TEMPERATURE EFFECTS ON LYSINE AVAILABILITY AND GERM VIABILITY IN CORN AT CONSTANT MOISTURE AND DURING DRYING

DISSERTATION FOR THE DEGREE OF Ph. D.
MICHIGAN STATE UNIVERSITY
RALPH ALLEN GYGAX
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ABSTRACT

Temperature Effects
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BY

Ralph Allen Gygax

The objectives of this study were to define two changes in corn quality as affected by temperature and moisture content and to use reaction kinetics in an attempt to predict the effect of the temperature-moisture histories of two types of corn driers on those quality changes. Success in obtaining both objectives paves the way for using the resulting quality models with existing grain drying models to design corn dryers that do not heat damage corn.

The thermal death model for the corn germ is derived through the use of statistical mechanics originally developed by Gumbel (1958) and applied by Rosenberg et al. (1973) and is the first model to date to successfully describe the thermal death of the corn germ. The model is fit to experimental data developed through the use of constant-moisture heat treatments; however, the model greatly over-estimates the thermal death of the corn germ when attached to a concurrent-flow drying model or to a fluidized-bed drying model. The most probable cause of this over-estimation is the existance of temperature gradients in the kernel because of the characteristic non-homogeniety of corn kernels and the large air-to-product temperature

gradients which exist in the initial portion of the drying process. The drying models predict only average kernel temperature.

The available lysine (AVL) model is a simple consecutive, first-order approximation of the actual reaction mechanisms. The first reaction represents the effect of protein denaturation in making available more lysine for reaction. The second reaction represents the effect of nonenzymatic browning in reducing lysine availability for nutritional use. The data gave plots characteristic of the model. Heating times less than 20 minutes at 270°F and at moistures less than 16% w.b. increased AVL by as much as 50%. Heating at higher temperatures decreased lysine availability while heating at lower temperatures slightly increased or did not change the availability of lysine. Significant decreases in AVL were only found when heating was sufficiently severe to cause significant darkening of the corn and when there was an associated "roasted" smell which has been reported in conjunction with other nonenzymatic browning reactions by previous investigators.

It was concluded that future work should focus on the detrimental effects of protein denaturation on processing quality. Future work on the nutritive values of corn as affected by high temperature drying should focus on the beneficial effects of protein denaturation. The thermal death model will be useful in predicting the quality of seed stock after drying or after storage under known temperature and moisture conditions. Correlation of any two quality parameters is not recommended because all modes of quality deterioration have their own characteristic rate mechanisms.

Approved: F. W. Bakker
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TEMPURATURE EFFECTS

ON

LYSINE AVAILABILITY AND GERM VIABILITY IN CORN

AT

CONSTANT MOISTURE AND DURING DRYING

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A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

Department of Agricultural Engineering

1977

DEDICATION

This dissertation is dedicated to my parents

Roy and Lucille Gygax

who lacked college degrees, but not the wisdom

and the vision to guarantee mine.

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ACKNOWLEDGMENTS

The author sincerely appreciates the assistance of all who have aided in this study. He is especially appreciative of the counsel and encouragement provided by his major professor, Dr. Fred W. Bakker-Arkema.

Appreciation is also extended to other members of the Guidance Committee, Dr. Martin Hawley (Chemical Engineering), Dr. Dennis Heldman (Food Science and Nutrition) and Dr. Debra Delmer (Biochemistry). The author is especially indebted to Dr. Delmer who gave unselfishly of her time and allowed him the use of laboratory facilities over an extended period of time.

Special appreciation is also extended to the Anderson Agricultural Research Foundation of Maumee, Ohio, for their financial support and to a wide variety of people too numerous to mention from various institutions to include The Pillsbury Company, The University of Minnesota, The University of Wisconsin, and numerous agricultural science departments at Michigan State University.

Thanks are extended to my wife, Beverly. Her encouragement and assistance during the years have been invaluable.

