.2	95.7	63.6	30.3	0.0283	0.9469	0.0379	1.345	0.986
						Std	1.1	1.0	1.9	28.9	5.3	0.0084	0.0980	0.0275	1.039	

Table C5. Summary of observed and predicted variables for Essex soybeans under absorption conditions in 1990.

YR	Vr	Wk	Rep	Exp	Cmb	Mo	T	RH	EMCH	EMCR	k	n	k'	k''	pseudo R ²	
90	E	1	1	7	A	8.4	19.3	98.4	103.6	40.8	0.0167	0.7805	0.0410	2.455	0.994	
90	E	1	2	8	A	8.4	18.9	93.8	41.8	43.0	0.0179	0.8519	0.0324	1.815	0.978	
90	E	1	3	3	A	9.6	18.9	98.6	114.1	42.6	0.0172	0.9563	0.0205	1.194	0.989	
90	E	2	1	7	B	8.6	19.0	95.6	52.7	26.4	0.0397	1.0000	0.0397	1.000	0.994	
90	E	2	2	8	B	7.4	19.1	96.2	57.8	27.3	0.0357	0.9442	0.0430	1.205	0.996	
90	E	2	3	3	B	8.5	23.2	93.7	40.7	24.8	0.0428	1.0000	0.0428	1.000	0.983	
90	E	3	1	4	A	9.1	19.0	98.8	122.9	37.7	0.0299	1.0000	0.0299	1.000	0.995	
90	E	3	2	9	A	9.1	18.5	93.7	41.5	30.6	0.0348	0.9952	0.0354	1.016	0.997	
90	E	3	3	6	A	5.7	19.7	98.5	109.6	31.5	0.0245	1.0000	0.0245	1.000	0.913	
90	E	4	1	4	B	9.6	19.0	96.2	58.4	31.3	0.0375	1.0000	0.0375	1.000	0.994	
90	E	4	2	9	B	8.2	19.2	95.6	52.8	24.7	0.0451	1.0000	0.0451	1.000	0.993	
90	E	4	3	6	B	5.6	19.5	95.9	55.3	25.7	0.0286	1.0000	0.0286	1.000	0.958	
90	E	5	1	7	A	8.8	19.5	95.8	54.0	34.2	0.0283	0.9762	0.0308	1.088	0.995	
90	E	5	2	8	A	8.3	18.9	93.6	41.0	33.0	0.0319	0.9217	0.0418	1.310	0.994	
90	E	6	1	7	B	9.1	19.1	92.1	35.4	28.0	0.0316	0.9390	0.0390	1.235	0.999	
90	E	6	2	8	B	8.3	19.1	96.0	56.4	29.6	0.0241	1.0000	0.0241	1.000	0.990	
90	E	6	3	3	B	8.9	23.2	93.5	39.9	26.8	0.0315	0.9006	0.0444	1.410	0.986	
90	E	7	1	4	A	8.8	19.0	98.7	121.0	37.1	0.0329	1.0000	0.0329	1.000	0.974	
90	E	7	2	9	A	10.0	18.5	93.6	40.9	28.9	0.0314	0.9861	0.0330	1.049	0.998	
90	E	7	3	6	A	6.3	19.8	98.5	106.0	30.6	0.0264	1.0000	0.0264	1.000	0.986	
90	E	8	1	4	B	9.3	18.9	96.1	57.2	30.6	0.0376	0.9992	0.0377	1.003	0.999	
90	E	8	2	9	B	8.7	19.2	95.6	52.3	26.0	0.0371	1.0000	0.0371	1.000	0.991	
90	E	8	3	6	B	5.8	19.5	95.8	54.3	25.1	0.0307	1.0000	0.0307	1.000	0.983	
90	E	9	1	4	A	8.4	19.1	98.7	121.0	39.1	0.0341	1.0000	0.0341	1.000	0.993	
90	E	9	2	9	A	8.8	18.6	93.5	40.6	30.9	0.0428	1.0000	0.0428	1.000	0.993	
90	E	9	3	6	A	6.3	19.8	98.5	105.6	33.3	0.0283	1.0000	0.0283	1.000	0.912	
90	E	10	1	4	B	8.5	18.8	96.1	57.4	31.5	0.0425	1.0000	0.0425	1.000	0.996	
90	E	10	2	9	B	7.7	19.3	95.5	51.4	27.9	0.0409	0.9766	0.0440	1.078	0.996	
90	E	11	1	7	A	8.8	19.6	95.3	49.9	39.6	0.0319	0.8338	0.0566	1.773	1.000	
90	E	11	2	8	A	7.9	18.9	93.5	40.5	38.0	0.0290	0.9635	0.0330	1.138	0.994	
90	E	11	3	3	A	12.6	19.0	98.6	111.5	45.1	0.0296	0.9762	0.0321	1.087	0.997	
90	E	12	1	7	B	8.8	19.0	91.4	33.4	27.2	0.0349	1.0000	0.0349	1.000	0.995	
90	E	12	2	8	B	7.8	19.1	96.0	55.7	32.1	0.0378	1.0000	0.0378	1.000	0.998	
90	E	12	3	3	B	8.2	23.2	93.3	39.2	27.1	0.0427	0.8186	0.0757	1.772	0.986	
90	E	13	1	10	A	9.6	18.4	93.7	41.3	28.1	0.0522	1.0000	0.0522	1.000	0.985	
90	E	13	2	10	B	9.3	18.7	95.6	52.7	24.1	0.0423	1.0000	0.0423	1.000	0.974	
90	E	13	3	11	A	6.9	18.3	93.2	39.3	27.1	0.0418	1.0000	0.0418	1.000	0.988	
90	E	14	1	10	A	9.5	18.5	93.7	41.3	26.2	0.0508	1.0000	0.0508	1.000	0.996	
90	E	14	2	10	B	8.6	18.7	95.5	52.2	23.2	0.0490	0.9484	0.0573	1.168	0.999	
90	E	14	3	11	A	7.9	18.3	93.1	39.0	25.7	0.0316	1.0000	0.0316	1.000	0.993	
90	E	15	1	10	A	10.4	18.5	93.5	40.7	29.1	0.0523	0.7490	0.1098	2.097	1.000	
90	E	15	2	10	B	9.5	18.7	95.5	51.9	26.7	0.0509	0.6894	0.1283	2.523	0.997	
90	E	16	1	11	B	7.1	18.8	95.7	53.3	25.1	0.0467	0.9751	0.0504	1.079	0.998	
90	E	16	3	11	B	7.4	18.9	95.5	51.8	28.4	0.0363	0.9831	0.0384	1.058	0.999	
Summary Statistics (n = 44)						Max	12.6	23.2	98.8	122.9	45.1	0.0523	1	0.1283	2.523	1.000
						Min	5.6	18.3	91.4	33.4	23.2	0.0167	0.6894	0.0205	1.000	0.912
						Avg	8.4	19.3	95.4	60.9	30.7	0.0355	0.9583	0.0423	1.194	0.988
						Std	1.3	1.1	2.0	27.3	5.6	0.0089	0.0746	0.0195	0.379	

Table C6. Summary of observed and predicted variables for Leflore soybeans under absorption conditions in 1990.

YR	Vr	Wk	Rep	Exp	Cmb	Mo	T	RH	EMCH	EMCR	k	n	k ^a	k ^m	pseudo R ²	
90	L	1	1	7	A	7.6	19.3	97.5	76.5	40.4	0.0154	0.6337	0.0711	4.610	0.996	
90	L	1	2	8	A	8.7	18.9	93.7	41.4	43.1	0.0152	0.8400	0.0297	1.953	0.992	
90	L	1	3	3	A	8.7	18.9	98.7	119.2	44.1	0.0154	0.8778	0.0257	1.665	0.968	
90	L	2	1	7	B	8.3	19.0	94.8	46.8	25.5	0.0233	0.8113	0.0474	2.032	0.999	
90	L	2	2	8	B	8.3	19.1	96.1	56.8	30.0	0.0238	1.0000	0.0238	1.000	0.986	
90	L	2	3	3	B	8.4	23.2	93.6	40.2	27.2	0.0233	0.8046	0.0485	2.085	0.968	
90	L	3	1	4	A	9.9	19.0	98.8	126.8	37.9	0.0318	1.0000	0.0318	1.000	0.986	
90	L	3	2	9	A	8.6	18.6	93.7	41.2	29.0	0.0295	1.0000	0.0295	1.000	0.983	
90	L	3	3	6	A	6.0	19.7	98.5	107.9	32.7	0.0264	1.0000	0.0264	1.000	0.944	
90	L	4	1	4	B	10.2	19.0	96.3	58.7	32.7	0.0298	1.0000	0.0298	1.000	0.998	
90	L	4	2	9	B	8.4	19.2	95.6	52.6	25.1	0.0275	0.9661	0.0310	1.130	0.992	
90	L	4	3	6	B	5.7	19.5	95.8	54.5	26.0	0.0254	1.0000	0.0254	1.000	0.988	
90	L	5	1	7	A	8.8	19.6	95.5	51.9	33.4	0.0419	0.8803	0.0612	1.462	0.994	
90	L	5	2	8	A	8.5	18.9	93.6	40.9	32.8	0.0327	1.0000	0.0327	1.000	0.986	
90	L	5	3	3	A	9.4	18.9	98.6	111.5	34.5	0.0281	1.0000	0.0281	1.000	0.982	
90	L	6	1	7	B	7.1	19.1	91.7	34.3	26.9	0.0315	0.9778	0.0340	1.080	0.999	
90	L	6	2	8	B	7.0	19.1	96.0	55.7	29.9	0.0310	0.9095	0.0424	1.369	0.985	
90	L	6	3	3	B	8.3	23.2	93.5	39.7	27.5	0.0387	1.0000	0.0387	1.000	0.989	
90	L	7	1	4	A	9.8	19.0	98.8	122.0	38.2	0.0350	1.0000	0.0350	1.000	0.996	
90	L	7	2	9	A	8.4	18.6	93.5	40.7	26.6	0.0399	1.0000	0.0399	1.000	0.991	
90	L	7	3	6	A	5.9	19.8	98.5	105.1	28.6	0.0287	1.0000	0.0287	1.000	0.931	
90	L	8	1	4	B	8.9	19.0	96.1	57.0	32.9	0.0498	1.0000	0.0498	1.000	0.995	
90	L	8	2	9	B	8.7	19.2	95.5	52.1	27.3	0.0632	1.0000	0.0632	1.000	0.981	
90	L	8	3	6	B	5.6	19.5	95.8	54.1	23.0	0.0306	1.0000	0.0306	1.000	0.969	
90	L	9	1	4	A	9.1	19.1	98.8	121.9	41.1	0.0322	1.0000	0.0322	1.000	0.990	
90	L	9	2	9	A	9.0	18.6	93.5	40.4	30.8	0.0372	1.0000	0.0372	1.000	0.998	
90	L	9	3	6	A	6.0	19.8	98.4	101.5	32.7	0.0266	1.0000	0.0266	1.000	0.935	
90	L	10	1	4	B	9.3	18.7	96.1	57.2	34.3	0.0377	1.0000	0.0377	1.000	0.999	
90	L	10	2	9	B	8.3	19.3	95.4	51.1	28.8	0.0345	1.0000	0.0345	1.000	0.998	
90	L	11	2	8	A	8.2	18.9	93.5	40.4	36.6	0.0325	0.9545	0.0380	1.169	0.998	
90	L	11	3	3	A	10.0	18.9	98.6	110.2	41.1	0.0358	1.0000	0.0358	1.000	0.970	
90	L	12	1	7	B	6.9	19.0	91.2	33.0	29.1	0.0402	0.9184	0.0522	1.300	0.995	
90	L	12	2	8	B	7.8	19.3	95.8	54.4	31.9	0.0347	0.9712	0.0382	1.102	0.999	
90	L	13	1	10	A	8.4	18.4	93.8	41.7	29.1	0.0454	1.0000	0.0454	1.000	0.997	
90	L	13	2	10	B	8.3	18.7	95.7	53.2	23.5	0.0433	1.0000	0.0433	1.000	0.999	
90	L	13	3	11	A	8.0	18.3	93.2	39.3	29.9	0.0356	0.8883	0.0517	1.451	0.995	
90	L	14	1	10	A	9.6	18.4	93.6	41.0	24.9	0.0590	0.8497	0.0902	1.530	0.996	
90	L	14	3	11	A	7.8	18.3	93.1	38.8	24.9	0.0402	1.0000	0.0402	1.000	0.993	
90	L	15	1	10	A	10.5	18.5	93.6	40.9	31.4	0.0441	0.8583	0.0686	1.556	0.996	
90	L	15	2	10	B	8.8	18.7	95.5	52.0	28.6	0.0350	0.8290	0.0620	1.775	0.999	
90	L	16	1	11	B	6.8	18.8	95.6	53.1	23.3	0.0375	0.9894	0.0389	1.035	0.990	
90	L	16	2	11	B	6.8	18.8	95.5	52.3	26.2	0.0385	1.0000	0.0385	1.000	0.991	
90	L	16	3	11	B	7.6	18.8	95.4	51.5	28.9	0.0322	1.0000	0.0322	1.000	0.998	
Summary Statistics (n = 43)						Max	10.5	23.2	98.8	126.8	44.1	0.0632	1	0.0902	4.610	0.999
						Min	5.6	18.3	91.2	33.0	23.0	0.0152	0.6337	0.0000	1.000	0.931
						Avg	8.2	19.2	95.5	61.9	31.0	0.0339	0.9526	0.0397	1.263	0.987
						Std	1.2	1.0	2.0	28.2	5.4	0.0097	0.0792	0.0152	0.601	

Table C7. Summary of observed and predicted variables for Tn4-86 soybeans under desorption conditions in 1989.

YR	Vr	Wk	Rep	Exp	Mo	T	RH	EMCH	EMCR	k	n	k ^a	k ^b	pseudo R ²
89	T	1	1	10	43.9	20.8	16.3	4.6	9.8	0.1170	0.7958	0.1813	1.550	1.000
89	T	1	2	11	46.6	19.0	14.8	4.5	9.2	0.0977	0.9102	0.1204	1.232	1.000
89	T	1	3	6	51.5	21.8	14.3	4.4	9.3	0.1207	1.0000	0.1207	1.000	0.995
89	T	2	1	10	40.7	21.0	16.3	4.6	10.9	0.1274	0.7805	0.2002	1.572	1.000
89	T	3	1	7	40.2	23.5	13.1	4.3	7.0	0.0772	0.8360	0.1175	1.522	1.000
89	T	3	3	9	36.6	19.6	17.2	4.7	8.6	0.0775	0.6724	0.1791	2.312	0.996
89	T	4	2	11	46.5	18.6	14.9	4.5	8.9	0.0890	0.9244	0.1069	1.201	1.000
89	T	4	3	12	60.0	22.3	16.7	4.6	8.7	0.0989	0.9239	0.1180	1.192	0.994
89	T	5	2	5	28.7	20.3	14.3	4.4	7.2	0.0919	0.7570	0.1642	1.786	0.998
89	T	6	1	7	40.0	24.1	13.4	4.3	6.2	0.0697	1.0000	0.0697	1.000	0.970
89	T	6	3	9	36.5	19.7	16.7	4.7	8.5	0.0731	0.6926	0.1634	2.234	1.000
89	T	7	2	11	45.9	18.7	14.9	4.5	10.5	0.1266	0.7626	0.2068	1.633	1.000
89	T	7	3	12	56.0	22.3	16.7	4.6	8.8	0.1042	0.7654	0.1771	1.700	0.997
89	T	8	1	1	43.4	24.6	15.8	4.5	5.5	0.1226	0.6377	0.2622	2.139	0.999
89	T	8	2	2	45.2	21.9	18.2	4.8	4.5	0.0727	0.9553	0.0817	1.124	0.998
89	T	8	3	3	36.4	21.5	13.7	4.3	10.5	0.0811	0.9245	0.0980	1.209	0.999
89	T	9	1	4	27.6	21.1	13.8	4.4	8.1	0.0690	0.7897	0.1211	1.755	0.999
89	T	9	2	5	27.4	20.4	14.2	4.4	7.5	0.0759	0.6984	0.1652	2.176	0.996
89	T	9	3	6	41.5	22.1	14.5	4.4	8.3	0.1299	0.6558	0.2623	2.019	0.986
89	T	11	1	7	39.8	24.0	13.0	4.2	7.4	0.0730	0.7929	0.1255	1.719	1.000
89	T	11	3	9	37.7	19.8	17.0	4.7	10.6	0.0767	0.7371	0.1507	1.964	0.997
89	T	12	1	10	42.6	21.0	16.3	4.6	10.5	0.1070	0.8243	0.1584	1.481	1.000
89	T	12	3	12	50.6	22.4	16.6	4.6	8.9	0.1151	0.8484	0.1598	1.388	0.996
89	T	13	1	4	33.7	21.3	13.7	4.4	7.7	0.0502	0.6937	0.1256	2.499	0.982
89	T	14	1	13	51.6	21.2	14.0	4.4	8.3	0.0915	0.8893	0.1193	1.303	0.999
89	T	14	2	13	53.1	21.2	14.0	4.4	8.8	0.0854	0.9631	0.0936	1.095	0.999
89	T	14	3	13	52.7	20.8	14.1	4.4	6.9	0.1165	0.7347	0.2060	1.769	1.000
89	T	16	2	2	48.2	22.1	18.6	4.8	7.1	0.0794	0.9715	0.0853	1.075	0.997
89	T	16	3	3	36.7	21.6	13.7	4.3	8.3	0.0920	0.9576	0.1018	1.107	0.994
Summary Statistics (n = 29)				Max	60	24.6	18.6	4.8	10.9	0.1299	1	0.2623	2.499	1.000
				Min	27.4	18.6	13	4.2	4.5	0.0502	0.6377	0.0697	1	0.970
				Avg	42.80	21.3	15.2	4.5	8.4	0.0934	0.8240	0.1463	1.578	0.996
				Std	8.15	1.50	1.55	0.16	1.52	0.0211	0.1097	0.0488	0.425	

Table C8. Summary of observed and predicted variables for Essex soybeans under desorption conditions in 1989.

YR	Vr	Wk	Rep	Exp	Mo	T	RH	EMCH	EMCR	k	n	k ^a	k ^b	pseudo R ²
89	E	2	2	2	52.9	21.8	17.7	4.8	4.0	0.0557	0.7873	0.1029	1.848	0.976
89	E	2	3	3	30.8	21.4	13.7	4.4	10.4	0.0836	1.0000	0.0836	1.000	0.998
89	E	3	1	7	42.7	23.9	13.1	4.2	10.6	0.1244	1.0000	0.1244	1.000	0.982
89	E	4	1	10	41.4	20.9	16.3	4.6	10.2	0.1287	0.8736	0.1668	1.296	1.000
89	E	4	2	11	44.6	18.5	15.0	4.5	9.4	0.1025	0.8374	0.1484	1.449	1.000
89	E	4	3	12	56.4	22.2	16.7	4.6	8.8	0.1050	0.8020	0.1641	1.562	0.991
89	E	5	3	6	50.4	21.9	14.3	4.4	10.7	0.1237	1.0000	0.1237	1.000	0.993
89	E	6	1	7	39.9	24.0	13.0	4.2	9.7	0.1172	0.9825	0.1217	1.038	0.990
89	E	6	3	9	38.9	19.7	16.6	4.7	9.4	0.0745	0.6952	0.1643	2.207	0.999
89	E	7	1	10	43.8	20.9	16.9	4.7	9.9	0.1280	0.7390	0.2189	1.710	1.000
89	E	7	2	11	44.7	18.8	14.8	4.5	8.7	0.0867	0.9373	0.1010	1.166	1.000
89	E	7	3	12	48.2	22.4	16.6	4.6	7.9	0.1056	0.7955	0.1672	1.584	0.998
89	E	8	2	2	47.6	22.1	18.5	4.8	4.0	0.0558	0.9379	0.0667	1.196	0.972
89	E	8	3	3	38.3	21.5	13.7	4.4	9.8	0.0901	1.0000	0.0901	1.000	0.994
89	E	9	1	4	27.4	21.0	13.7	4.4	9.1	0.0829	0.8135	0.1318	1.591	0.998
89	E	9	3	6	48.2	22.1	14.4	4.4	10.6	0.1716	0.5881	0.3547	2.067	0.988
89	E	11	1	7	40.5	24.1	13.0	4.2	7.4	0.0729	0.7260	0.1494	2.050	1.000
89	E	11	3	9	33.1	19.7	17.0	4.7	6.6	0.0859	0.5465	0.2614	3.044	0.999
89	E	12	1	10	43.9	21.0	16.3	4.6	10.8	0.1208	0.7960	0.1860	1.539	0.999
89	E	12	2	11	45.8	18.4	15.0	4.5	8.7	0.0896	0.9064	0.1123	1.253	1.000
89	E	12	3	12	57.4	22.4	16.7	4.6	14.9	0.1122	0.7897	0.1777	1.584	0.998
89	E	13	1	4	28.7	21.4	13.7	4.4	8.3	0.0765	0.6877	0.1708	2.232	0.999
89	E	13	2	5	27.9	20.1	14.4	4.4	7.3	0.0890	0.6257	0.2201	2.473	0.997
89	E	13	3	6	45.0	22.0	14.4	4.4	8.4	0.1567	0.8737	0.1981	1.264	0.991
89	E	15	1	13	46.1	21.1	14.0	4.4	8.6	0.1064	0.7591	0.1825	1.716	0.999
89	E	15	2	13	52.4	21.1	14.0	4.4	9.3	0.0808	0.9798	0.0850	1.052	0.999
89	E	15	3	13	43.6	21.1	14.0	4.4	7.3	0.0899	0.7509	0.1638	1.822	0.999
89	E	16	2	2	50.0	22.2	19.2	4.9	4.0	0.0601	0.9572	0.0678	1.128	0.982
89	E	16	3	3	36.6	21.6	13.7	4.3	8.3	0.0892	0.9825	0.0930	1.043	0.994
Summary Statistics (n = 29)	Max				57.4	24.1	19.2	4.9	14.9	0.1716	1	0.3547	3.044	1.000
	Min				27.4	18.4	13	4.2	4	0.0557	0.5465	0.0667	1	0.972
	Avg				43.01	21.4	15.2	4.5	8.7	0.0988	0.8335	0.152	1.549	0.994
	Std				7.88	1.41	1.69	0.18	2.21	0.0271	0.1299	0.061	0.505	

Table C9. Summary of observed and predicted variables for Leflore soybeans under desorption conditions in 1989.

YR	Vr	Wk	Rep	Exp	Mo	T	RH	EMCH	EMCR	k	n	k ^a	k ^m	pseudo R ²	
89	L	2	1	1	46.8	24.6	15.4	4.5	5.2	0.1119	0.6308	0.2512	2.244	1.000	
89	L	2	2	2	51.7	21.8	18.0	4.8	7.3	0.0656	0.9667	0.0718	1.095	0.997	
89	L	2	3	3	38.6	21.4	13.7	4.4	11.3	0.0804	0.9093	0.1010	1.257	0.984	
89	L	3	1	7	43.9	23.8	13.4	4.3	9.5	0.0943	0.8402	0.1375	1.459	0.998	
89	L	3	3	9	39.5	19.6	17.2	4.7	6.2	0.0556	0.5225	0.2209	3.976	0.999	
89	L	6	1	7	42.1	23.9	13.4	4.3	9.8	0.0921	1.0000	0.0921	1.000	0.989	
89	L	6	3	9	33.0	19.7	16.5	4.7	8.1	0.0530	0.6431	0.1512	2.853	1.000	
89	L	7	1	10	45.9	21.0	16.3	4.6	9.4	0.1446	0.7774	0.2224	1.538	1.000	
89	L	7	2	11	46.4	18.7	14.9	4.5	8.9	0.0903	0.8353	0.1342	1.486	1.000	
89	L	7	3	12	57.2	22.3	16.6	4.6	8.7	0.0965	0.9149	0.1177	1.220	0.994	
89	L	8	1	1	47.2	24.7	16.1	4.5	4.6	0.1235	0.6133	0.2773	2.245	0.999	
89	L	8	2	2	49.2	21.9	18.7	4.9	6.1	0.0720	0.9163	0.0897	1.247	0.998	
89	L	8	3	3	36.7	21.7	14.3	4.4	11.4	0.0968	0.9390	0.1117	1.153	0.999	
89	L	9	1	4	34.5	21.0	13.8	4.4	9.3	0.0578	0.9653	0.0638	1.104	0.947	
89	L	9	3	6	50.7	21.9	14.4	4.4	9.0	0.1187	0.9043	0.1455	1.226	0.995	
89	L	11	1	7	41.4	24.2	13.5	4.3	4.0	0.0518	0.8106	0.0907	1.752	0.996	
89	L	11	3	9	37.9	19.7	17.0	4.7	8.3	0.0640	0.6462	0.1693	2.645	1.000	
89	L	12	1	10	45.8	21.0	16.3	4.6	9.0	0.1198	0.7452	0.2058	1.717	1.000	
89	L	12	2	11	47.8	18.8	14.9	4.5	9.6	0.0990	0.8458	0.1414	1.429	1.000	
89	L	12	3	12	49.0	22.4	16.5	4.6	8.2	0.0914	0.7929	0.1500	1.641	0.997	
89	L	13	1	4	34.9	21.3	13.8	4.4	11.0	0.0735	0.7528	0.1401	1.906	0.999	
89	L	13	2	5	29.7	20.2	14.4	4.4	7.6	0.0786	0.6917	0.1721	2.191	0.997	
89	L	13	3	6	45.6	22.0	14.4	4.4	7.7	0.1110	0.9529	0.1231	1.109	0.994	
89	L	14	1	13	51.3	20.8	14.1	4.4	7.5	0.0955	0.7931	0.1552	1.626	1.000	
89	L	14	2	13	62.8	21.1	14.2	4.4	7.1	0.0997	0.7869	0.1629	1.635	1.000	
89	L	15	1	13	52.3	21.0	14.0	4.4	7.5	0.0912	0.7957	0.1488	1.631	1.000	
89	L	15	2	13	52.0	21.0	14.0	4.4	6.7	0.0947	0.7405	0.1746	1.843	1.000	
89	L	15	3	13	53.6	21.2	14.0	4.4	8.0	0.0783	1.0000	0.0783	1.000	0.998	
89	L	16	1	1	48.8	24.8	15.7	4.5	6.0	0.1326	0.6466	0.2708	2.042	0.999	
89	L	16	3	3	37.4	21.8	14.3	4.4	11.2	0.0897	0.8649	0.1242	1.385	0.999	
Summary Statistics (n = 30)					Max	62.8	24.8	18.7	4.9	11.4	0.1446	1	0.2773	3.976	1.000
					Min	29.7	18.7	13.4	4.3	4	0.0518	0.5225	0.0638	1.000	0.947
					Avg	45.12	21.6	15.1	4.5	8.1	0.0908	0.8081	0.1498	1.688	0.996
					Std	7.50	1.63	1.44	0.15	1.88	0.0232	0.1249	0.0554	0.631	

Table C10. Summary of observed and predicted variables for Tn4-86 soybeans under desorption conditions in 1990.

YR	Vr	Wk	Rep	Exp	Cmb	Mo	T	RH	EMCH	EMCR	k	n	k ^a	k ^b	pseudo R ²
90	T	1	1	7	A	33.6	21.2	19.7	5.0	7.3	0.0484	0.7031	0.1190	2.457	0.998
90	T	1	2	8	A	32.1	21.9	14.6	4.4	6.7	0.0592	0.7093	0.1346	2.275	1.000
90	T	1	3	3	A	31.4	21.3	14.4	4.4	10.2	0.0667	0.7123	0.1454	2.179	1.000
90	T	2	1	7	B	25.0	17.9	17.2	4.8	7.8	0.0380	0.7868	0.0764	2.008	1.000
90	T	2	2	8	B	25.7	21.0	13.7	4.4	7.8	0.0669	0.7540	0.1301	1.946	1.000
90	T	3	1	4	A	35.1	20.9	14.6	4.5	8.2	0.0742	0.7600	0.1386	1.867	1.000
90	T	3	2	9	A	26.6	21.9	19.6	5.0	7.3	0.0584	0.7261	0.1271	2.177	1.000
90	T	3	3	6	A	32.8	21.6	19.9	5.0	5.8	0.0701	0.6390	0.1830	2.611	1.000
90	T	4	1	4	B	27.0	17.3	15.0	4.6	8.1	0.0658	0.7821	0.1190	1.810	1.000
90	T	4	2	9	B	24.5	18.5	15.4	4.6	5.9	0.0518	0.6996	0.1260	2.434	0.999
90	T	4	3	6	B	23.2	19.3	18.1	4.8	4.1	0.0468	0.6253	0.1474	3.149	0.999
90	T	5	1	7	A	34.4	21.1	20.8	5.1	9.4	0.0491	1.0000	0.0491	1.000	0.998
90	T	5	2	8	A	30.0	22.0	14.8	4.5	7.7	0.0681	0.8521	0.1013	1.488	1.000
90	T	5	3	3	A	31.2	20.9	14.3	4.4	9.1	0.0748	0.8412	0.1129	1.509	1.000
90	T	6	1	7	B	26.1	17.9	18.6	4.9	7.5	0.0392	1.0000	0.0392	1.000	1.000
90	T	6	2	8	B	27.2	21.1	13.7	4.4	6.3	0.0658	0.7447	0.1318	2.003	1.000
90	T	6	3	3	B	23.7	21.5	13.5	4.3	8.8	0.0814	0.7935	0.1367	1.679	0.997
90	T	7	1	4	A	35.8	21.0	14.6	4.4	9.3	0.0719	0.8082	0.1191	1.657	1.000
90	T	7	2	9	A	27.1	21.9	19.6	4.9	6.0	0.0487	0.7538	0.1024	2.105	0.998
90	T	7	3	6	A	32.0	21.7	18.2	4.8	5.9	0.0972	0.5614	0.2702	2.780	0.993
90	T	8	1	4	B	24.9	17.3	15.0	4.6	8.2	0.0609	0.7409	0.1257	2.065	1.000
90	T	8	2	9	B	26.6	18.5	15.4	4.6	6.1	0.0641	0.7418	0.1303	2.033	1.000
90	T	8	3	6	B	24.1	19.2	17.0	4.7	4.4	0.0758	0.6169	0.2037	2.686	0.990
90	T	9	1	4	A	37.2	21.1	14.6	4.4	9.0	0.0963	0.8141	0.1488	1.545	1.000
90	T	9	2	9	A	32.1	21.9	19.5	4.9	8.0	0.0677	0.8325	0.1063	1.570	1.000
90	T	9	3	6	A	34.8	21.6	18.3	4.8	4.7	0.0698	0.7562	0.1335	1.914	0.999
90	T	10	1	4	B	28.5	17.3	15.0	4.6	8.7	0.0729	0.7302	0.1477	2.027	1.000
90	T	10	2	9	B	26.9	18.5	15.4	4.6	5.8	0.0632	0.7943	0.1115	1.765	1.000
90	T	10	3	6	B	23.9	19.2	17.1	4.7	3.8	0.0545	0.5810	0.1844	3.384	0.999
90	T	11	1	7	A	33.6	21.1	21.8	5.2	6.8	0.0419	0.6456	0.1289	3.080	0.999
90	T	11	2	8	A	34.8	22.0	14.9	4.5	7.3	0.0838	0.7374	0.1607	1.918	1.000
90	T	11	3	3	A	35.4	21.0	14.4	4.4	7.8	0.0776	0.7974	0.1302	1.679	0.997
90	T	12	2	8	B	28.2	21.2	13.7	4.4	5.5	0.0572	0.6659	0.1488	2.601	1.000
90	T	12	3	3	B	26.8	21.4	13.5	4.3	8.9	0.0736	0.8184	0.1181	1.606	0.999
90	T	13	1	10	A	27.6	21.7	18.0	4.8	6.8	0.0657	1.0000	0.0657	1.000	1.000
90	T	13	2	10	B	22.3	18.6	15.0	4.5	5.9	0.0663	0.9188	0.0826	1.247	0.994
90	T	13	3	11	A	28.0	20.9	16.8	4.7	6.4	0.0607	0.7556	0.1203	1.984	1.000
90	T	14	1	10	A	27.4	21.7	18.0	4.8	3.3	0.0475	0.5182	0.2062	4.340	1.000
90	T	14	2	10	B	23.3	18.6	15.0	4.5	6.4	0.0681	0.8117	0.1129	1.659	0.999
90	T	14	3	11	A	26.2	20.9	16.9	4.7	6.5	0.0589	0.8488	0.0904	1.534	1.000
90	T	15	1	10	A	28.9	21.6	18.1	4.8	6.8	0.0662	0.8928	0.0886	1.338	1.000
90	T	15	3	11	A	29.9	20.8	17.1	4.7	7.2	0.0654	0.7732	0.1214	1.856	0.999
90	T	16	1	11	B	23.6	18.6	14.7	4.5	6.9	0.0696	0.8133	0.1145	1.645	1.000
90	T	16	2	11	B	24.3	18.8	14.7	4.5	6.3	0.0696	0.7662	0.1298	1.865	0.999
90	T	16	3	11	B	27.6	18.7	14.7	4.5	6.4	0.0643	0.7181	0.1394	2.168	1.000
Summary Statistics (n = 45)					Max	37.2	22.0	21.8	5.2	10.2	0.0972	1	0.2702	4.340	1.000
					Min	22.3	17.3	13.5	4.3	3.3	0.0380	0.5182	0.0392	1	0.990
					Avg	28.7	20.3	16.3	4.6	7.0	0.0650	0.7658	0.1280	1.998	0.999
					Std	4.1	1.5	2.2	0.2	1.6	0.0127	0.1054	0.0405	0.647	

Table C11. Summary of observed and predicted variables for Essex soybeans under desorption conditions in 1990.

YR	Vr	Wk	Rep	Exp	Cmb	Mo	T	RH	EMCH	EMCR	k	n	k ^a	k ^m	pseudo R ²
90	T	1	1	7	A	33.6	21.2	19.7	5.0	7.3	0.0484	0.7031	0.1190	2.457	0.998
90	T	1	2	8	A	32.1	21.9	14.6	4.4	6.7	0.0592	0.7093	0.1346	2.275	1.000
90	T	1	3	3	A	31.4	21.3	14.4	4.4	10.2	0.0667	0.7123	0.1454	2.179	1.000
90	T	2	1	7	B	25.0	17.9	17.2	4.8	7.8	0.0380	0.7868	0.0764	2.008	1.000
90	T	2	2	8	B	25.7	21.0	13.7	4.4	7.8	0.0669	0.7540	0.1301	1.946	1.000
90	T	3	1	4	A	35.1	20.9	14.6	4.5	8.2	0.0742	0.7600	0.1386	1.867	1.000
90	T	3	2	9	A	26.6	21.9	19.6	5.0	7.3	0.0584	0.7261	0.1271	2.177	1.000
90	T	3	3	6	A	32.8	21.6	19.9	5.0	5.8	0.0701	0.6390	0.1830	2.611	1.000
90	T	4	1	4	B	27.0	17.3	15.0	4.6	8.1	0.0658	0.7821	0.1190	1.810	1.000
90	T	4	2	9	B	24.5	18.5	15.4	4.6	5.9	0.0518	0.6996	0.1260	2.434	0.999
90	T	4	3	6	B	23.2	19.3	18.1	4.8	4.1	0.0468	0.6253	0.1474	3.149	0.999
90	T	5	1	7	A	34.4	21.1	20.8	5.1	9.4	0.0491	1.0000	0.0491	1.000	0.998
90	T	5	2	8	A	30.0	22.0	14.8	4.5	7.7	0.0681	0.8521	0.1013	1.488	1.000
90	T	5	3	3	A	31.2	20.9	14.3	4.4	9.1	0.0748	0.8412	0.1129	1.509	1.000
90	T	6	1	7	B	26.1	17.9	18.6	4.9	7.5	0.0392	1.0000	0.0392	1.000	1.000
90	T	6	2	8	B	27.2	21.1	13.7	4.4	6.3	0.0658	0.7447	0.1318	2.003	1.000
90	T	6	3	3	B	23.7	21.5	13.5	4.3	8.8	0.0814	0.7935	0.1367	1.679	0.997
90	T	7	1	4	A	35.8	21.0	14.6	4.4	9.3	0.0719	0.8082	0.1191	1.657	1.000
90	T	7	2	9	A	27.1	21.9	19.6	4.9	6.0	0.0487	0.7538	0.1024	2.105	0.998
90	T	7	3	6	A	32.0	21.7	18.2	4.8	5.9	0.0972	0.5614	0.2702	2.780	0.993
90	T	8	1	4	B	24.9	17.3	15.0	4.6	8.2	0.0609	0.7409	0.1257	2.065	1.000
90	T	8	2	9	B	26.6	18.5	15.4	4.6	6.1	0.0641	0.7418	0.1303	2.033	1.000
90	T	8	3	6	B	24.1	19.2	17.0	4.7	4.4	0.0758	0.6169	0.2037	2.686	0.990
90	T	9	1	4	A	37.2	21.1	14.6	4.4	9.0	0.0963	0.8141	0.1488	1.545	1.000
90	T	9	2	9	A	32.1	21.9	19.5	4.9	8.0	0.0677	0.8325	0.1063	1.570	1.000
90	T	9	3	6	A	34.8	21.6	18.3	4.8	4.7	0.0698	0.7562	0.1335	1.914	0.999
90	T	10	1	4	B	28.5	17.3	15.0	4.6	8.7	0.0729	0.7302	0.1477	2.027	1.000
90	T	10	2	9	B	26.9	18.5	15.4	4.6	5.8	0.0632	0.7943	0.1115	1.765	1.000
90	T	10	3	6	B	23.9	19.2	17.1	4.7	3.8	0.0545	0.5810	0.1844	3.384	0.999
90	T	11	1	7	A	33.6	21.1	21.8	5.2	6.8	0.0419	0.6456	0.1289	3.080	0.999
90	T	11	2	8	A	34.8	22.0	14.9	4.5	7.3	0.0838	0.7374	0.1607	1.918	1.000
90	T	11	3	3	A	35.4	21.0	14.4	4.4	7.8	0.0776	0.7974	0.1302	1.679	0.997
90	T	12	2	8	B	28.2	21.2	13.7	4.4	5.5	0.0572	0.6659	0.1488	2.601	1.000
90	T	12	3	3	B	26.8	21.4	13.5	4.3	8.9	0.0736	0.8184	0.1181	1.606	0.999
90	T	13	1	10	A	27.6	21.7	18.0	4.8	6.8	0.0657	1.0000	0.0657	1.000	1.000
90	T	13	2	10	B	22.3	18.6	15.0	4.5	5.9	0.0663	0.9188	0.0826	1.247	0.994
90	T	13	3	11	A	28.0	20.9	16.8	4.7	6.4	0.0607	0.7556	0.1203	1.984	1.000
90	T	14	1	10	A	27.4	21.7	18.0	4.8	3.3	0.0475	0.5182	0.2062	4.340	1.000
90	T	14	2	10	B	23.3	18.6	15.0	4.5	6.4	0.0681	0.8117	0.1129	1.659	0.999
90	T	14	3	11	A	26.2	20.9	16.9	4.7	6.5	0.0589	0.8488	0.0904	1.534	1.000
90	T	15	1	10	A	28.9	21.6	18.1	4.8	6.8	0.0662	0.8928	0.0886	1.338	1.000
90	T	15	3	11	A	29.9	20.8	17.1	4.7	7.2	0.0654	0.7732	0.1214	1.856	0.999
90	T	16	1	11	B	23.6	18.6	14.7	4.5	6.9	0.0696	0.8133	0.1145	1.645	1.000
90	T	16	2	11	B	24.3	18.8	14.7	4.5	6.3	0.0696	0.7662	0.1298	1.865	0.999
90	T	16	3	11	B	27.6	18.7	14.7	4.5	6.4	0.0643	0.7181	0.1394	2.168	1.000
Summary Statistics (n = 45)					Max	37.2	22.0	21.8	5.2	10.2	0.0972	1	0.2702	4.340	1.000
					Min	22.3	17.3	13.5	4.3	3.3	0.0380	0.5182	0.0392	1	0.990
					Avg	28.7	20.3	16.3	4.6	7.0	0.0650	0.7658	0.1280	1.998	0.999
					Std	4.1	1.5	2.2	0.2	1.6	0.0127	0.1054	0.0405	0.647	

Table C12. Summary of observed and predicted variables for Leflore soybeans under desorption conditions in 1990.

YR	Vr	Wk	Rep	Exp	Cmb	Mo	T	RH	EMCH	EMCR	k	n	k ^a	k ^m	pseudo R ²
90	L	1	1	7	A	33.7	21.1	20.6	5.1	6.5	0.0344	0.7626	0.0766	2.225	0.996
90	L	1	2	8	A	32.9	21.9	14.7	4.4	6.5	0.0567	0.7380	0.1202	2.121	1.000
90	L	1	3	3	A	33.2	21.0	14.3	4.4	10.0	0.0721	0.8394	0.1100	1.526	0.999
90	L	2	1	7	B	24.2	17.9	18.3	4.9	8.5	0.0362	1.0000	0.0362	1.000	0.999
90	L	2	2	8	B	27.6	21.1	13.7	4.4	6.5	0.0513	0.7263	0.1156	2.255	0.999
90	L	2	3	3	B	26.1	21.5	13.5	4.3	9.0	0.0649	0.8370	0.1014	1.562	1.000
90	L	3	1	4	A	36.6	20.9	14.6	4.4	9.4	0.0608	0.7247	0.1315	2.162	1.000
90	L	3	2	9	A	28.9	21.8	19.5	4.9	6.3	0.0523	0.8048	0.0931	1.778	1.000
90	L	3	3	6	A	34.4	21.8	18.2	4.8	4.9	0.0698	0.6801	0.1636	2.343	0.999
90	L	4	1	4	B	30.7	17.3	15.0	4.6	9.8	0.0646	0.8327	0.1022	1.581	1.000
90	L	4	2	9	B	25.4	18.5	15.4	4.6	4.8	0.0467	0.7017	0.1165	2.495	1.000
90	L	4	3	6	B	25.7	19.3	17.0	4.7	5.0	0.0617	0.7036	0.1409	2.283	0.997
90	L	5	1	7	A	33.0	21.2	21.4	5.1	8.8	0.0440	1.0000	0.0440	1.000	0.994
90	L	5	2	8	A	30.7	21.9	14.8	4.5	7.5	0.0647	0.8399	0.1003	1.550	1.000
90	L	5	3	3	A	33.6	20.9	14.3	4.4	9.3	0.0676	0.8876	0.0915	1.354	1.000
90	L	6	1	7	B	26.7	17.8	19.6	5.0	6.9	0.0360	1.0000	0.0360	1.000	0.999
90	L	6	2	8	B	28.3	21.2	13.7	4.3	6.0	0.0680	0.7005	0.1521	2.238	1.000
90	L	6	3	3	B	25.9	21.4	13.5	4.3	8.1	0.0932	0.8056	0.1479	1.586	0.998
90	L	7	1	4	A	37.4	21.0	14.6	4.5	10.3	0.0814	0.9077	0.1026	1.261	1.000
90	L	7	2	9	A	27.0	21.8	19.6	5.0	4.2	0.0414	0.7076	0.1051	2.537	0.998
90	L	7	3	6	A	30.0	21.6	18.3	4.8	5.7	0.0984	0.5269	0.2947	2.995	0.992
90	L	8	1	4	B	32.4	17.3	15.0	4.6	8.3	0.0822	0.7127	0.1685	2.050	1.000
90	L	8	2	9	B	26.4	18.5	15.5	4.6	6.5	0.0646	0.7590	0.1250	1.935	1.000
90	L	8	3	6	B	23.0	19.2	17.1	4.7	5.0	0.0837	0.6648	0.1922	2.297	0.996
90	L	9	1	4	A	39.9	21.0	14.6	4.5	9.7	0.0688	0.8161	0.1125	1.636	1.000
90	L	9	2	9	A	31.3	21.8	19.6	4.9	6.7	0.0565	0.7875	0.1041	1.842	1.000
90	L	9	3	6	A	35.2	21.5	18.3	4.8	5.1	0.0842	0.6441	0.2032	2.413	0.994
90	L	10	1	4	B	33.4	17.3	15.1	4.6	9.2	0.0650	0.6996	0.1478	2.273	1.000
90	L	10	2	9	B	28.8	18.5	15.5	4.6	5.3	0.0477	0.8268	0.0808	1.694	1.000
90	L	11	2	8	A	34.9	22.1	15.0	4.5	7.3	0.0749	0.7895	0.1293	1.726	1.000
90	L	11	3	3	A	40.0	20.9	14.4	4.4	9.6	0.0789	0.7651	0.1432	1.816	1.000
90	L	12	1	7	B	27.9	17.8	20.2	5.1	7.5	0.0416	1.0000	0.0416	1.000	0.995
90	L	12	2	8	B	31.4	21.2	13.7	4.4	6.4	0.0676	0.7492	0.1328	1.966	0.999
90	L	13	1	10	A	28.8	21.6	18.0	4.8	6.0	0.0618	0.8544	0.0926	1.500	1.000
90	L	13	2	10	B	23.3	18.6	15.0	4.5	6.6	0.0533	0.8490	0.0830	1.557	1.000
90	L	13	3	11	A	28.9	20.9	17.0	4.7	6.3	0.0541	0.7779	0.1034	1.911	0.997
90	L	14	1	10	A	25.4	21.6	18.0	4.8	6.0	0.0553	0.7809	0.1042	1.886	1.000
90	L	14	3	11	A	24.2	20.8	17.0	4.7	6.2	0.0556	0.7529	0.1136	2.042	1.000
90	L	15	1	10	A	31.8	21.6	18.2	4.8	7.4	0.0617	0.8122	0.1041	1.687	1.000
90	L	15	2	10	B	27.9	18.6	15.0	4.5	5.5	0.0658	0.7579	0.1271	1.933	1.000
90	L	16	1	11	B	22.0	18.8	14.7	4.5	5.9	0.0622	0.8280	0.1003	1.612	1.000
90	L	16	2	11	B	26.3	18.7	14.7	4.5	5.2	0.0694	0.7734	0.1270	1.831	1.000
90	L	16	3	11	B	28.6	18.6	14.8	4.5	5.5	0.0569	0.7380	0.1205	2.119	1.000
Summary Statistics (n = 43)					Max	40.0	22.1	21.4	5.1	10.3	0.0984	1	0.2947	2.995	1.000
					Min	22.0	17.3	13.5	4.3	4.2	0.0344	0.5269	0.0360	1.000	0.992
					Avg	29.9	20.2	16.3	4.6	7.0	0.0623	0.7876	0.1172	1.851	0.999
					Std	4.4	1.6	2.2	0.2	1.7	0.0146	0.0969	0.0450	0.442	