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LIST OF SYMBOLS

A	a lysine molecule
A_D	temperature dependent death rate constant, $hr.^{-1}$
a	convective heat transfer area, 5g. m.
C	a reducing substance, mole per mole proteinaceous nitrogen
C^*	concentration of the forward transition state species, mole per mole proteinaceous nitrogen
C_A	concentration of available lysine, mole per mole proteinaceous nitrogen
C_c	concentration of reducing substance, mole per mole proteinaceous nitrogen
C_N	concentration of native protein, mole per mole proteinaceous nitrogen
C_N^*	concentration of molecules of protein in which all side-chain hydrogen bonds are broken, mole per mole proteinaceous nitrogen
C_p	concentration of additional produce, mole per mole proteinaceous nitrogen
C_s	concentration of Schiff's base, mole per mole proteinaceous nitrogen
C_w	concentration of water, mole per mole proteinaceous nitrogen
c	average specific heat, Kcal. per kg.
c_a	specific heat of drying air, Kcal. per Kg.
c_v	specific heat of water vapor, Kcal. per Kg.
c_w	specific heat of grain moisture, Kcal. per Kg.

c_1 and c_2	half life viability constants, (% w.b.)$^{-1}$ and $^{o}C^{-1}$, respectively
D_i	the difference between two measurements, units dependent on measurements
df	degrees of freedom, dimensionless
$\dot{E}_s$	the rate of energy storage within an object, Kcal. per hour
$F_j(t)$	probability that the transformation from stage j is accomplished in a time interval of t, dimensionless
$f(t)$	probability density function for all stages of deterioration, hr.$^{-1}$
$f_j(t)$	probability density function for the j^{th} stage of deterioration, hr.$^{-1}$
G	energy of the system, cal. per mole
G_a	air flow rate, Kg. per hour
G_p	product flow rate, Kg. dry matter per hour
G_s	free energy of the solution phase, cal. per mole
G_w	partial molar free energy of water, cal. per mole
ΔG	free energy of a system, cal. per mole
H	free enthalpy of a system, cal. per mole
H_a	absolute humidity, g. H_2O per g. dry air
ΔH	enthalpy of activation, cal. per mole
h	Plank's constant, Joule sec.
h_c	convective heat transfer coefficient, Kcal. per sq. m.
h_{g_f}	heat of vaporization, Kcal. per Kg.
K	transmission coefficient, dimensionless
K^*	equilibrium constant for the activated complex, dimensionless
K_{ij}	the hydrogen bond equilibrium constant, dimensionless
k	Boltzmann's constant, Joule per ^{o}K

k^*	activated complex theory reaction rate, $hr.^{-1}$
k_v	half-life viability constant, dimensionless
k_1, k_2, k_3 & k_4	appropriate rate constants, $hr.^{-1}$
L	lysine masked by the protein matrix, mole per mole proteinaceous nitrogen
M	moisture, % d.b. unless otherwise specified
M_e	equilibrium moisture content, % d.b. unless otherwise specified
M_o	original moisture content, % d.b. unless otherwise specified
m	number of means averaged, dimensionless
m_v	number of variances pooled, dimensionless
N_o	initial population
N_w	the number of moles of water, moles
N(t)	the population as a function of time
n	power law constant, dimensionless
n_i	the number of samples read against one blank to determine the mean
n_j	the number of moles of j constituents of a solution, moles per liter
n_t	total number of sample-blank comparisons, dimensionless
P	an addition product, mole per mole proteinaceous nitrogen
p	pressure, Kg. per sq. cm.
$p^{\frac{1}{2}}$	half viability period, days
Q^*	partition function for stable degrees of freedom, dimensionless
Q_N	partition function for native protein, dimensionless
Q_{trans}	partition function for the transition state, dimensionless