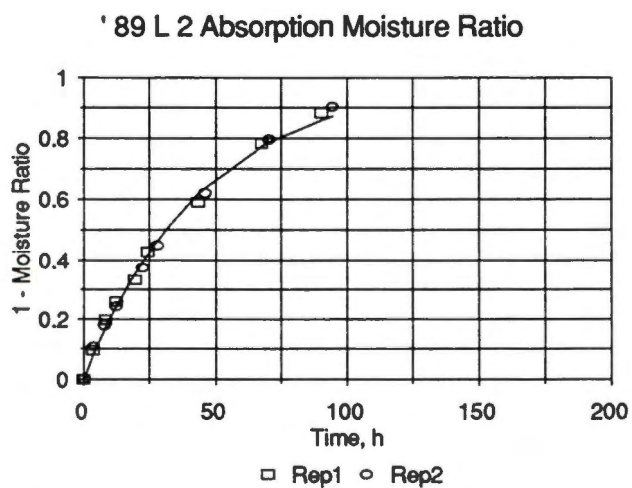
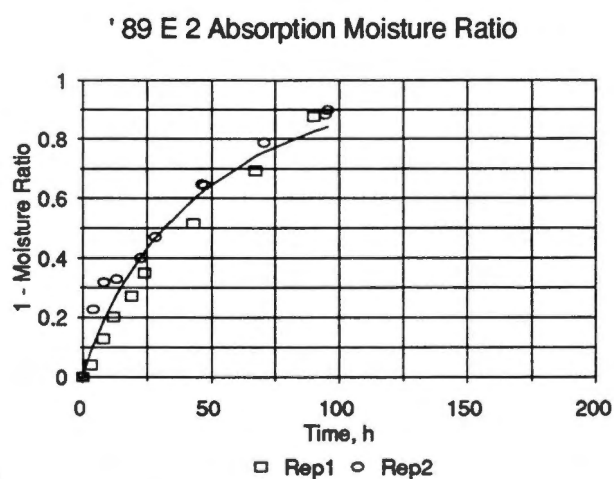
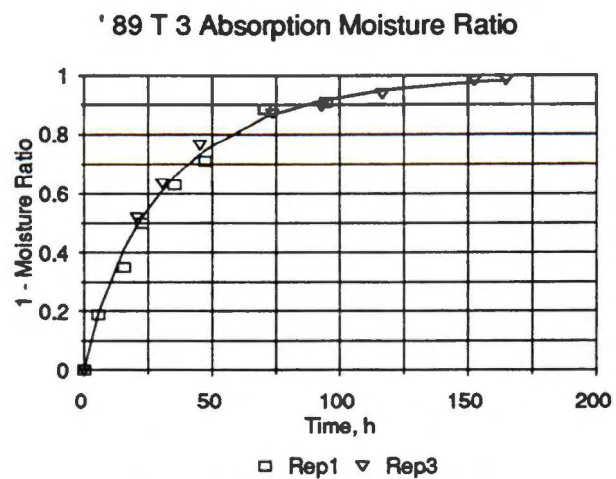


Figure C1. Observed and predicted moisture ratios for absorption tests during harvest week 3 for Tn4-86, and week 2 for Essex and Leflore soybeans in 1989.

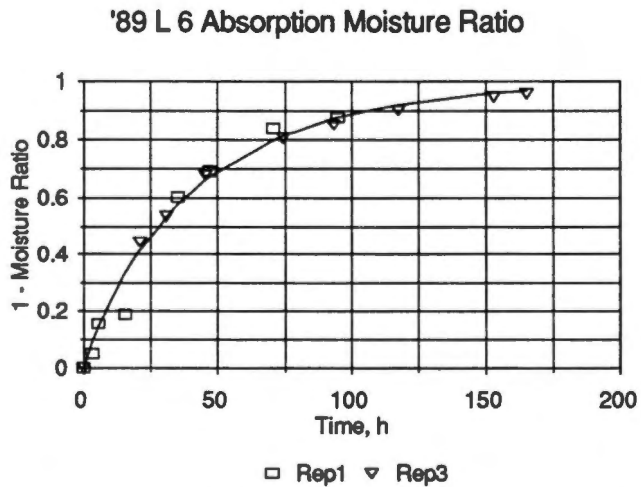
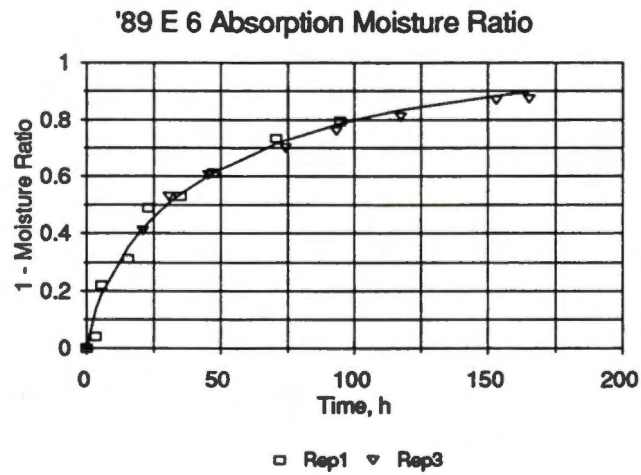
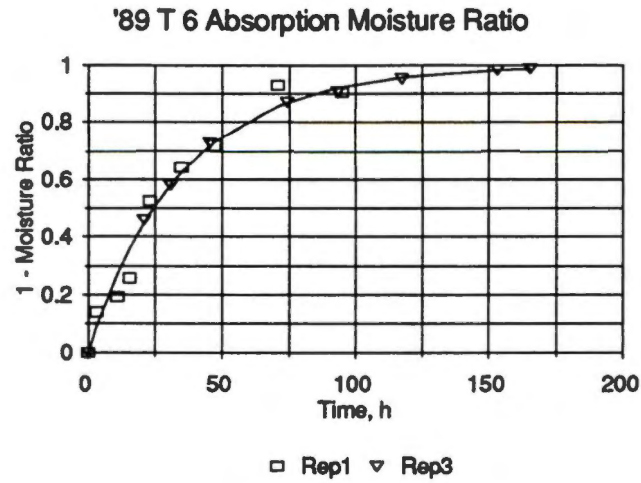


Figure C2. Observed and predicted moisture ratios for absorption tests during harvest week 6 for Tn4-86, Essex, and Leflore soybeans in 1989.

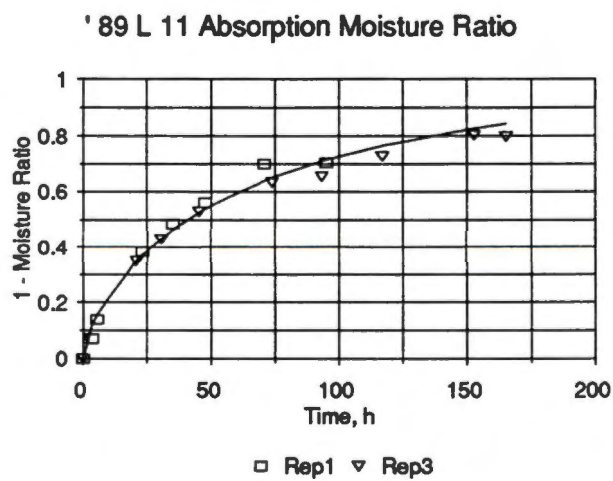
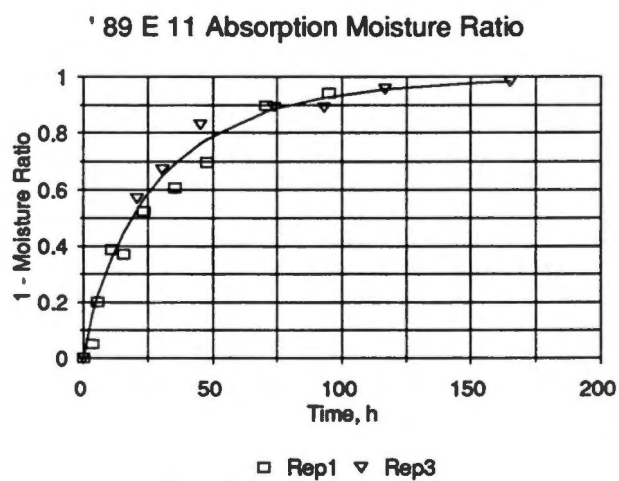
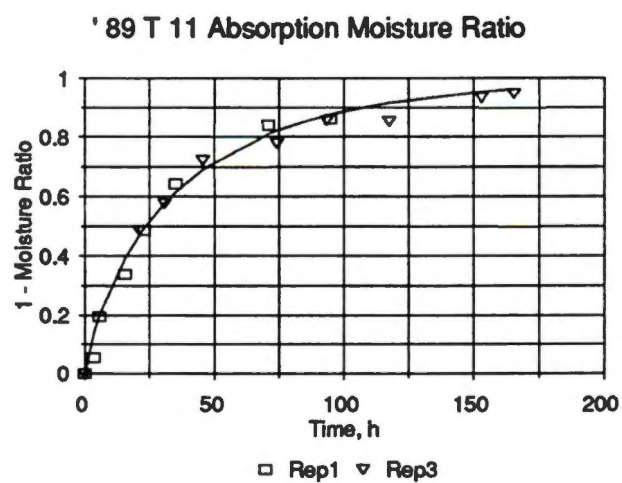
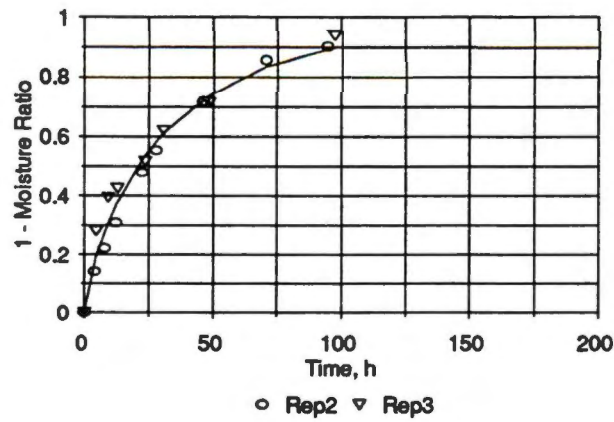
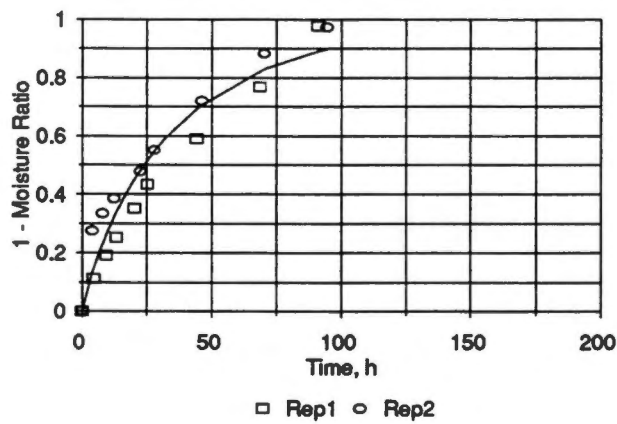


Figure C3. Observed and predicted moisture ratios for absorption tests during harvest week 11 for Tn4-86, Essex, and Leflore soybeans in 1989.

' 89 T 16 Absorption Moisture Ratio



' 89 E 16 Absorption Moisture Ratio



' 89 L 16 Absorption Moisture Ratio

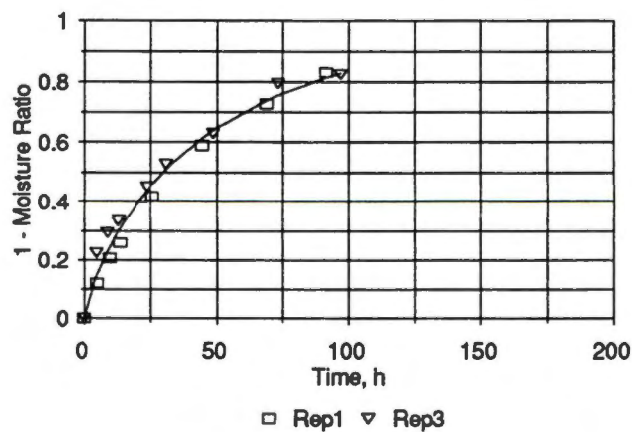


Figure C4. Observed and predicted moisture ratios for absorption tests during harvest week 16 for Tn4-86, Essex, and Leflore soybeans in 1989.

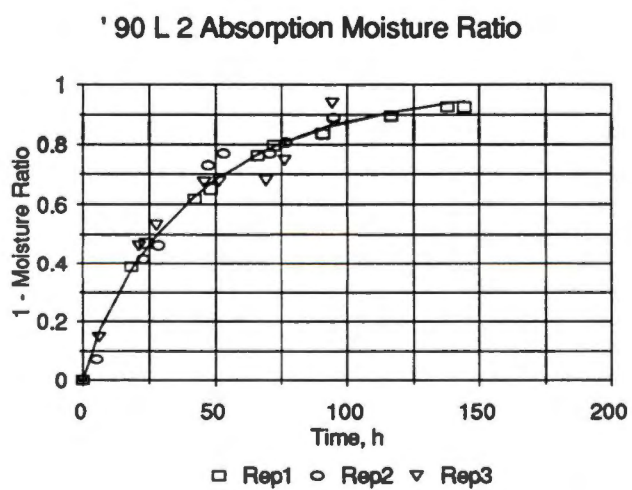
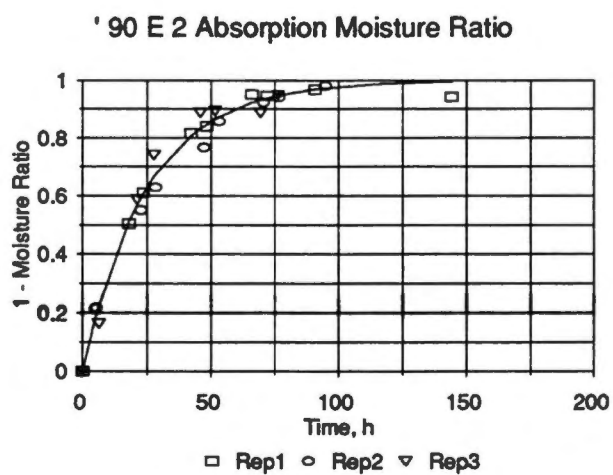
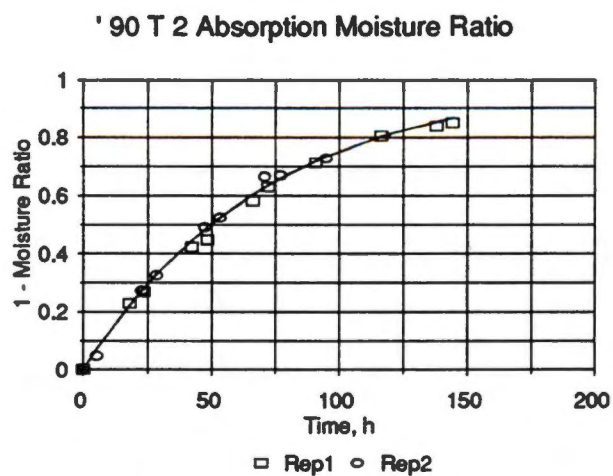


Figure C5. Observed and predicted moisture ratios for absorption tests during harvest week 2 for Tn4-86, Essex, and Leflore soybeans in 1990.

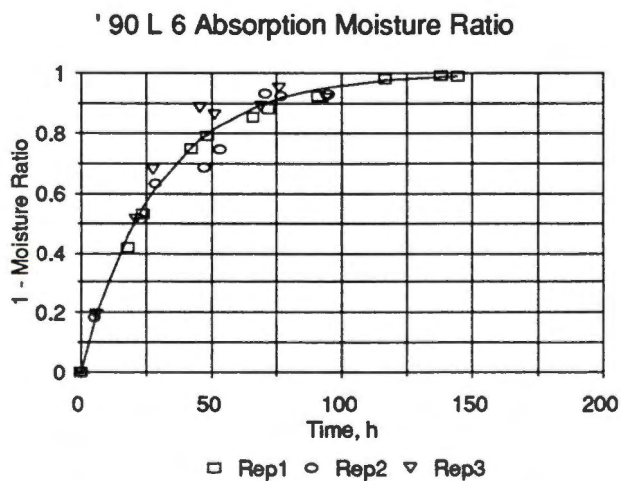
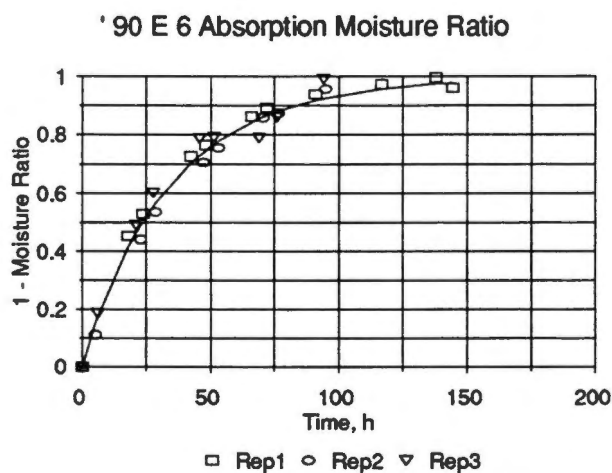
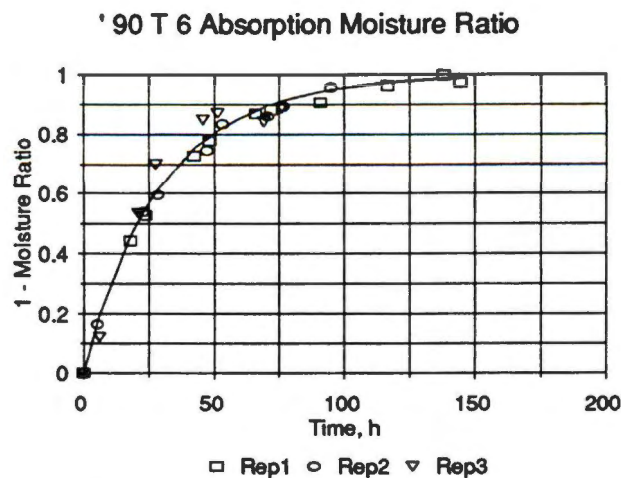


Figure C6. Observed and predicted moisture ratios for absorption tests during harvest week 6 for Tn4-86, Essex, and Leflore soybeans in 1990.

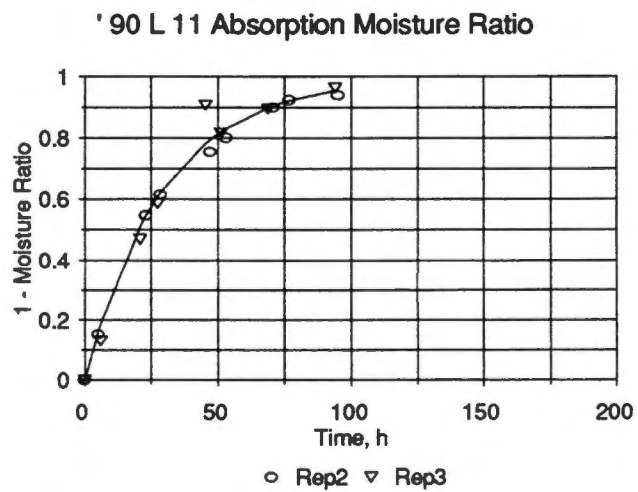
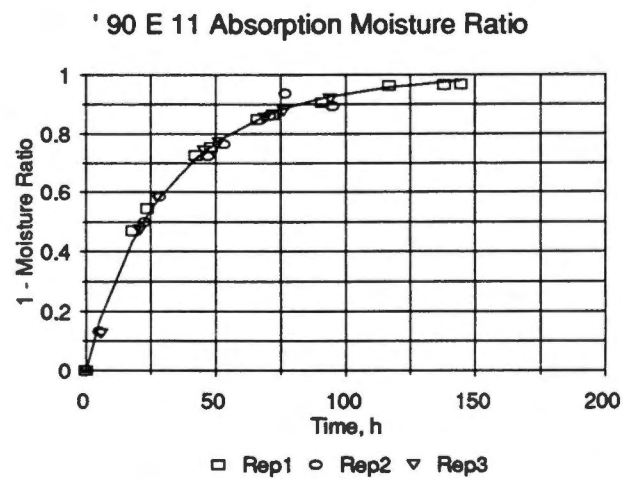
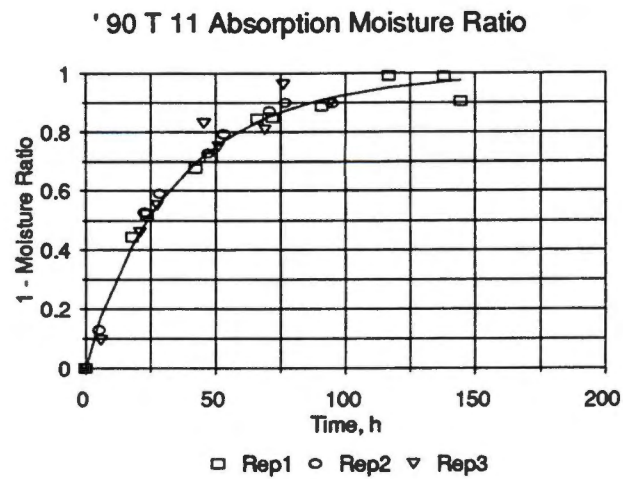


Figure C7. Observed and predicted moisture ratios for absorption tests during harvest week 11 for Tn4-86, Essex, and Leflore soybeans in 1990.

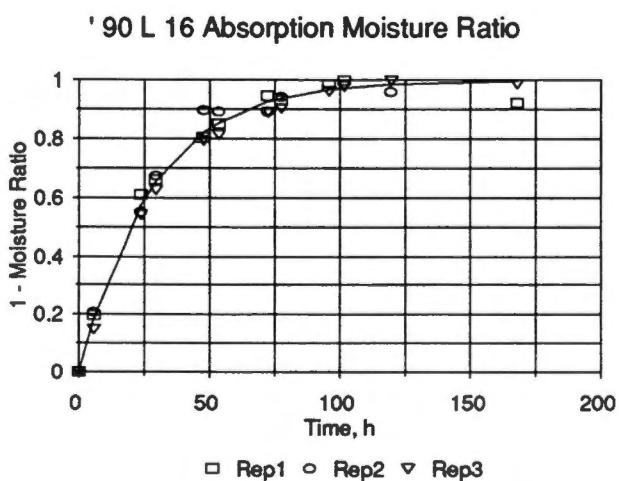
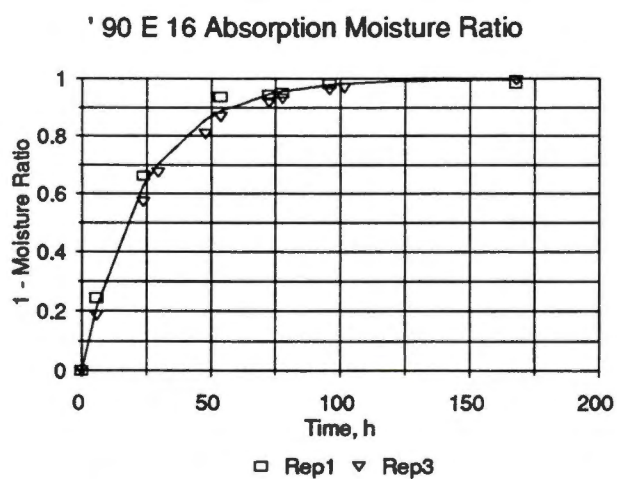
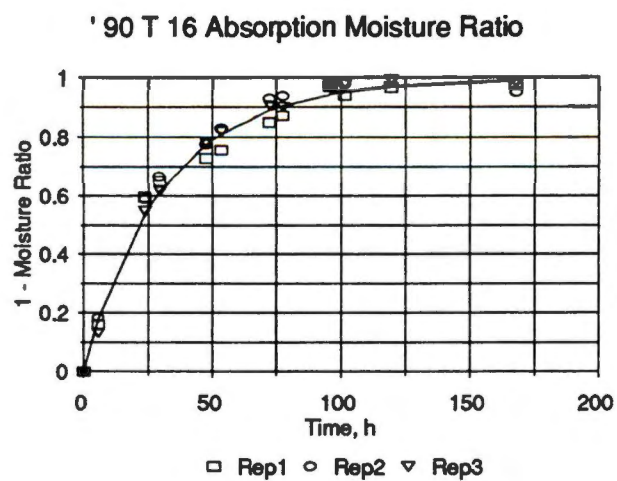


Figure C8. Observed and predicted moisture ratios for absorption tests during harvest week 16 for Tn4-86, Essex, and Leflore soybeans in 1990.

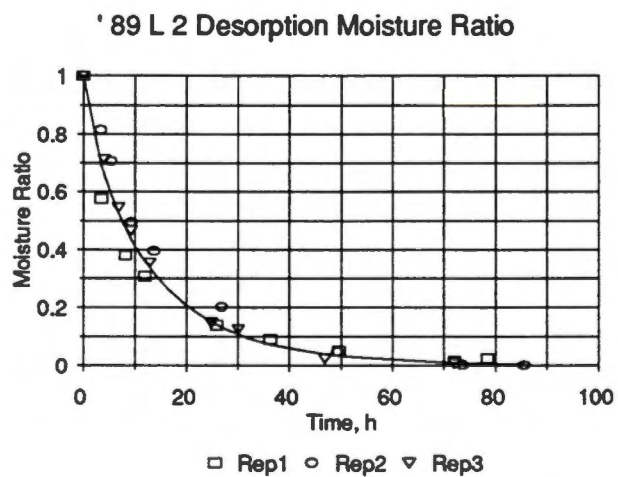
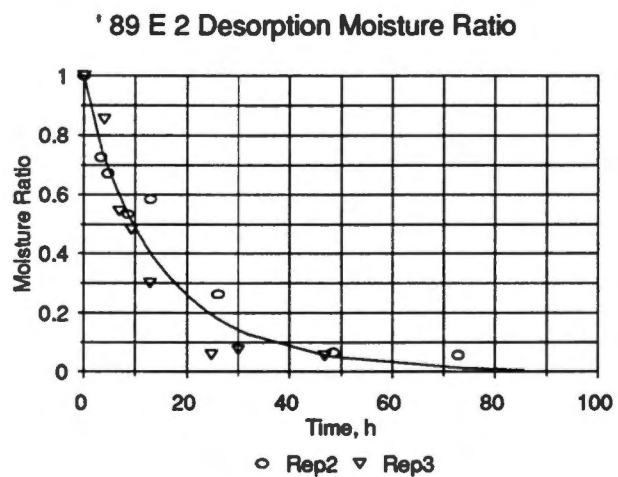
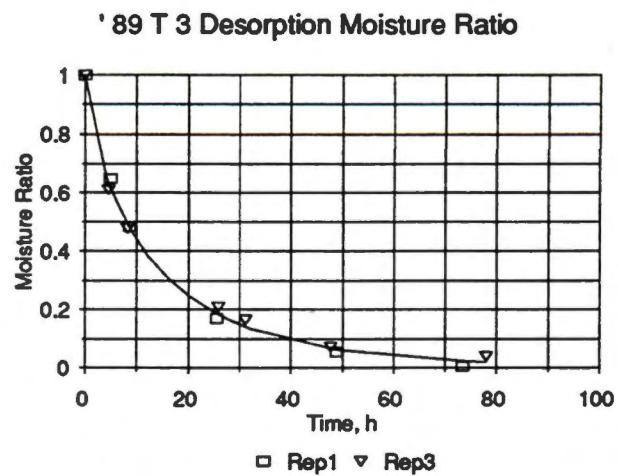


Figure C9. Observed and predicted moisture ratios for desorption tests during harvest week 3 for Tn4-86, and week 2 for Essex and Leflore soybeans in 1989.

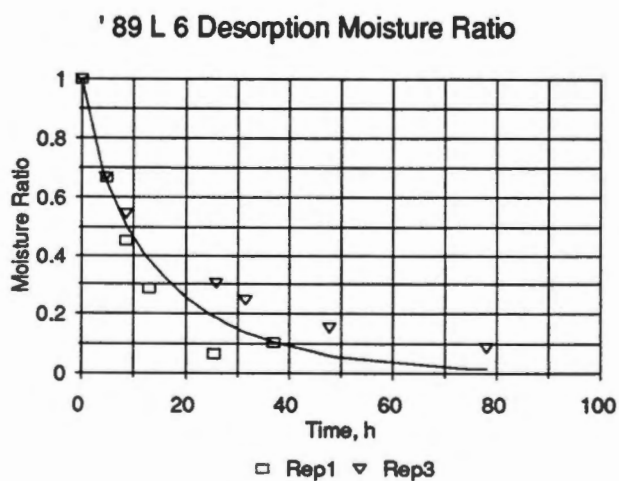
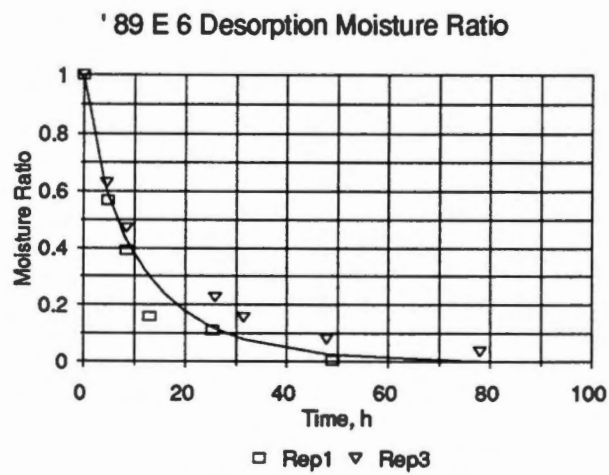
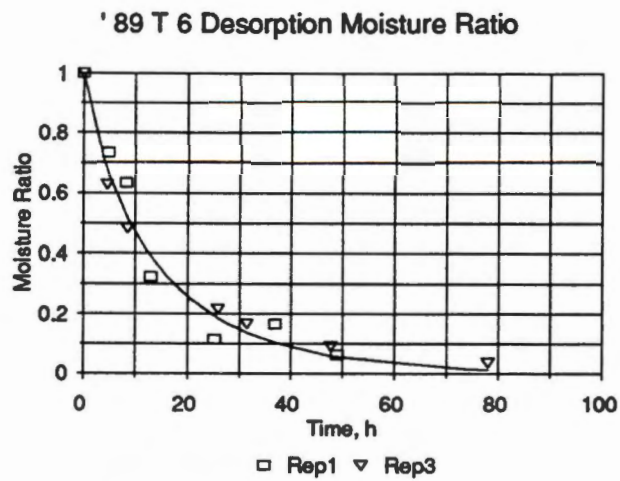
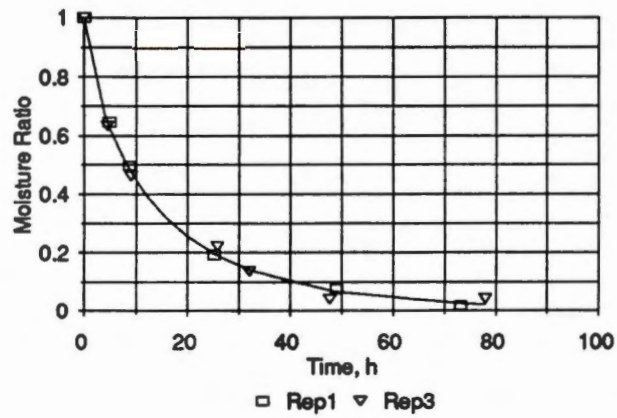
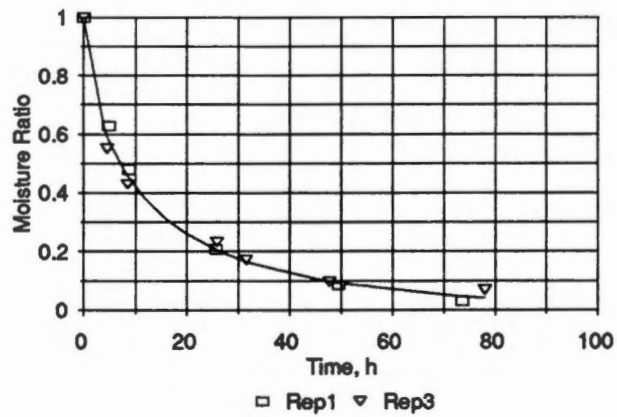


Figure C10. Observed and predicted moisture ratios for desorption tests during harvest week 6 for Tn4-86, Essex, and Leflore soybeans in 1989.

' 89 T 11 Desorption Moisture Ratio



' 89 E 11 Desorption Moisture Ratio



' 89 L 11 Desorption Moisture Ratio

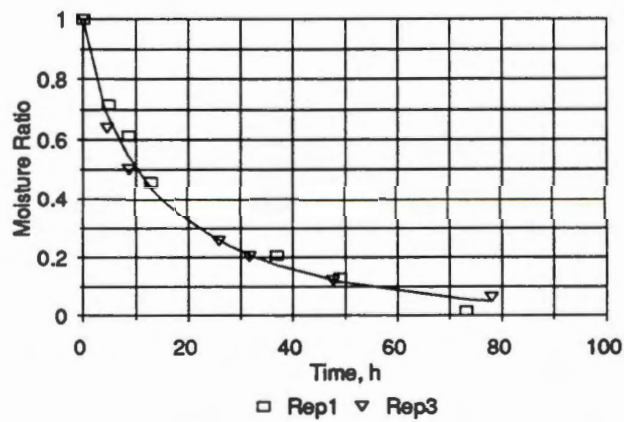
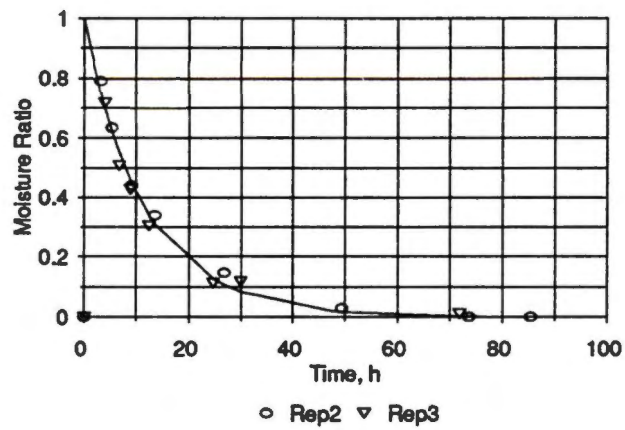
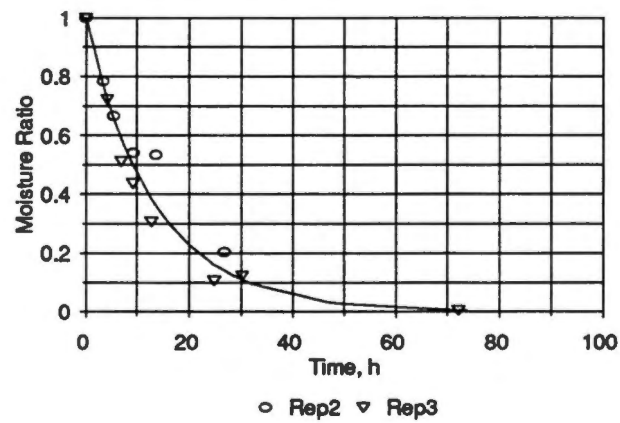


Figure C11. Observed and predicted moisture ratios for desorption tests during harvest week 11 for Tn4-86, Essex, and Leflore soybeans in 1989.

' 89 T 16 Desorption Moisture Ratio



' 89 E 16 Desorption Moisture Ratio



' 89 L 16 Desorption Moisture Ratio

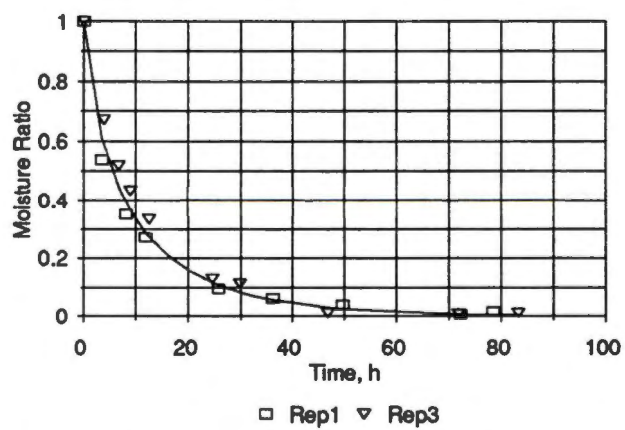


Figure C12. Observed and predicted moisture ratios for desorption tests during harvest week 16 for Tn4-86, Essex, and Leflore soybeans in 1989.

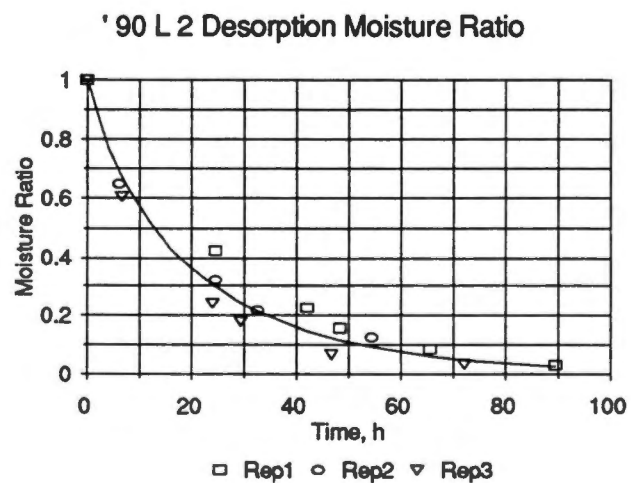
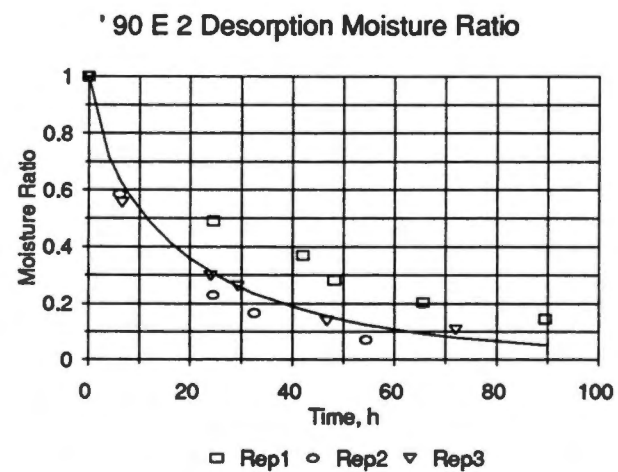
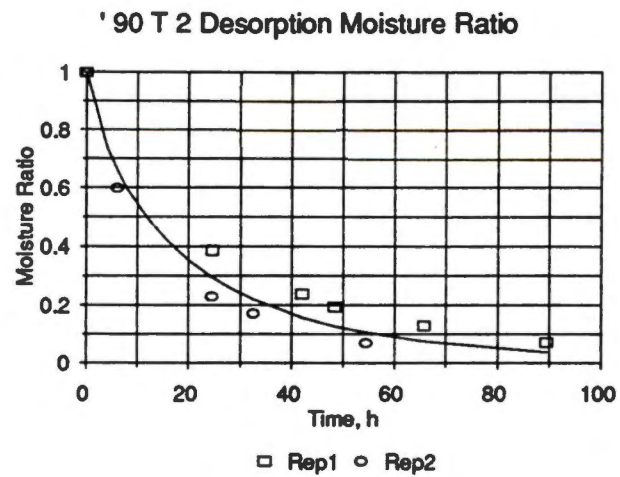


Figure C13. Observed and predicted moisture ratios for desorption tests during harvest week 2 for Tn4-86, Essex, and Leflore soybeans in 1990.

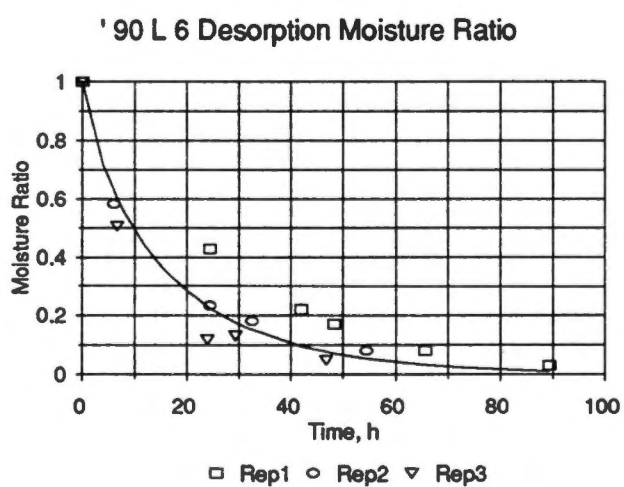
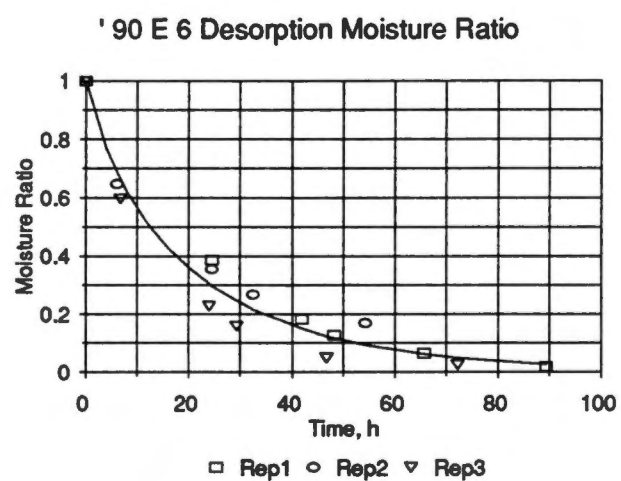
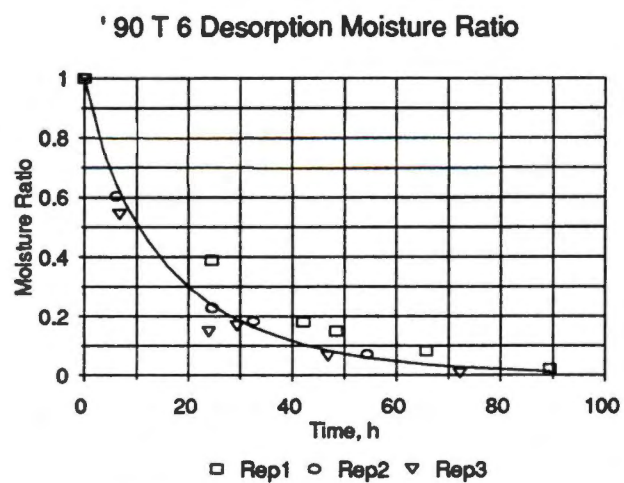
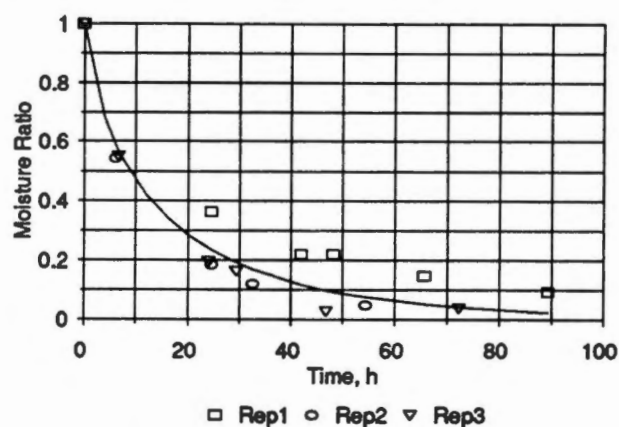
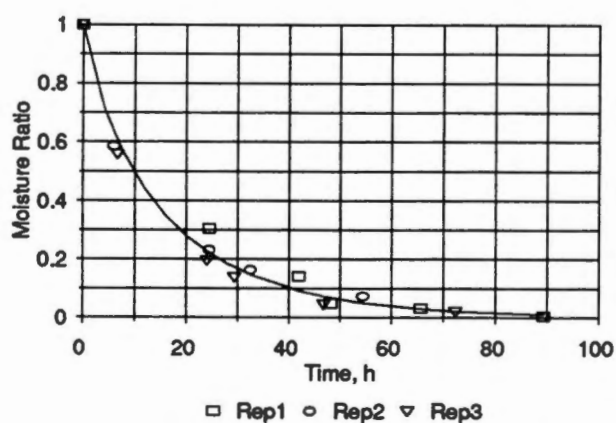


Figure C14. Observed and predicted moisture ratios for desorption tests during harvest week 6 for Tn4-86, Essex, and Leflore soybeans in 1990.