Q_u	partition function for unstable degrees of freedom, dimensionless
$\dot{q}_c$	the rate of convective heat transfer to an object, Kcal. per hour
R	gas constant, Joule per mole ^oK
S	total enthalpy of the system, Kcal.
ΔS	entropy of activation, cal. per mole
s_i^2	the variance of each determination, units dependent on measurement
s_p^2	pooled estimate of variance, units dependent on measurement
T	temperature, ^oC, ^oK, and ^oF
t	time, hr., min. or sec.
v_i	the number of degrees of freedom associated with each s_i^2 and s_p^2, dimensionless
v^*	velocity of motion along the reaction coordinate, mole per hour
W	water molecule, dimensionless
X_i	the mean of each determination, units dependent on measurement
$\overline{X}$	overall mean, units dependent on measurement
$\overline{X}_i$	the average of the determinations at the i^{th} heat treatment, units dependent on measurement
X_{i1}	first determination for the i^{th} heat treatment, units dependent on measurement
X_{i2}	second determination for the i^{th} heat treatment, units dependent on measurement
X_{ij}	probabilities that single hydrogen bonds exist, dimensionless
X_{rs}	probabilities that cooperative hydrogen bonds exist, dimensionless
X_{zm}	probabilities that double hydrogen bonds exist, dimensionless

$\epsilon_{o\ reag}$	energy level of native protein, cal. per mole
$\epsilon_{o\ trans}$	energy level of the transition state, cal. per mole
θ	product temperature, ^{o}C, ^{o}K, and ^{o}F
$\mu(t)$	thermal death rate as a function of time, $hr.^{-1}$
ρ_c	density, Kg./cu. m.
ρ_j	the probability of a immediate transformation, dimensionless
τ	time constant, $hr.^{-1}$

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I. INTRODUCTION

1.1 Overview of the Corn Industry

Corn is a major feed crop for the United States with an average of 93% of annual production being used for animal feeds. Corn is advantageous as a feed grain. It exhibits high digestability; it is a good energy source; it is well-suited as a constituent of nutritionally balanced, mixed feeds; and it is an economical feed constituent because of its high yield per acre.

Since 1955 food consumption of corn increased at an average annual rate of 3.5% with 5% of the 1970 harvest being dry milled into corn meal, flour and grits or wet milled into starch, syrups, and dextrose. Meal is used for pancakes, snacks, mush, cereals, muffins, and corn breads; flour is used for pancakes, baby foods, bakery products, cereals and snacks; and grits are used for breakfast cereal, snack foods and malt beverages. The uses of starch and starch in modified forms include: thickening agents, stabilizers for oil-in-water emulsions, gel-forming agents in confections, moisture retention agents in toppings and cake icings, bonding agents for foods, coating and glazing agents for nut meals and candies, encapsulation of materials such as coffee sweeteners, dry dusting of bakery products and candies, and anticaking agents in materials such as powdered sugar. The increased use of corn sweetening agents (which are more economical in comparison to cane sugar) has been largely responsible for the recent increase in the use of corn products in food. The largest use of corn syrups is in the confectionary industry.

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Corn oil is recovered from the germ, a by-product of the wet-and dry-milling industries. Approximately half of the oil is used in cooking and salad oils. Increased awareness of the importance of polyunsaturated fatty acids has caused a sharp increase in the use of corn oil in margarines.

Corn has a wide variety of industrial uses. Corn starch and flour have functional properties such as viscosity, film formation, adhesive properties, and ability to suspend particles. The growth of industrial applications has resulted both from these properties and from the ability of chemists to adapt starch to fit specific industrial requirements through alteration of the starch (Senti and Schaefer, 1972).

When corn is traded in the open market, official grades assigned by government inspectors provide the basis for pricing. The grade is based on a minimum acceptable test weight and on maximum acceptable levels of moisture, foreign matter, damaged kernels, and heat damaged kernels. A given lot of corn cannot be graded above the grade for which any of the factors considered (except moisture content) is at less than acceptable levels.

One of the primary short-comings of the present grading system is that chemical and physical properties are not reflected in the grade. Since the grade is used at the point of initial sale of the product and reflects quality deterioration caused by subsequent handling, drying, and storage, there is little incentive to the farmer to produce higher quality corn. Also, there is no method by which the purchaser can discriminate through factors other than those included in the official grade unless he deals outside of the normal trade channels. This is not practical at this time.

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Use of high-temperature dryers is the primary cause of differences in the behavior of corn during dry-and wet-milling. This is necessitated by a required rapid, mechanized harvest. At the present time, major improvements in quality cannot come about through the present grain quality standards or through changes in the standards--which would be rigorously resisted by some sellers. Under present circumstances improvements in quality will be most feasible through improved equipment and education of equipment users (Freeman, 1971).