' 90 T 11 Desorption Moisture Ratio



' 90 E 11 Desorption Moisture Ratio



' 90 L 11 Desorption Moisture Ratio

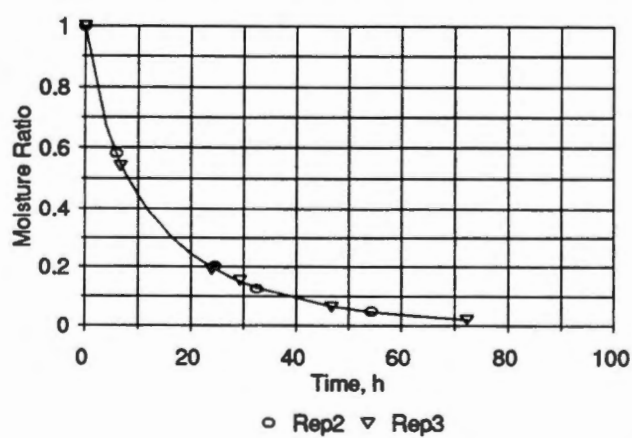
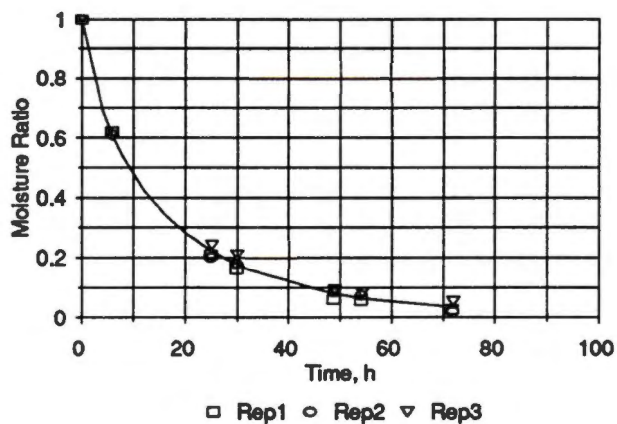
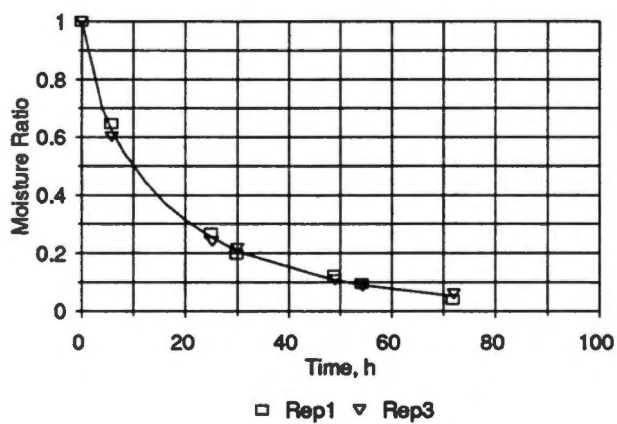


Figure C15. Observed and predicted moisture ratios for desorption tests during harvest week 11 for Tn4-86, Essex, and Leflore soybeans in 1990.

' 90 T 16 Desorption Moisture Ratio



' 90 E 16 Desorption Moisture Ratio



' 90 L 16 Desorption Moisture Ratio

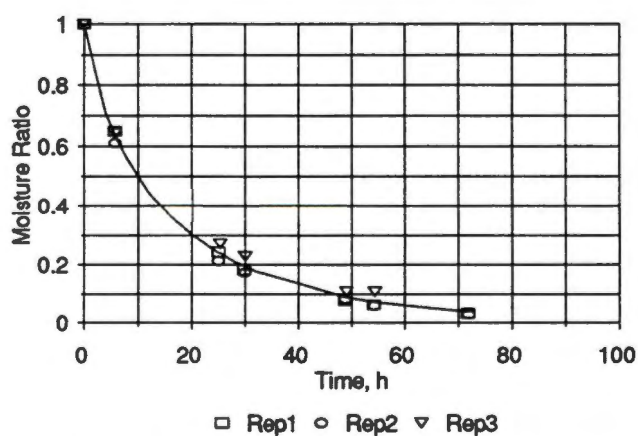
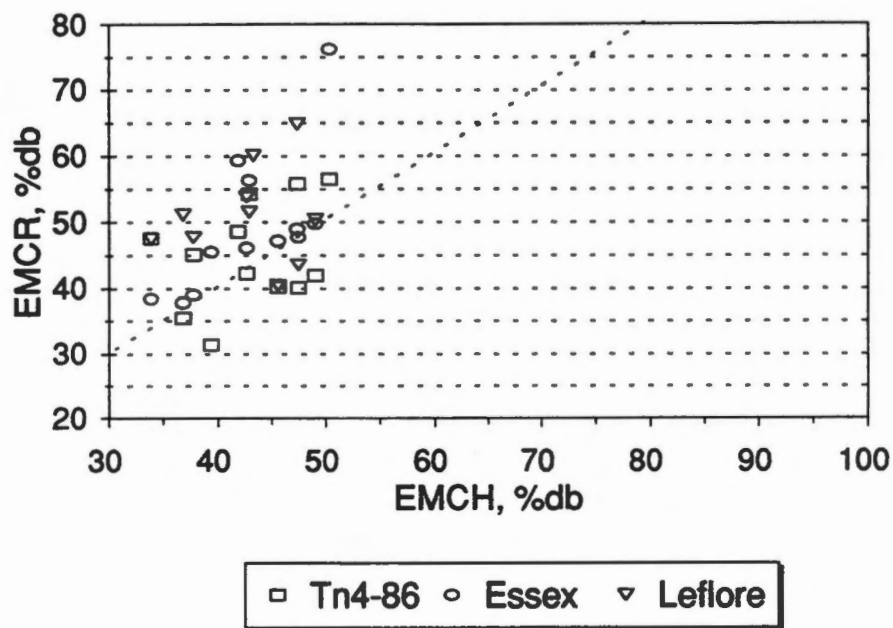
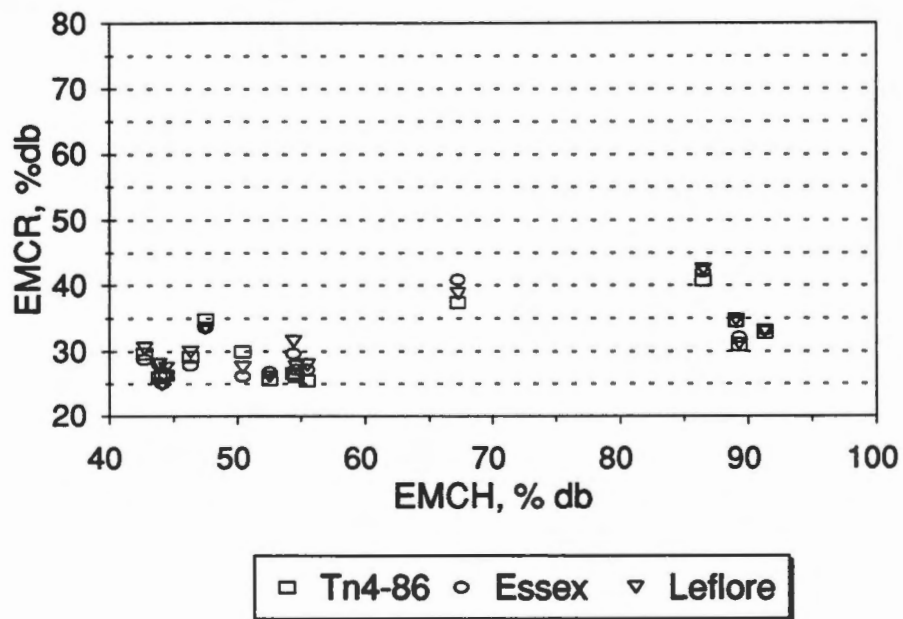


Figure C16. Observed and predicted moisture ratios for desorption tests during harvest week 16 for Tn4-86, Essex, and Leflore soybeans in 1990.

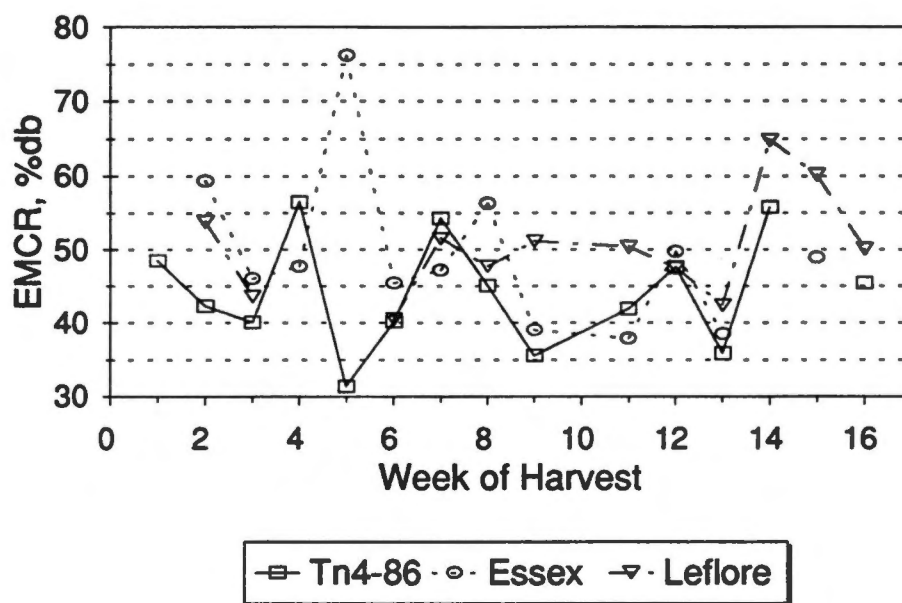


(a)

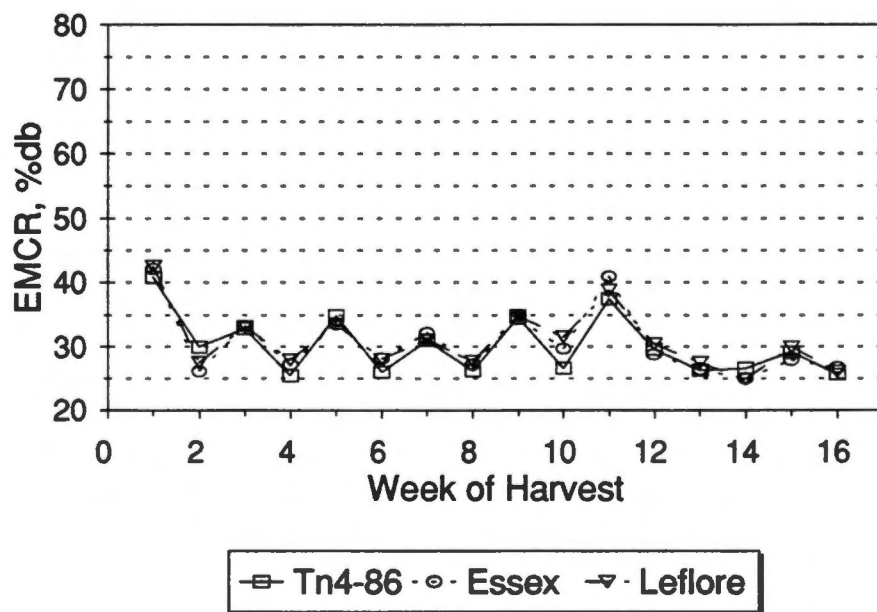


(b)

Figure C17. Comparison of mean regression equilibrium moisture content (EMCR) values with values predicted by the modified Halsey equation (EMCH) for 1989 (a) and 1990 (b) absorption tests.

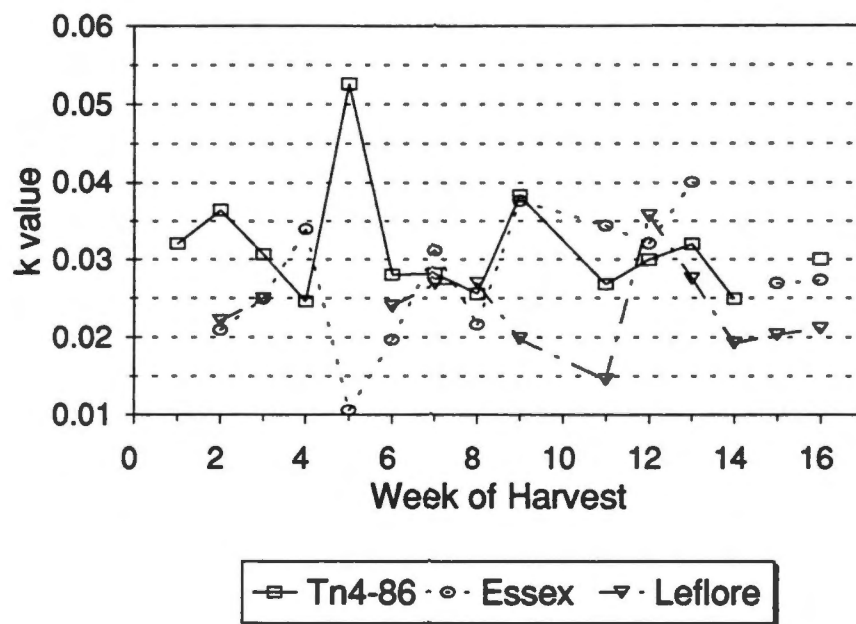


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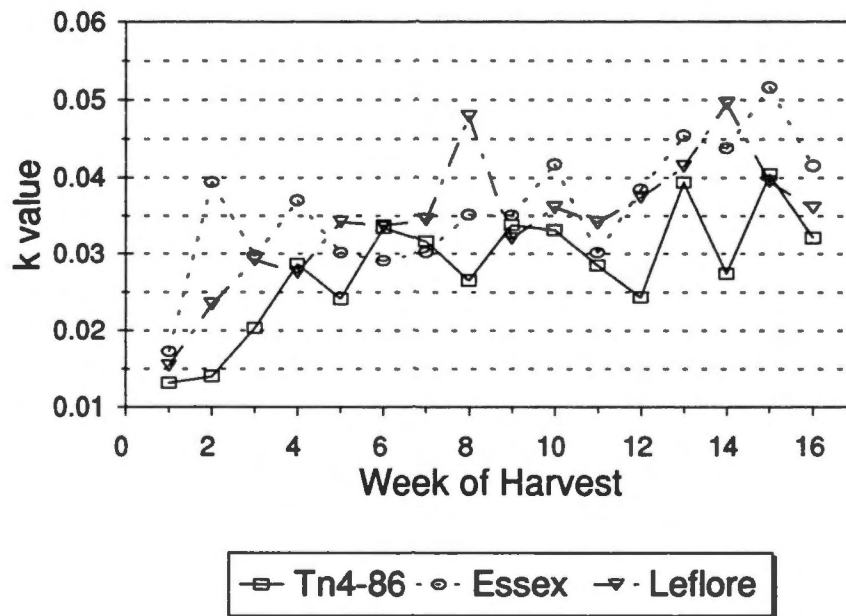


(b)

Figure C18. Variations in the regression equilibrium moisture content (EMCR) values by harvest week and variety for 1989 (a) and 1990 (b) absorption tests.

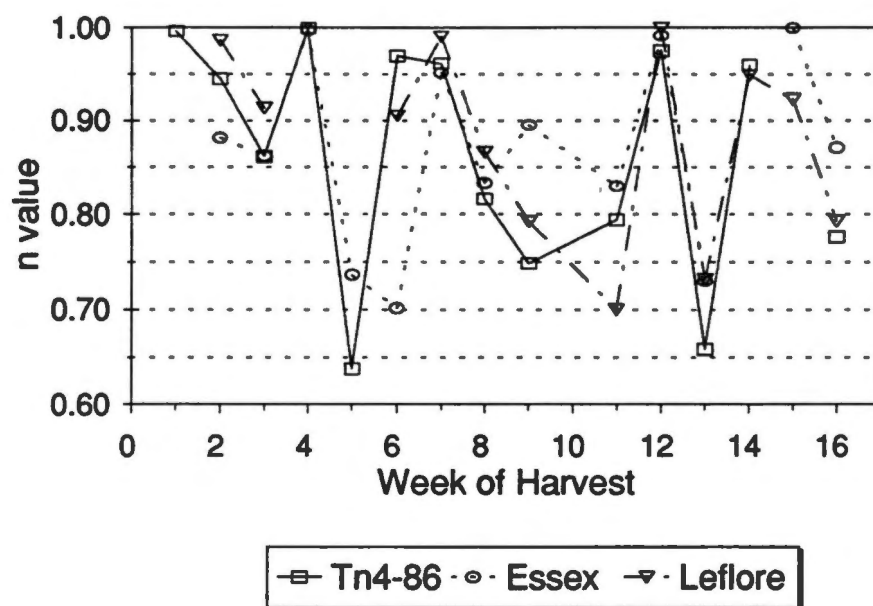


(a)

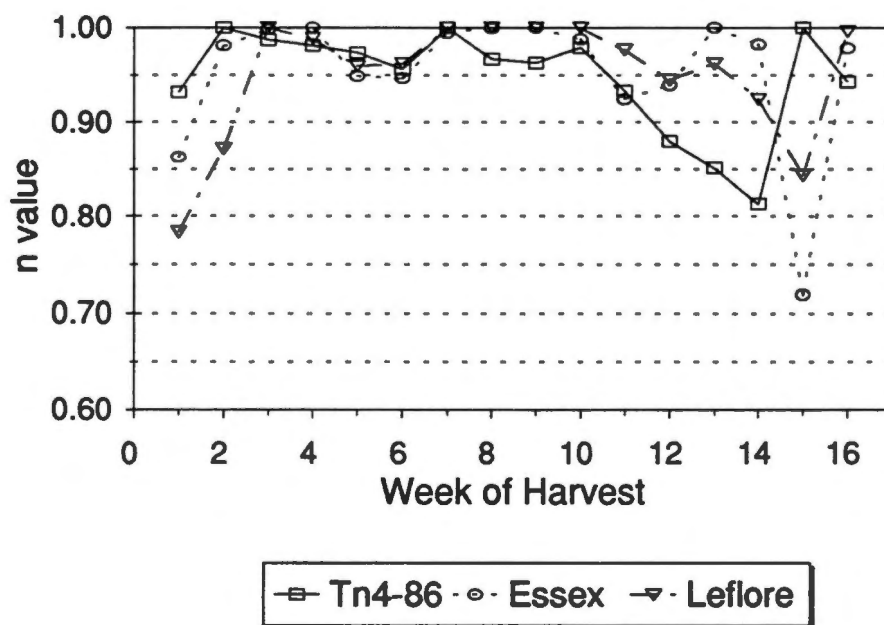


(b)

Figure C19. Mean k values for each harvest week and variety for 1989 (a) and 1990 (b) absorption tests.

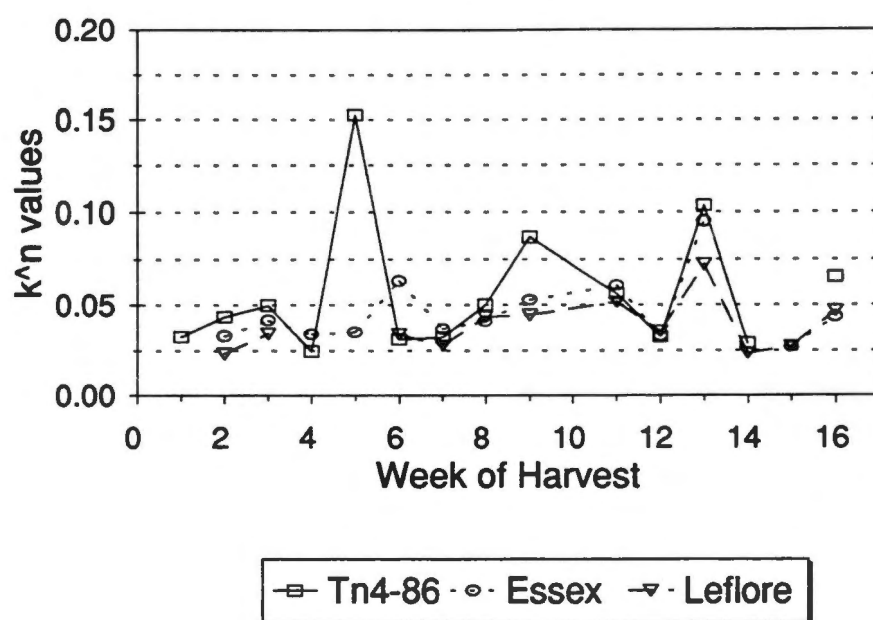


(a)

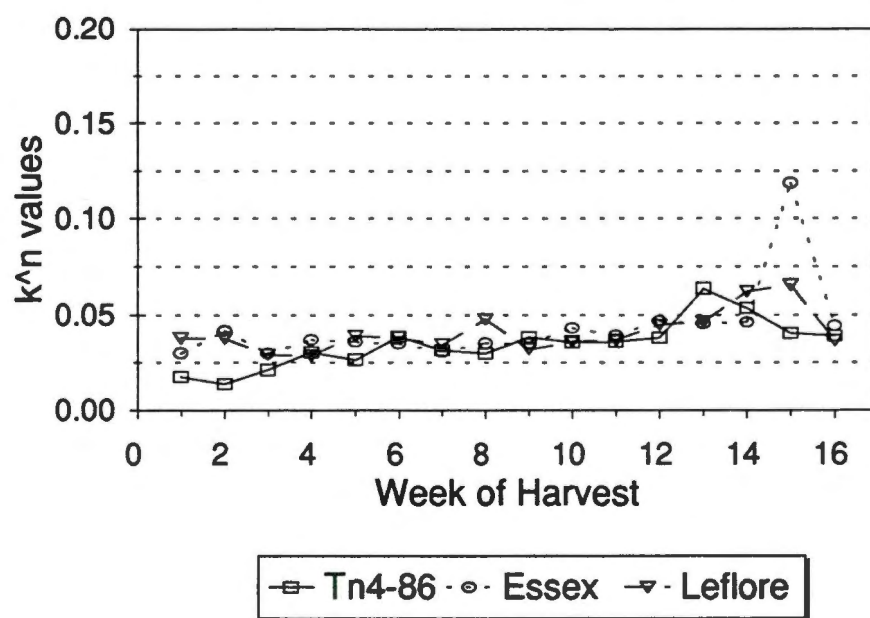


(b)

Figure C20. Mean n values for each harvest week and variety for 1989 (a) and 1990 (b) absorption tests.

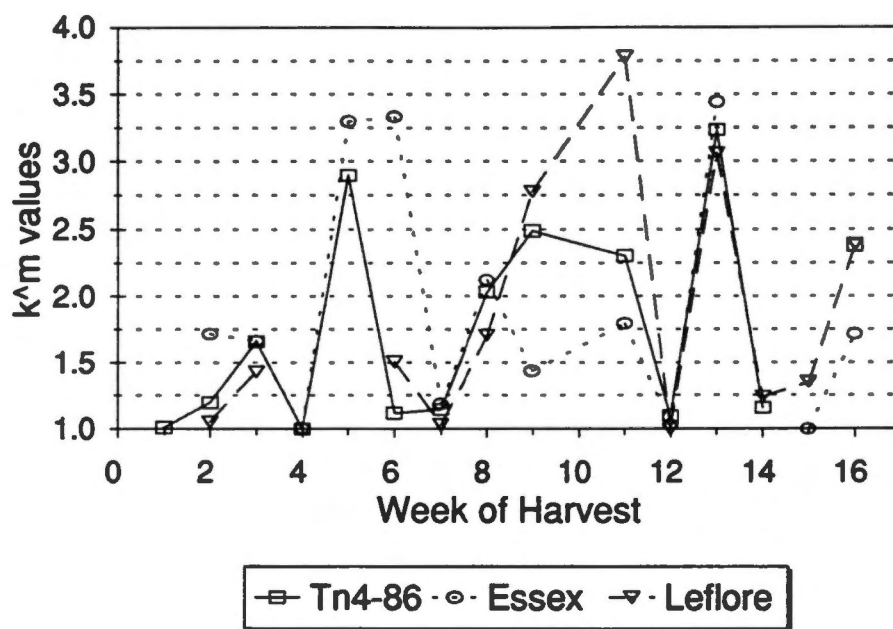


(a)

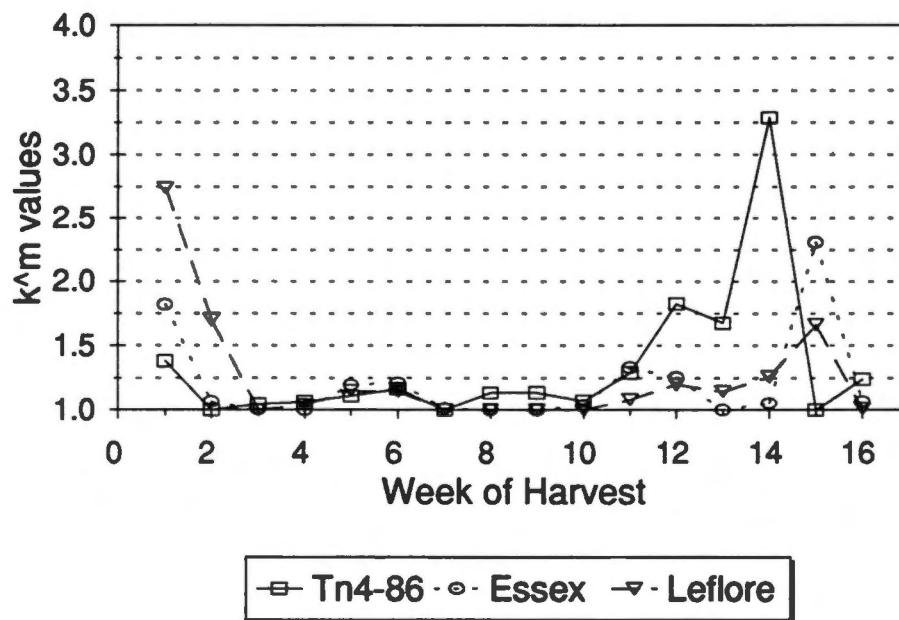


(b)

Figure C21. Mean k^n values for each harvest week and variety for 1989 (a) and 1990 (b) absorption tests.

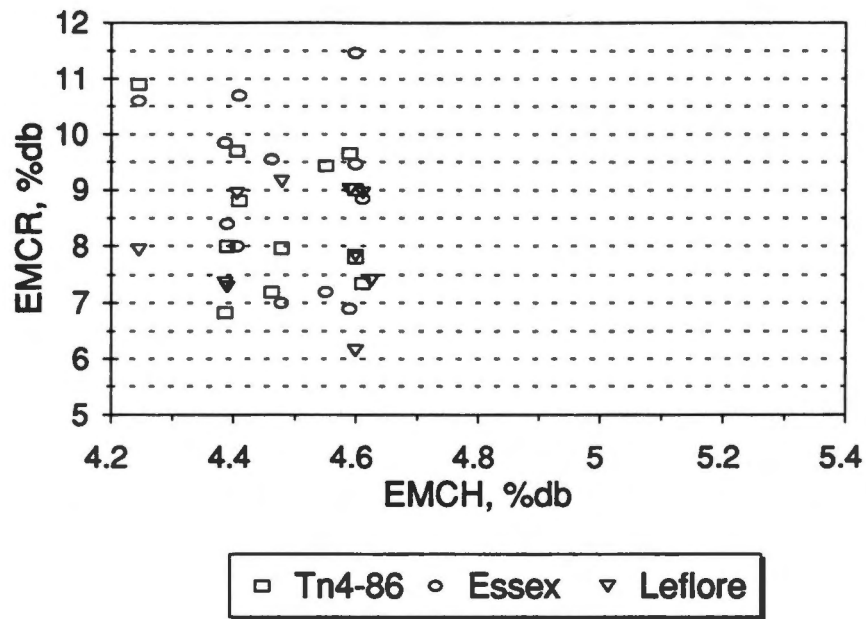


(a)

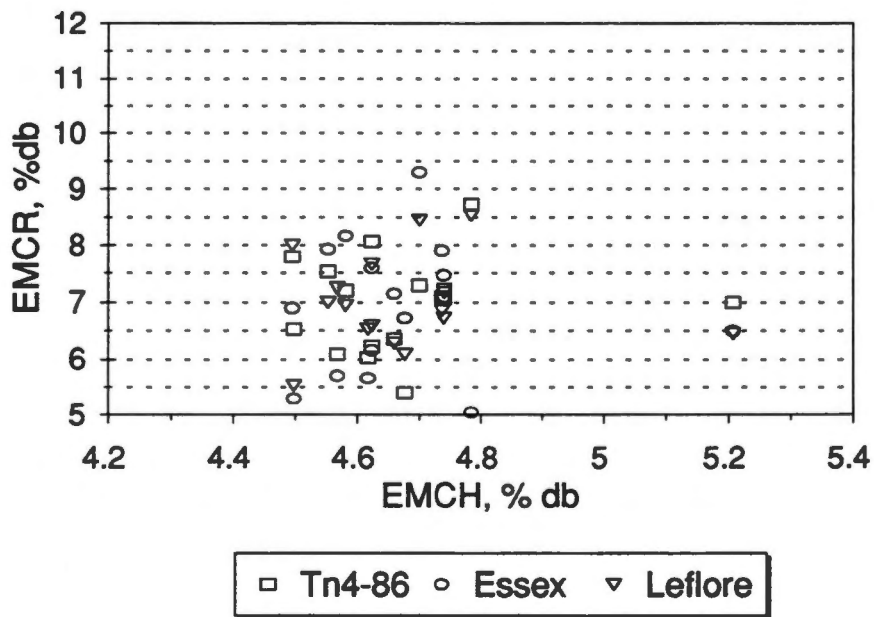


(b)

Figure C22. Mean k^m values for each harvest week and variety for 1989 (a) and 1990 (b) absorption tests.

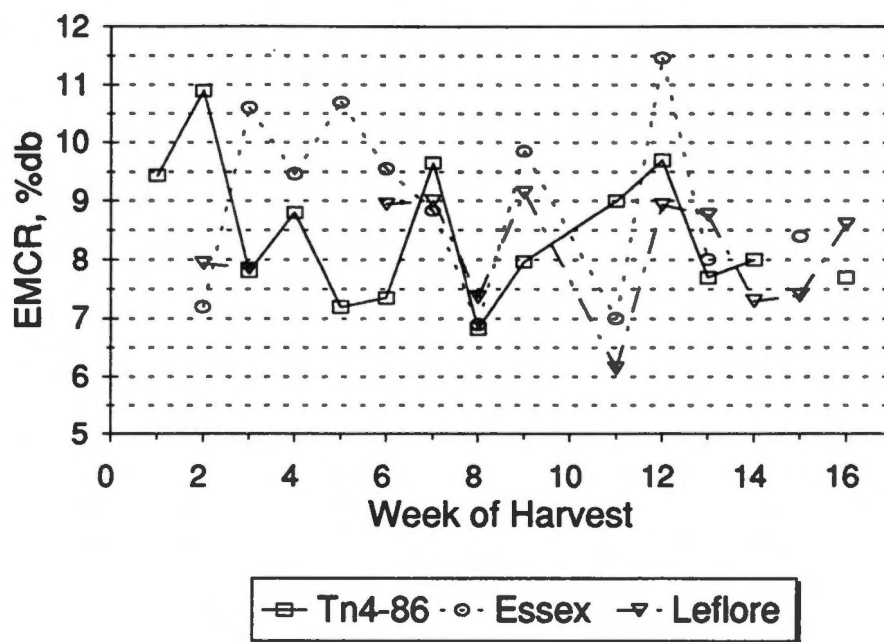


(a)

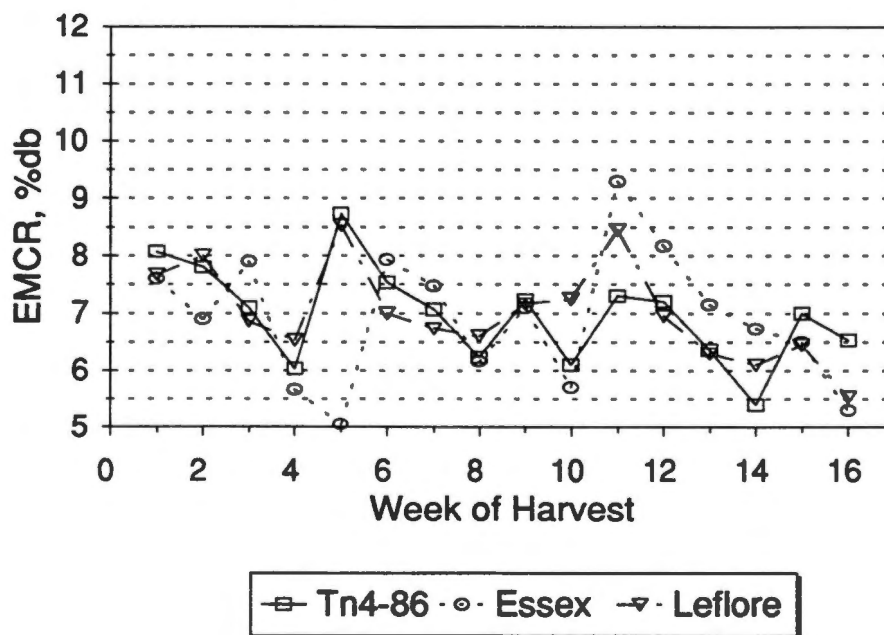


(b)

Figure C23. Comparison of mean regression equilibrium moisture content (EMCR) values with values predicted by the modified Halsey equation (EMCH) for 1989 (a) and 1990 (b) desorption tests.

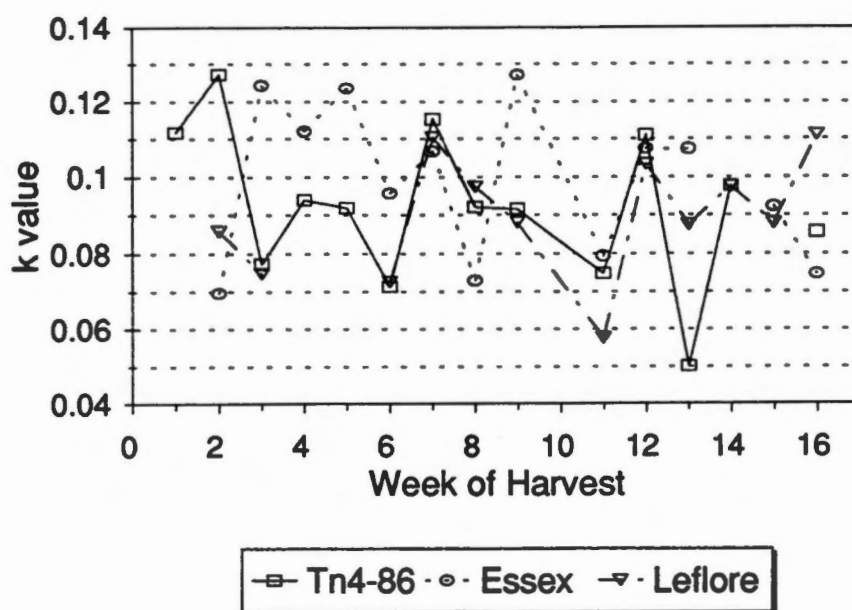


(a)

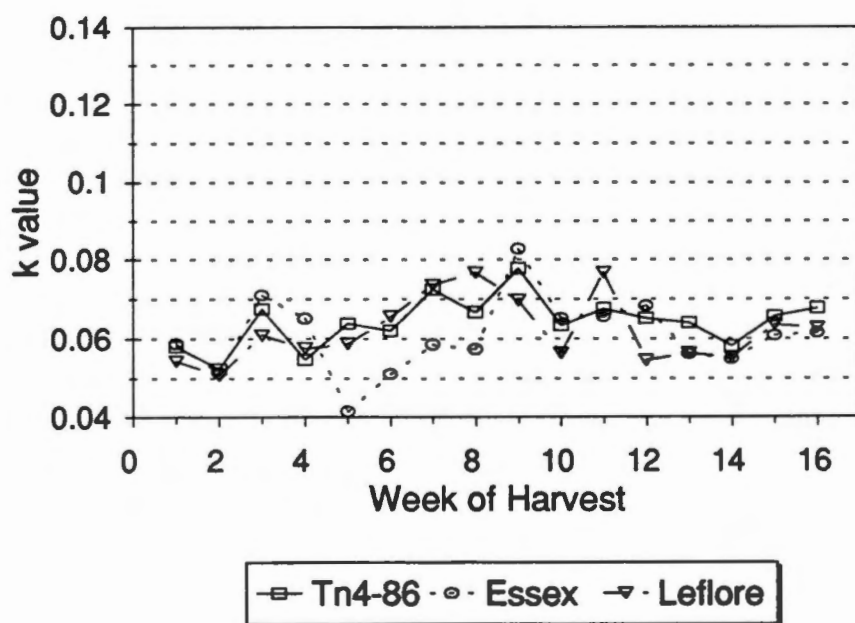


(b)

Figure C24. Variations in regression equilibrium moisture content (EMCR) values for each harvest week and variety for 1989 (a) and 1990 (b) desorption tests.

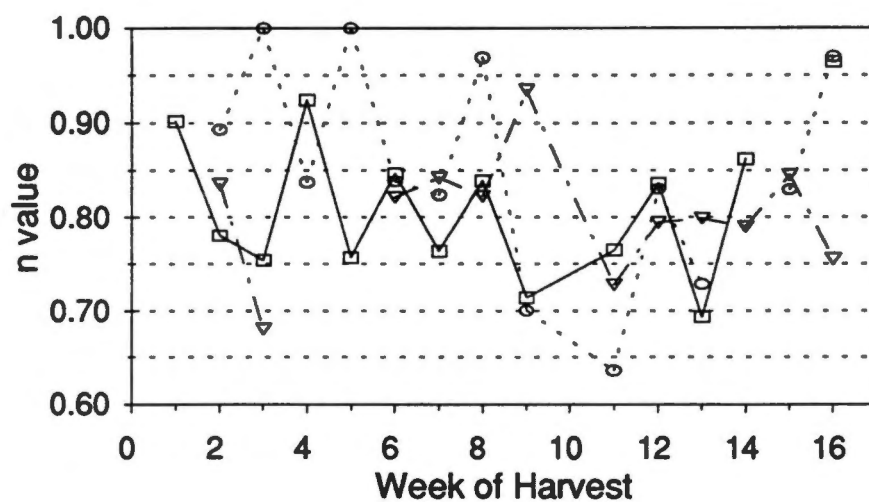


(a)

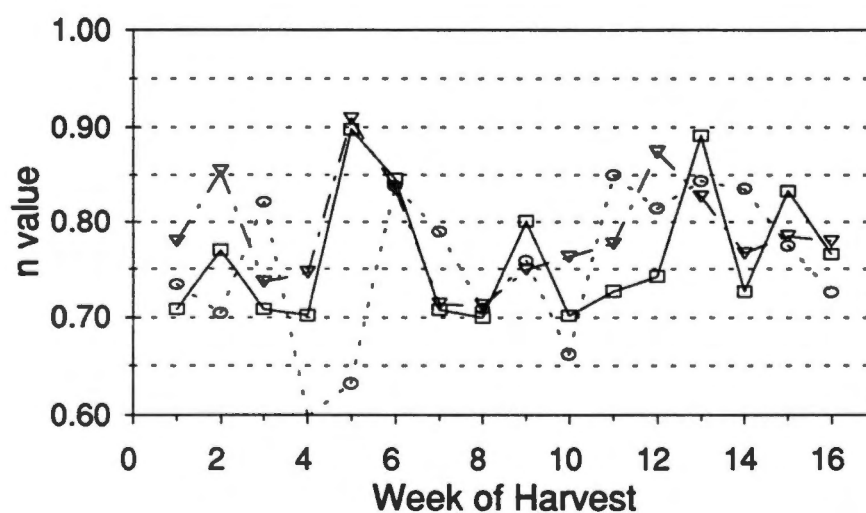


(b)

Figure C25. Mean k values for each harvest week and variety for 1989 (a) and 1990 (b) desorption tests.

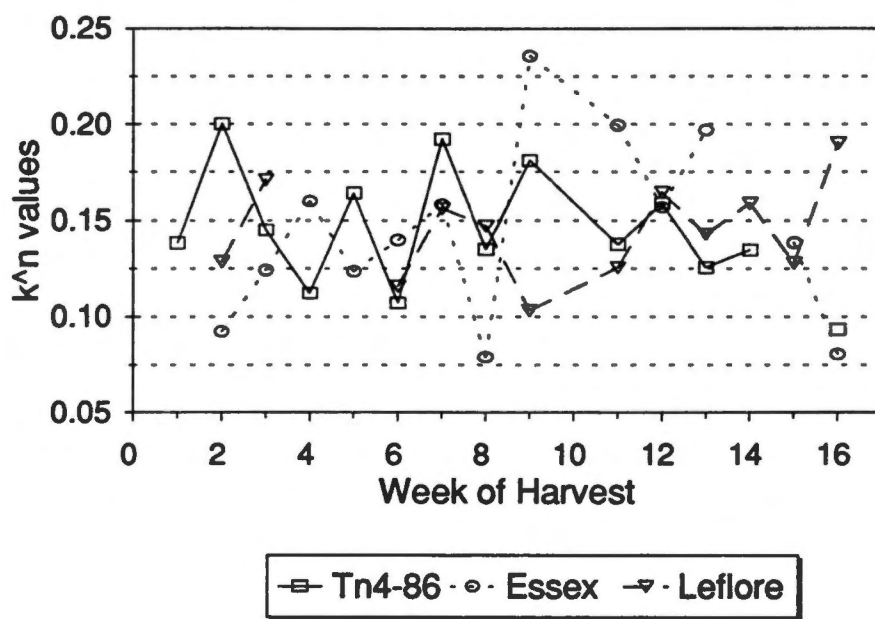


(a)

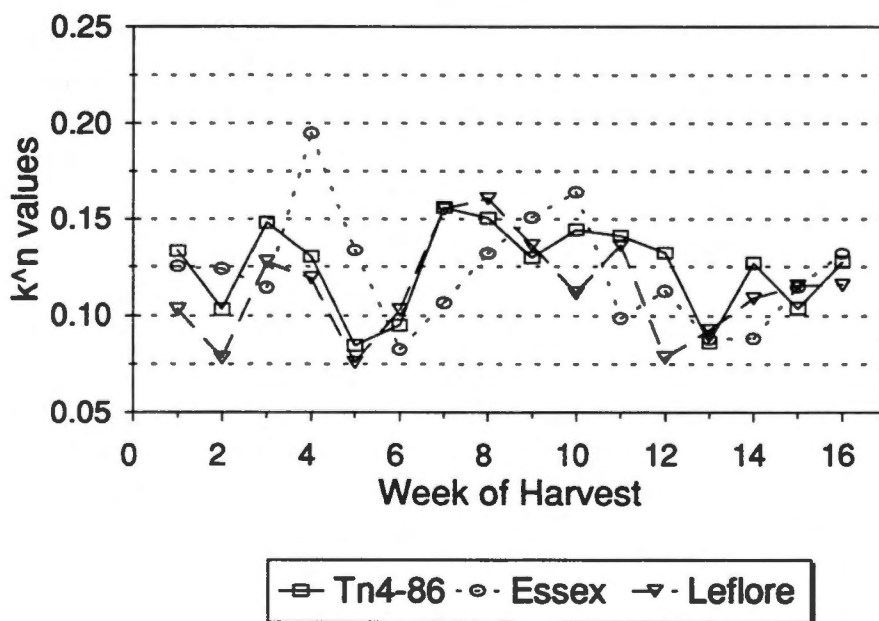


(b)

Figure C26. Mean n values for each harvest week and variety for 1989 (a) and 1990 (b) desorption tests.

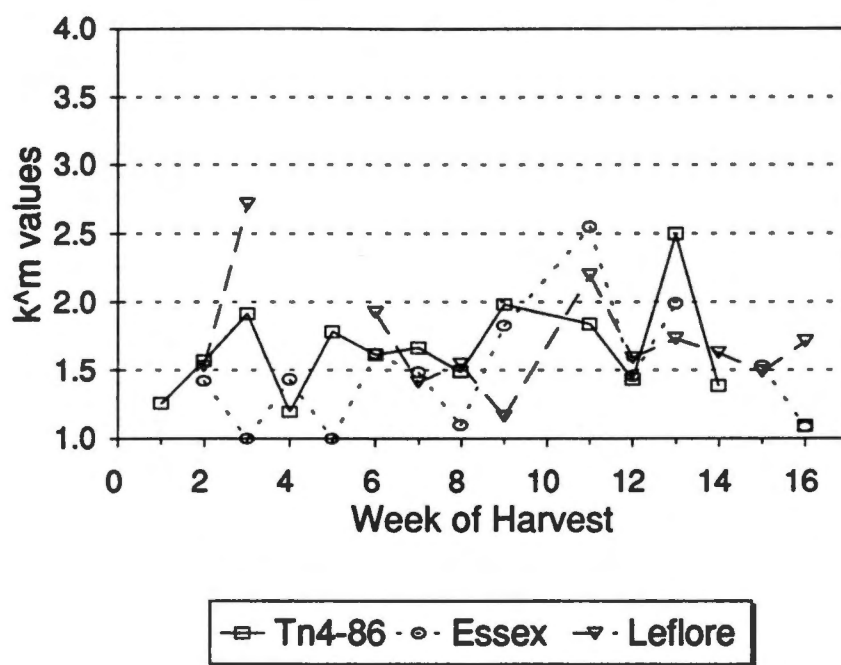


(a)

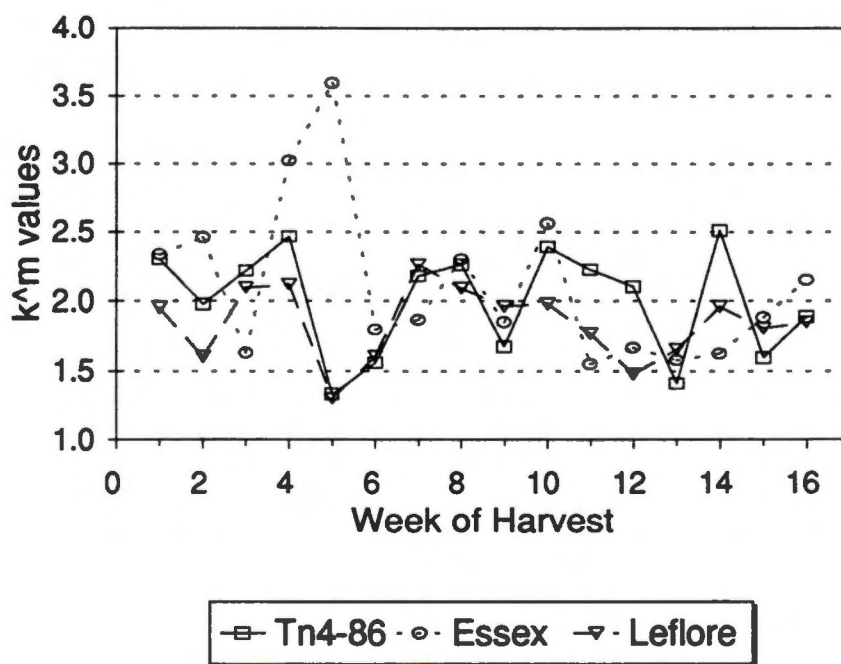


(b)

Figure C27. Mean k^n values for each harvest week and variety for 1989 (a) and 1990 (b) desorption tests.

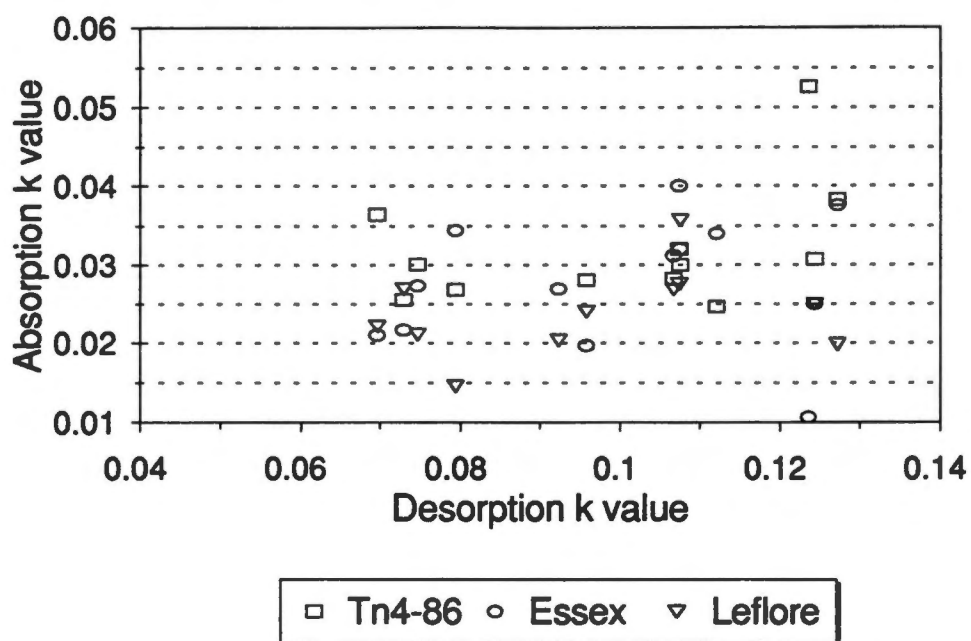


(a)

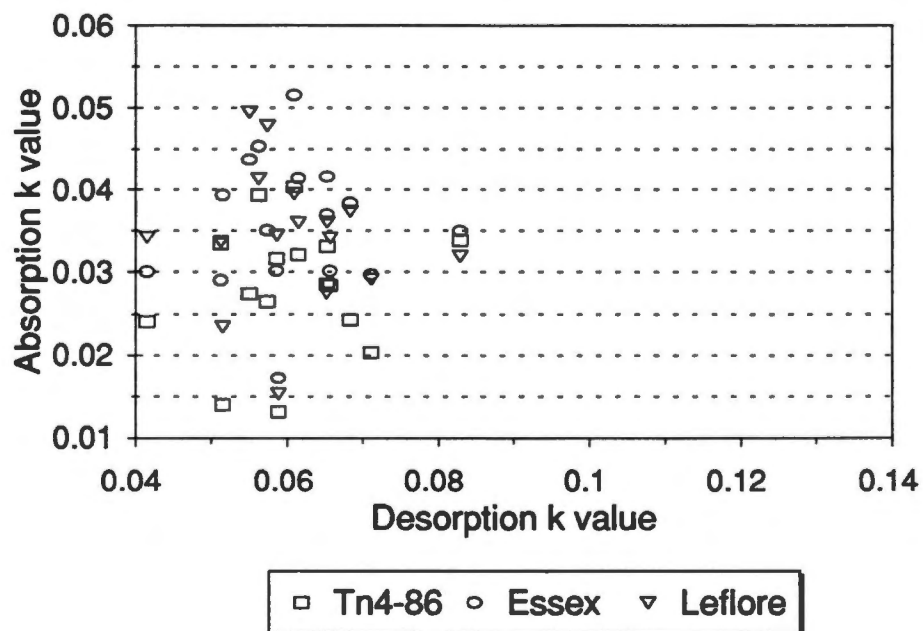


(b)

Figure C28. Mean k^m values for each harvest week and variety for 1989 (a) and 1990 (b) desorption tests.

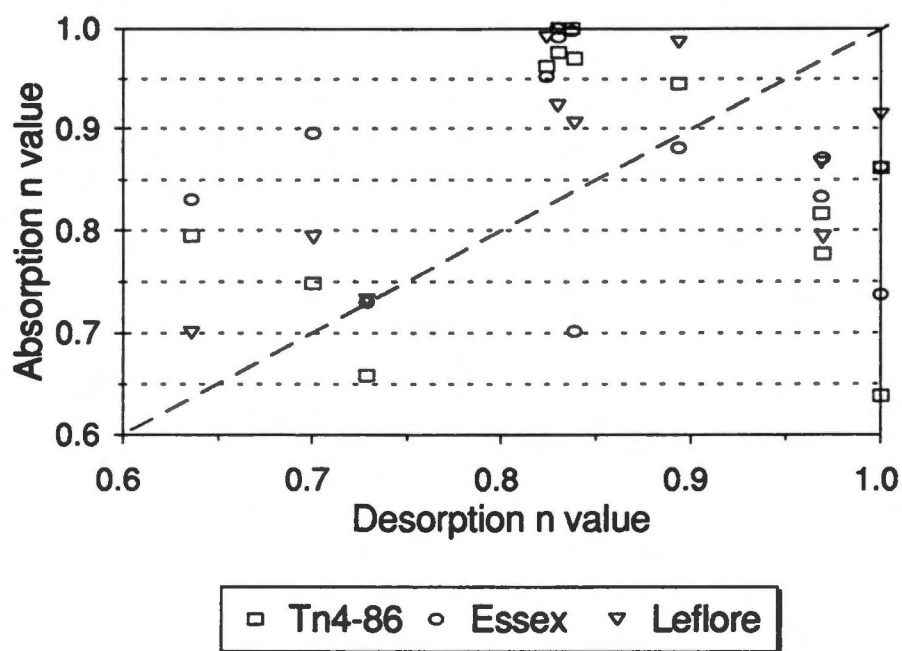


(a)

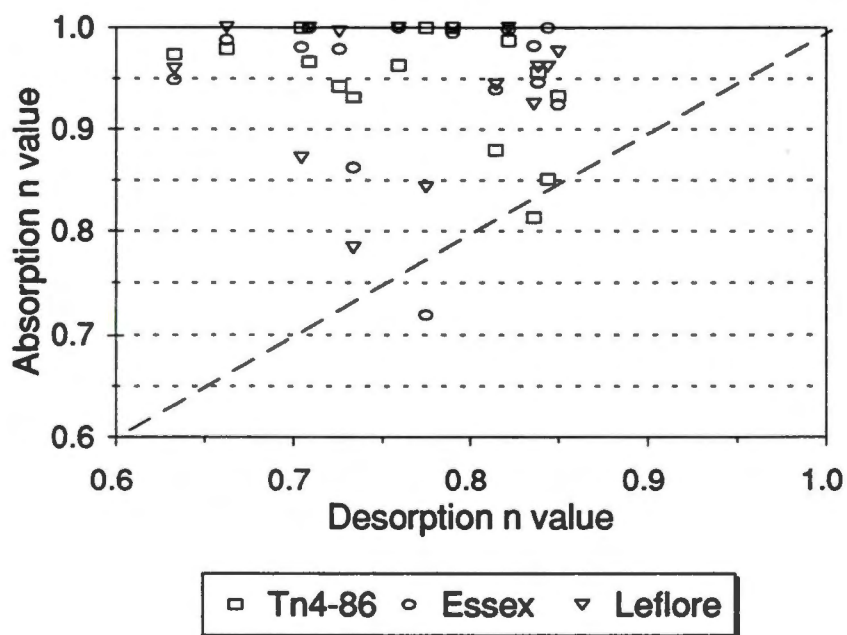


(b)

Figure C29. Comparison of mean k values for absorption and desorption for 1989 (a) and 1990 (b) tests. Each point represents the replication average for one harvest week and variety.

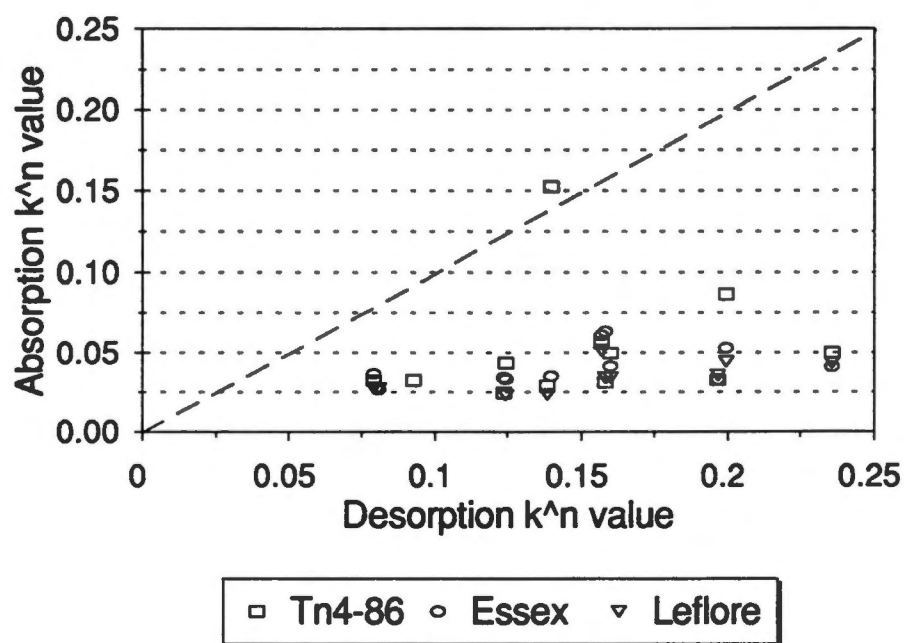


(a)

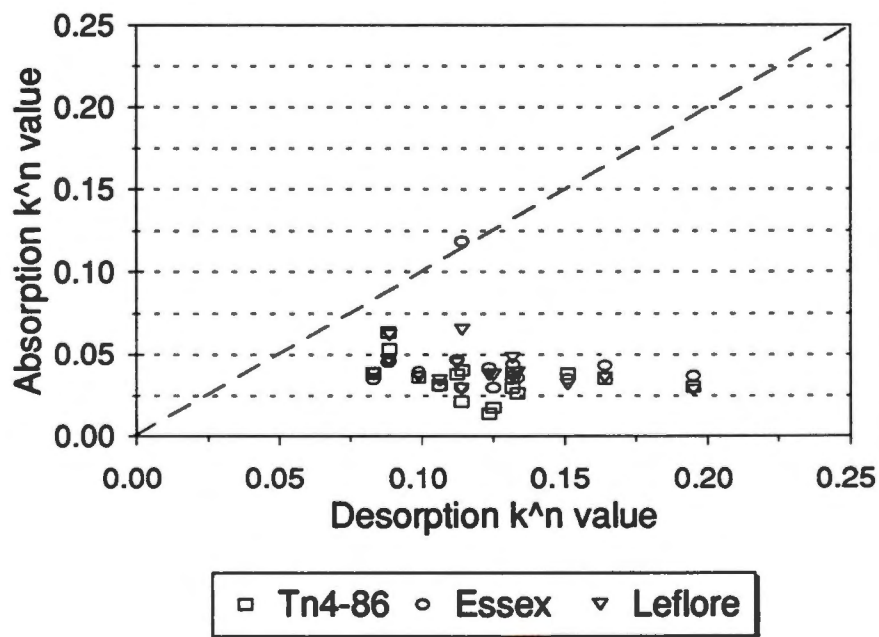


(b)

Figure C30. Comparison of mean n values for absorption and desorption for 1989 (a) and 1990 (b) tests. Each point represents the replication average for one harvest week and variety.

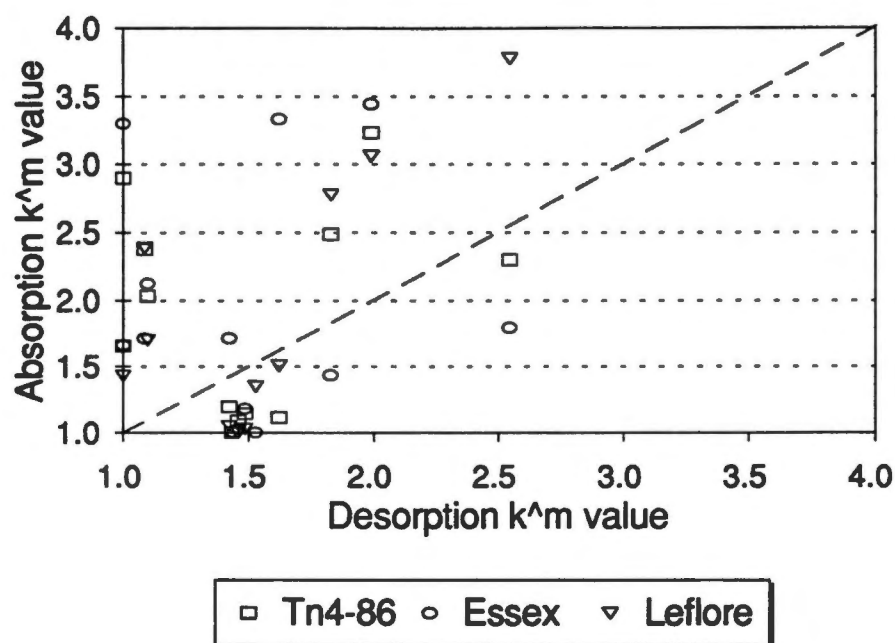


(a)

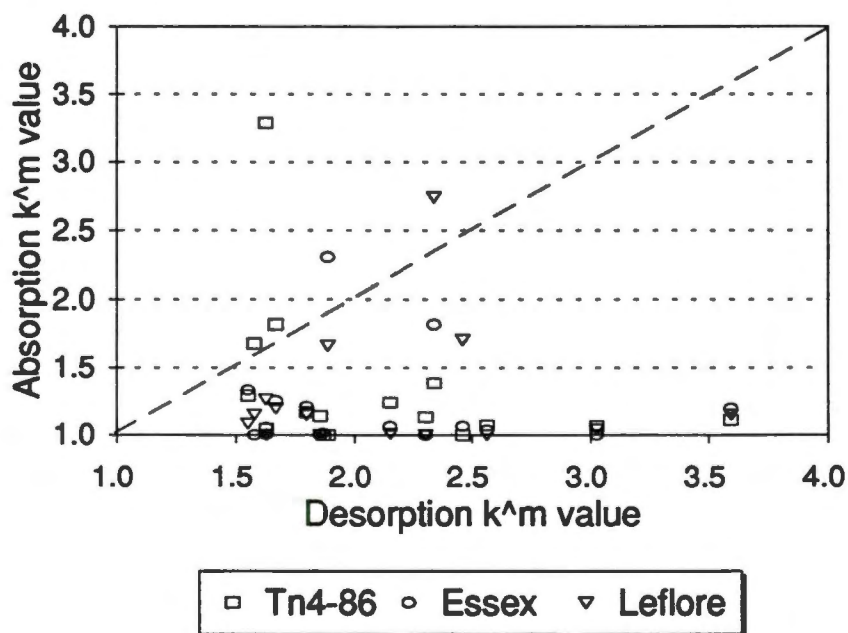


(b)

Figure C31. Comparison of mean k^n values for absorption and desorption for 1989 (a) and 1990 (b) tests. Each point represents the replication average for one harvest week and variety.



(a)



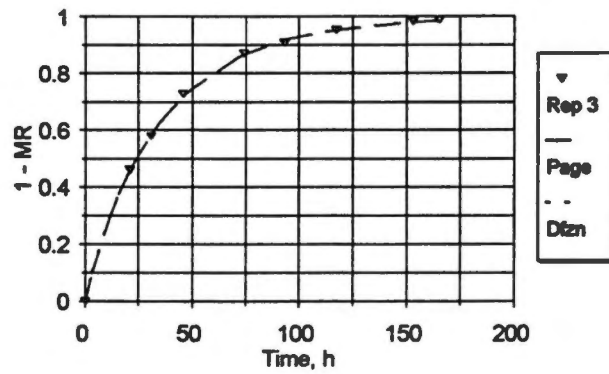
(b)

Figure C32. Comparison of mean k^m values for absorption and desorption for 1989 (a) and 1990 (b) tests. Each point represents the replication average for one harvest week and variety.

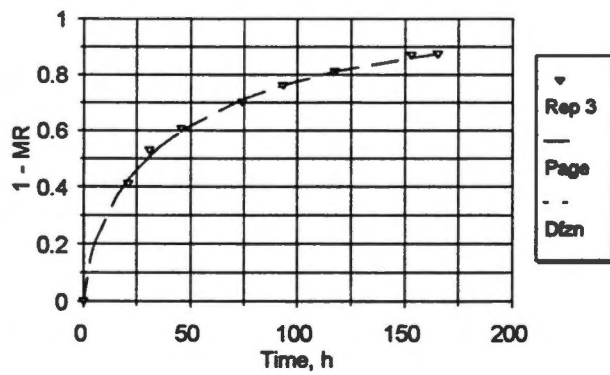
APPENDIX D

Comparison of Empirical and Theoretical Models

'89 Tn4-86 Absorption Week 6 / Rep 3



'89 Essex Absorption Week 6 / Rep 3



'89 Leflore Absorption Week 6 / Rep 3

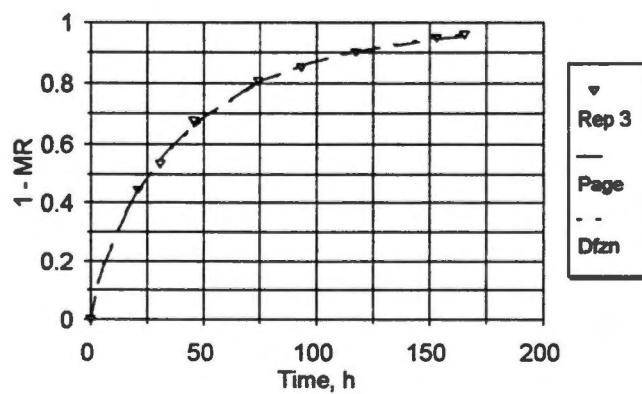
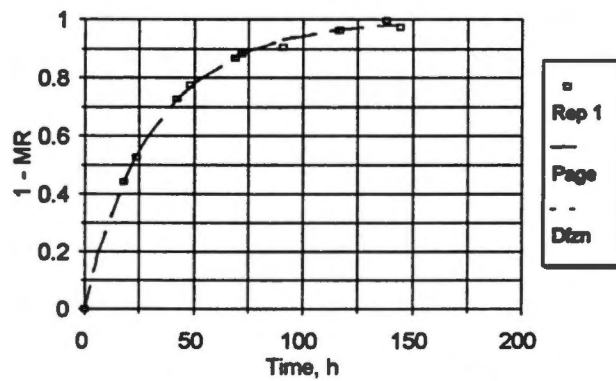
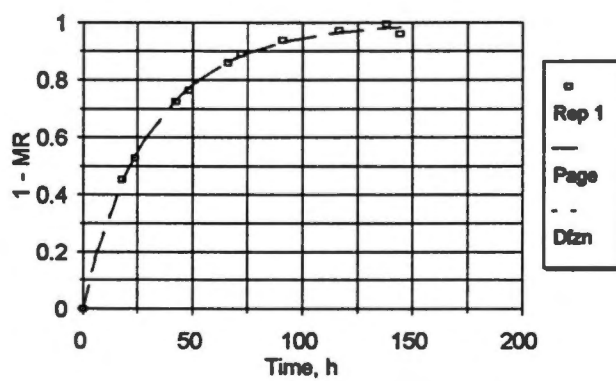


Figure D1. Comparison of the modified Page equation and the diffusion equation for absorption tests during harvest week 6 (Rep 3) for Tn4-86, Essex, and Leflore soybeans in 1989.

'90 Tn4-86 Absorption Week 6 / Rep 1



'90 Essex Absorption Week 6 / Rep 1



'90 Leflore Absorption Week 6 / Rep 1

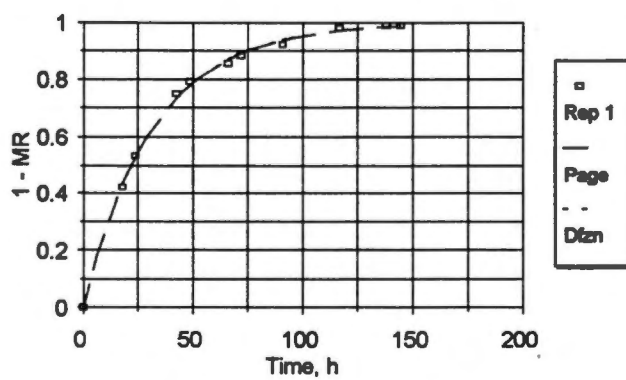
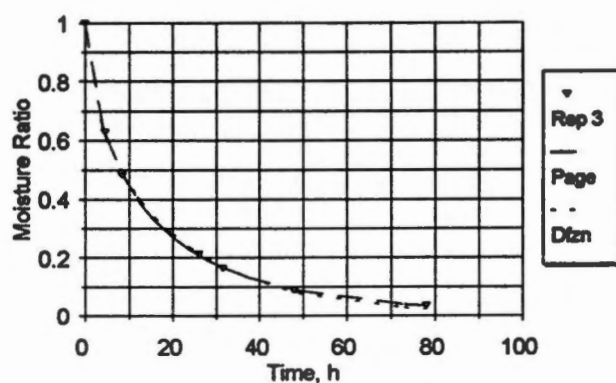
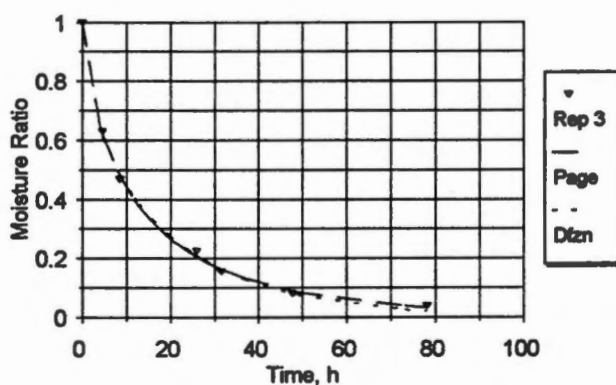


Figure D2. Comparison of the modified Page equation and the diffusion equation for absorption tests during harvest week 6 (Rep 1) for Tn4-86, Essex, and Leflore soybeans in 1990.

'89 Tn4-86 Desorption Week 6 / Rep 3



'89 Essex Desorption Week 6 / Rep 3



'89 Leflore Desorption Week 6 / Rep 3

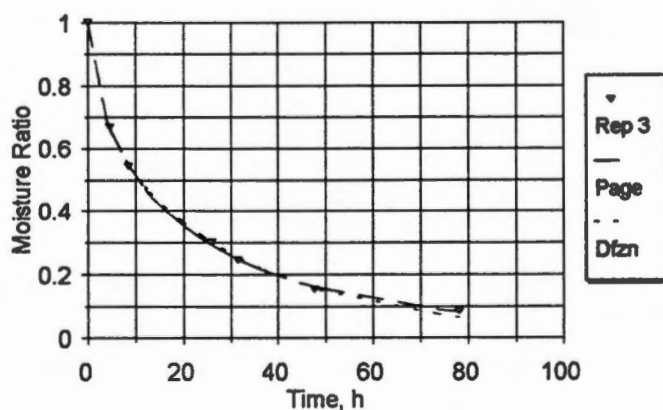
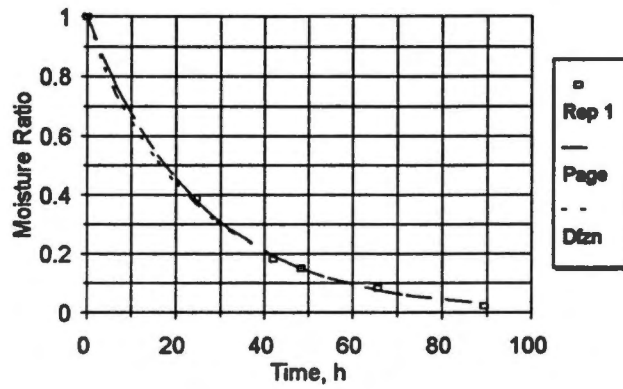
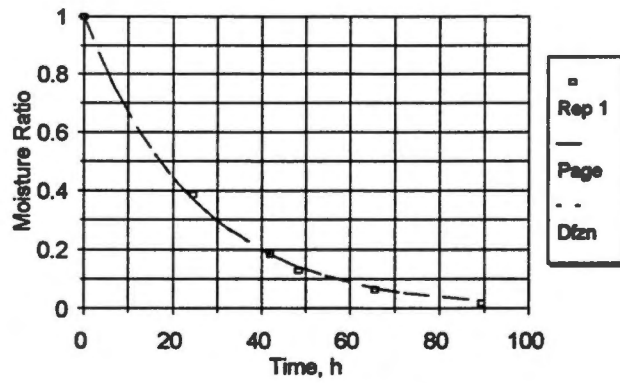


Figure D3. Comparison of the modified Page equation and the diffusion equation for desorption tests during harvest week 6 (Rep 3) for Tn4-86, Essex, and Leflore soybeans in 1989.

'90 Tn4-86 Desorption Week 6 / Rep 1



'90 Essex Desorption Week 6 / Rep 1



'90 Leflore Desorption Week 6 / Rep 1

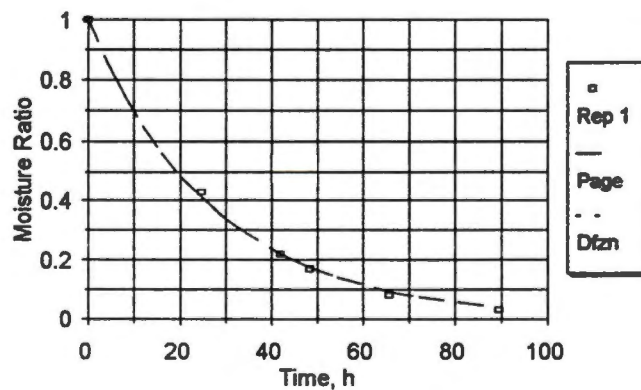


Figure D4. Comparison of the modified Page equation and the diffusion equation for desorption tests during harvest week 6 (Rep 1) for Tn4-86, Essex, and Leflore soybeans in 1990.

Biot Nos. and n values for soybean absorption and desorption

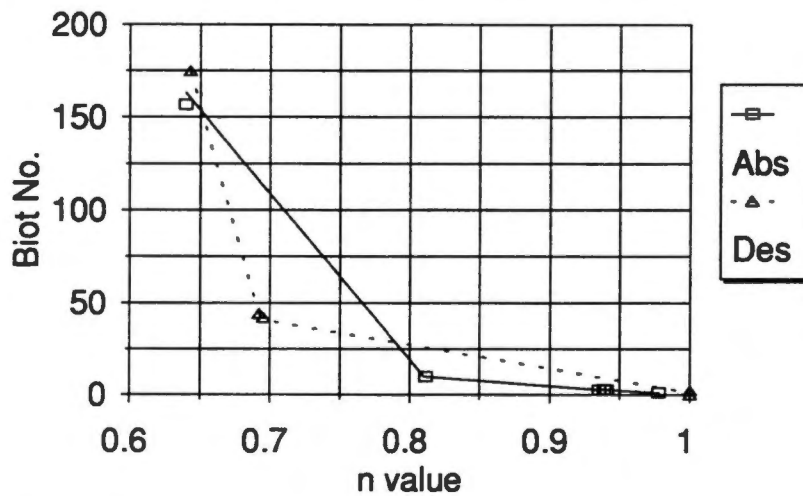


Figure D5. Biot numbers and n values for absorption and desorption conditions for Tn4-86, Essex, and Leflore soybeans harvested during week 6 in 1989 and 1990.

D'/R^2 and k values for soybean absorption and desorption

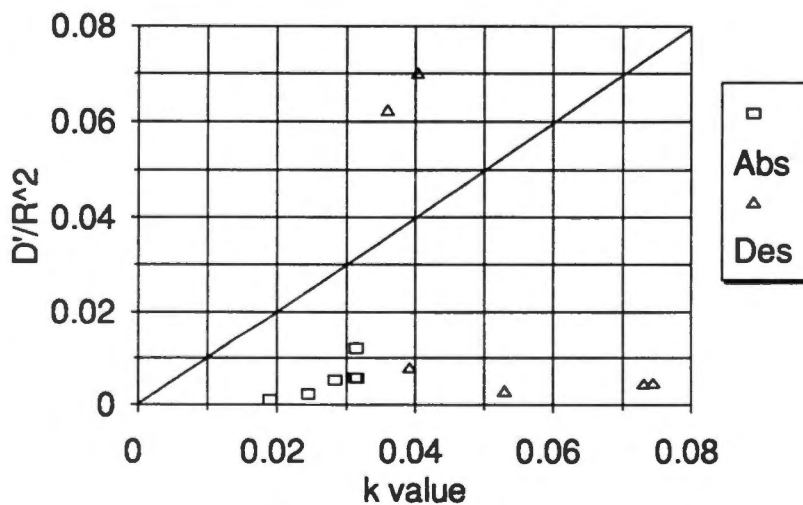


Figure D6. D'/R^2 and k values for absorption and desorption conditions for Tn4-86, Essex, and Leflore soybeans harvested during week 6 in 1989 and 1990.

APPENDIX E

Computer Program and Sample Output for Theoretical Model

Computer Program Used to Compare the Cellular Diffusion
Model with the Modified Page Equation

```

400 DIM ALAM(101),MDB(101),MHAT(101),T(101),TE(101),TT(101)
450 GOSUB 1000
500 GOSUB 3000
550 GOSUB 4000
600 GOSUB 5000
650 PRINT "The MR sum of squares for Bi and D/R^2 terms ";BI, DRSQ
700 PRINT "are ";MRESS, MRTSS
750 GOSUB 6000
800 PRINT "The MC sum of squares for Bi and D/R^2 terms ";BI, DRSQ
850 PRINT "are ";MESS, MTSS
900 END
1000 CLS
1010 ***** PART I *****
1020 'P1: 1) Input sorption data,
1030 " 2) Select output device, and
1040 " 3) Compute the modified Halsey EMC value given Temp and RH
1050 JMAX=7
1060 FOR K=1 TO JMAX
1070 READ T(K), MDB(K)
1080 PRINT K, T(K), MDB(K)
1090 NEXT K
1100 DATA 0,36.50,4.57,26.09,8.5,22.04,25.87,14.56,31.45,13.17,47.77,11.01
1110 DATA 78.00,9.53
1120 PRINT
1130 PRINT TAB(5)"1) Screen print only"
1140 PRINT TAB(5)"2) Screen and (ASCII) file printout"
1150 PRINT TAB(5)"3) Screen and line printer output"
1160 PRINT
1170 INPUT "Which option do you prefer (1 2 or 3)";IOUT
1180 'IOUT=1
1190 ON IOUT GOTO 1250,1200,1250
1200 PRINT:INPUT "Which drive do you want to use (A B C D a b c d)";A3$
1210 IF (A3$="A") OR (A3$="a"), THEN OPEN "O",#1,"A:MR.OUT"
1220 IF (A3$="B") OR (A3$="b"), THEN OPEN "O",#1,"B:MR.OUT"
1230 IF (A3$="C") OR (A3$="c"), THEN OPEN "O",#1,"C:MR.OUT"
1240 IF (A3$="D") OR (A3$="d"), THEN OPEN "O",#1,"D:MR.OUT"
1250 CLS
1260 RETURN
3000 ***** PART II *****
3010 'P2: Empirical model for determining the moisture ratio of soybeans.
3020 ' Rewetting equation parameters via thesis by Osborn (UKY '88).
3030 ' Drying equation parameters via thesis by Overhults (UKY '75).
3040 ' Inputs are the conditioning air T (C), RH (%), and grain Mo (%db).
3050 ' The equation parameters k, and n are derived from experimental data.
3060 ' Equilibrium moisture content is determined by the Halsey equation,
3070 ' with constants b, c, and rc computed from combined wetting and drying
3080 ' data from Osborn (UKy '88) and Sulaiman (UKy '86).
3090 ' Outputs are k, n, Meq, and M(t) and MRemp with changes in time.

```

```

3100 MEQ=8.5:K=.07312:N=.6926
3110 TC=20:RH=20:MO=MDB(1)
3120 B=-.0053636:C=2.866532:RC=1.378753:A=1/RC
3130 TI=0!
3140 DTI=1
3150 'OSBORN'S (WET) TEST VALUES: T=10:RH=73.3:MO=11.2
3155 'OVERHULT'S (DRY) TEST VALUES: T=37.78:RH=16.1:MO=29.7
3160 'INPUT "ENTER Average T(C), RH(%), and Mo(%db)";TC,RH,MO
3170 EMCH=(-EXP(TC*B+C)/LOG(RH/100))^(1/RC)
3180 'IF (MEQ>MO) THEN GOSUB 3400
3190 'IF (MEQ<MO) THEN GOSUB 3470
3200 ON IOUT GOTO 3280,3250,3210
3210 LPRINT
3220 LPRINT" Temp RH EMCH Mo Meq k n"
3230 LPRINT USING" ###.## ###.## ###.## ###.## ###.## ###.##"
###.##";TC,RH,EMCH,MO,MEQ,K,N:LPRINT
3240 GOTO 3280
3250 PRINT #1,
3260 PRINT #1," Temp RH EMCH Mo Meq k n"
3270 PRINT #1, USING" ###.## ###.## ###.## ###.## ###.## ###.##"
###.##";TC,RH,EMCH,MO,MEQ,K,N
3280 PRINT
3290 PRINT" Temp RH EMCH Mo Meq k n"
3300 PRINT USING" ###.## ###.## ###.## ###.## ###.## ###.##"
";TC,RH,EMCH,MO,MEQ,K,N:PRINT
3310 PRINT
3330 FOR J=1 TO JMAX
3340 TI=T(J)
3350 TE(J)=EXP(-(K*TI)^N)
3355 'PRINT USING" ###.####";J,TI,TE(J)
3360 ' MET=MEQ+TE(J)*(MO-MEQ)
3370 ' IF ABS(MET-MEQ) < .1, THEN PRINT "M(t)-Meq <0.1":GOTO 3390:ELSE
3380 NEXT J
3390 RETURN
3400 ' Wetting subroutine parameters determined by Osborn (UKy '88)
3410 ' For TN test conditions, k and n are determined by reg. from exp. data.
3430 IF (TC<26) AND (RH>90), THEN K=.003138:N=.4672:GOTO 3460:ELSE
3440 N=.8267
3450 K=-.2625+.004916*TC+.003033*RH
3460 RETURN
3470 ' Drying subroutine parameters determined by Overhults (UKy '75)
3480 ' For TN test conditions, k and n are determined by reg. from exp. data.
3500 IF (TC<30) AND (RH<20), THEN K=.0669:N=.6915:GOTO 3570:ELSE
3510 TF=TC*9/5+32
3520 TR=TF+460
3530 N=.3529+.00136*TF
3540 IF (MO=<27) THEN K=EXP(11.752-7912.7/TR)
3550 IF (MO>27) AND (MO<50) THEN K=EXP(10.906-7357!/TR)
3560 IF (MO>=50) THEN K=EXP(10.375-6779.3/TR)
3570 RETURN

```

```

4000 ***** PART III *****
4010 'P3: Compute the eigenvalues for spherical geometry then use them
4020 ' in the theoretical diffusion model (DIFUZN) to calculate MRt.
4030 PRINT"Enter the Biot number and diffusivity term of the cotyledon"
4040 PRINT
4050 INPUT "A suggested range is 5< Bi <15 and 0.001< D' <0.015";BI,DRSQ
4060 PI=3.141592654#
4070 TOL=.0002
4100 NMAX=10
4110 IF BI>3, THEN NMAX=70
4120 IMAX=50
4130 ON IOUT GOTO 4170,4160,4140
4140 LPRINT "The following are eigenvalues for Bi =";BI
4150 GOTO 4170
4160 PRINT #1, "The following are eigenvalues for Bi =";BI
4170 PRINT
4180 PRINT "The following are eigenvalues and eignfunctions for Bi =";BI
4190 PRINT
4200 FOR N=1 TO NMAX
4210 P=PI*(N-3/2)+.1
4220 FP=P/(1-BI)-TAN(P)
4230 DERFP=1/(1-BI)-(1/COS(P))^2
4260 FOR I=1 TO IMAX
4270 P1=P-FP/DERFP
4280 DIFF=ABS(P1-P)
4290 IF DIFF<TOL GOTO 4370
4300 P=P1
4310 FP=P/(1-BI)-TAN(P)
4320 DERFP=1/(1-BI)-(1/COS(P))^2
4340 NEXT I
4350 PRINT " Newton-Raphson algorithm failed after";I;"iterations!"
4360 GOTO 4430
4370 ALAM(N)=P1
4380 ON IOUT GOTO 4420,4410,4390
4390 LPRINT " LnR(";N;") ="; P1, FP
4400 GOTO 4420
4410 PRINT #1, " LnR(";N;") ="; P1, FP
4420 PRINT " LnR(";N;") ="; P1, FP
4430 NEXT N
4440 PRINT
4460 FOR J=1 TO JMAX
4470 SUM=0!
4480 FOR N=2 TO NMAX
4490 Z=ALAM(N)
4500 S=SIN(Z)
4510 C=COS(Z)
4520 SUM=SUM+(S-Z*C)^2*EXP(-DRSQ*Z^2*T(J))/((Z-S*C)*Z^3)
4530 NEXT N
4540 TT(J)=6*SUM
4550 ' TI=TI+DT
4560 NEXT J
4570 RETURN

```



```

5000 ***** PART IV *****
5010 ' P4: Results of the above calculations are summarized in tabular form.
5020 MRESS=0:MRTSS=0
5030 DNOM=(MO-MEQ)
5040 ON IOUT GOTO 5110,5080,5050
5050 LPRINT "The moisture ratio for each time step is:"
5060 LPRINT " Time   MRO   MRe   Diffe   MRt   Difft"
5070 GOTO 5110
5080 PRINT "Computational results are listed in the file _:MR.OUT"
5090 PRINT #1, "The moisture ratio for each time step is:"
5100 PRINT #1, " Time   MRO   MRe   Diffe   MRt   Difft"
5110 PRINT "The moisture ratio for each time step is:"
5120 PRINT " Time   MRO   MRe   Diffe   MRt   Difft"
5130 FOR J=1 TO JMAX
5140   MRO=(MDB(J)-MEQ)/DNOM
5150   MREDIF=MRO-TE(J)
5160   MRTDIF=MRO-TT(J)
5170   MRESS=MRESS+MREDIF^2
5180   MRTSS=MRTSS+MRTDIF^2
5190   ON IOUT GOTO 5230,5220,5200
5200   LPRINT USING"###.#### "; T(J), MRO, TE(J), MREDIF, TT(J), MRTDIF
5210   GOTO 5230
5220   PRINT #1, T(J), MRO, TE(J), MREDIF, TT(J), MRTDIF
5230   PRINT USING"###.#### "; T(J), MRO, TE(J), MREDIF, TT(J), MRTDIF
5240 NEXT J
5250 RETURN
6000 ***** PART V *****
6010 ' P5: A Comparison of the observed and estimated moisture values is made.
6020 MESS=0:MTSS=0:PRINT
6030 ON IOUT GOTO 6100,6070,6040
6040 LPRINT "The moisture content for each time step is:"
6050 LPRINT " Time   MdbObs   Mdbe   Diffe   Mdbt   Difft"
6060 GOTO 6100
6070 PRINT "Computational results are listed in the file _:MR.OUT"
6080 PRINT #1, "The moisture content for each time step is:"
6090 PRINT #1, " Time   MdbObs   Mdbe   Diffe   Mdbt   Difft"
6100 PRINT "The moisture content for each time step is:"
6110 PRINT " Time   MdbObs   Mdbe   Diffe   Mdbt   Difft"
6120 FOR J=1 TO JMAX
6130   MET=MEQ+TE(J)*(MO-MEQ)
6140   MTT=MEQ+TT(J)*(MO-MEQ)
6150   EDIFF=MDB(J)-MET
6160   TDIFF=MDB(J)-MTT
6170   MESS=MESS+EDIFF^2
6180   MTSS=MTSS+TDIFF^2
6190   ON IOUT GOTO 6230,6220,6200
6200   LPRINT USING"###.## "; T(J), MDB(J), MET, EDIFF, MTT, TDIFF
6210   GOTO 6230
6220   PRINT #1, T(J), MDB(J), MET, EDIFF, MTT, TDIFF
6230   PRINT USING"###.## "; T(J), MDB(J), MET, EDIFF, MTT, TDIFF
6240 NEXT J
6250 RETURN

```

Output from the computer program which compares the observed moisture ratios (Mro) to the empirical (MRe) and the theoretical (Mrt) solutions for Rep 3 of harvest week 6 for Tn4-86 in 1989. Observed and predicted moisture content levels are also shown to compare the two models for this test and the sum of squared residuals is printed for each model. Results are shown in Figure D3.

Temp RH EMCH Mo Meq k n
20.0 20.0 5.24 36.50 8.50 0.07312 0.6926

The following are eigenvalues and eigenfunctions for Bi = 44

LnR(1) = 0	5.369097E-06	LnR(2) = 3.070311	4.409999E-05
LnR(3) = 6.141323	9.019673E-05	LnR(4) = 9.213698	1.328588E-04
LnR(5) = 12.28802	1.646578E-04	LnR(6) = 15.36478	1.826584E-04
LnR(7) = 18.44436	1.854003E-04	LnR(8) = 21.527	1.752973E-04
LnR(9) = 24.61287	1.593232E-04	LnR(10) = 27.70202	1.38402E-04
LnR(11) = 30.79444	1.152754E-04	LnR(12) = 33.89005	9.196997E-05
LnR(13) = 36.98873	7.486343E-05	LnR(14) = 40.09031	5.292893E-05
LnR(15) = 43.19464	3.814697E-05	LnR(16) = 46.30154	2.765656E-05
LnR(17) = 49.41083	2.300739E-05	LnR(18) = 52.52232	1.549721E-05
LnR(19) = 55.63586	1.239777E-05	LnR(20) = 58.75128	4.649163E-06
LnR(21) = 61.86844	-2.384186E-07	LnR(22) = 64.98718	4.649163E-06
LnR(23) = 68.1074	-7.152558E-07	LnR(24) = 71.22896	1.0252E-05
LnR(25) = 74.35176	4.649163E-06	LnR(26) = 77.4757	1.394749E-05
LnR(27) = 80.6007	9.11355E-04	LnR(28) = 83.72666	7.377863E-04
LnR(29) = 86.85351	5.793572E-04	LnR(30) = 89.98119	4.446507E-04
LnR(31) = 93.10962	3.335476E-04	LnR(32) = 96.23877	2.791882E-04
LnR(33) = 99.36857	2.067089E-04	LnR(34) = 102.499	1.5611642E-04

The moisture ratio for each time step is:

Time	Mro	Mre	Diffe	Mrt	Diff
0	1	1	0	.9990	.0010
4.57	.6282	.6262	.0020	.6209	.0073
8.50	.4836	.4871	-.0035	.4919	-.0083
25.87	.2164	.2112	.0052	.2177	-.0013
31.45	.1668	.1686	-.0018	.1709	-.0042
47.77	.0896	.0927	-.0031	.0851	.0046
78.00	.0368	.0355	.0013	.0235	.0133

The MR sum of squares for Bi and D/R^2 terms 44 .00451
are 5.824551E-05 3.3888E-04

The moisture content for each time step is:

Time	MdbObs	Mdbe	Diffe	Mdbt	Diff
0	36.50	36.50	0	36.47	0.03
4.57	26.09	26.03	0.06	25.88	0.21
8.50	22.04	22.14	-0.10	22.27	-0.23
25.87	14.56	14.41	0.15	14.60	-0.04
31.45	13.17	13.22	-0.05	13.29	-0.12
47.77	11.01	11.10	-0.09	10.88	0.13
78.00	9.53	9.49	0.04	9.16	0.37

The MC sum of squares for Bi and D/R^2 terms 44 .00451
are .04566439 .2656815

VITA

Samuel Gaither McNeill was born on September 5, 1952 in West Jefferson, North Carolina. He is the second child of Peter Thurman McNeill, Jr. and Anna Lou Planck McNeill. The family moved to a farm in Fleming County, Kentucky in the spring of 1953. He graduated from Hillsboro Consolidated School, Hillsboro, Ky in 1966, attended the International School of Bangkok, Thailand from 1966 to 1968, and returned to Fleming County High School his senior year where he graduated in 1970. He received a BS and MS in Agricultural Engineering from the University of Kentucky in Lexington in 1974 and 1979, respectively. The topic of his masters thesis was "Drying Characteristics of Formed Poultry Excreta in a Deep Bed."

He was employed as an Extension Agricultural Engineer at the University of Kentucky Research and Education Center in Princeton, Ky in 1979. It was there that he established an extension program in crop and livestock production with emphasis on grain conditioning and storage. Field projects have included an evaluation of evaporative cooling pads for gestation swine housing in the mid-south; a direct-fired biomass gasifier/combustor for drying grain; equilibrium moisture and thin-layer drying tests for corn cobs; a smoke generator for curing dark-fired tobacco; bench-top compression tests for shelled corn, corn mixed with fines, and ground feed products; a demonstration field sprayer to illustrate new application techniques; a pesticide applicator survey; and a ground water monitoring study to measure the levels of agricultural chemicals in the mixing/loading vicinity of farmsteads with different soil types.

In August 1988, he accepted a research assistantship at the University of Tennessee in Knoxville, where he entered the Graduate School. He expects to receive a Doctor of Philosophy degree in Agricultural Engineering in December 1996 and return to his position with the University of Kentucky. He is a member of the American Society of Agricultural Engineers, the Gamma Sigma Delta honor society, the Kentucky Association of Extension Specialists, and the University of Kentucky Ag Alumni Association.

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