1.2 Objectives of this Investigation

The need for studies of corn quality as affected by currently available high-temperature dryers is well-recognized. In spite of the energy situation, the rapidity with which grain must be harvested makes high-temperature drying imperative, especially in the humid, north-central region of the corn belt. Grain quality is greatly dependent on the time-temperature-moisture relationship which varies with the specific configuration of each dryer.

This study is the first application of process modeling to high-temperature grain drying with respect to grain quality. To date all drying studies have involved exposing corn to drying processes of varying dryer configurations, drying-air conditions, initial grain moistures and air to grain ratios. This study attempts to relate grain temperature and grain moisture to the rate of change of grain quality.

The quality parameters chosen for study are at opposite ends of the grain-drying temperature spectrum in terms of sensitivity to temperature. Germ viability is most sensitive to small changes in temperature and begins to decrease at approximately 140°F (60°C) (Watson and Hirata, 1962); whereas, lysine availability begins to decrease at relatively high grain temperatures 176°F - 260°F (80°C - 126.6°C) (Mulhbäuer and Christ, 1974 and Wall, 1975)

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and is relatively insensitive to temperature increases depending on moisture content. These two quality parameters were chosen because they do represent opposite extremes in terms of grain drying temperatures and because it was felt that these are sensitive to temperature and moisture levels only and not to rates of heating and drying.

The objectives of this investigation are two-fold: First, to define some changes in corn quality as affected by temperature and moisture content; and, second, to use reaction kinetics in an attempt to predict the effect of the temperature - moisture history on grain quality during any drying treatments. Success in obtaining both objectives will pave the way for using the resulting quality models with existing grain drying models to design dryers. Thus, a design analysis will allow not only for the consideration of the economics of capital investment and energy, but also for the consideration of the economics of quality deterioration caused by the drying process.

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II. SURVEY OF LITERATURE

Much of today's corn is artificially dried with excessive heat which, while accelerating the drying process, produces detrimental side effects. Viability, nutritional quality, and millability of the seed are reduced; water-soluble proteins are denatured; browning reactions involving amino acids and carbohydrates produce some nutritional defects; and alteration of the wet-milling characteristics of gluten (a primarily saline-insoluble protein) occurs (Wall, 1964).

Numerous investigations have been conducted by exposing corn to drying processes of varying dryer configurations, drying-air conditions, initial grain moistures, and air-to-grain ratios. Attempts to find a general index of thermal damage as related to the behavior of the product during processing and to its nutritive value as food and feed have been unsuccessful. The recommendations of most investigators regarding the effect of drying on grain quality have been conservative largely due to their methods of investigation. The result has been that operators have slowly increased drying air temperatures far beyond limitations specified in the literature without readily apparent damage to the product.

It has been recognized that an investigation which considers the temperature-moisture history of the product during the drying process is needed (Freeman, 1973). If the deterioration of important nutritive and chemical constituents is to be predicted, a knowledge of the rate of deterioration as a function of temperature and moisture must be known (Labuza, 1972).

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The following literature review presents investigations of the past and methods which have been applied in food processing, to include: standard indices of thermal damage; seed viability as a quality index; processing characteristics affected by heat and moisture; nutritive degradation; and determination of available lysine--the limiting amino acid in whole grain corn.

2.1 Indices of Thermal Damage

A number of investigations have been carried out in an attempt to find a general index of thermal damage to corn. Some of the indices, while affected by heat, are also affected by varietal and cultural factors, have different characteristic sensitivities to heat and moisture, and change according to their own particular stoichiometry. In a biological system such as corn, these stoichiometric relationships are either unknown or very complex (Labuza, 1972).

2.1.1 Chemical Indices

French and Kingsolver (1964), in search of an index of heat damage, investigated dehydrogenase activity as determined by tetrazolium salts, diastase activity and esterase activity. Diastase activity is inversely correlated with drying-air temperature at the 1% level. Esterase activity and dehydrogenase activity are less sensitive to inactivation by heat than diastase activity, but varietal and cultural differences appeared to make the measurement of heat damage inaccurate. MacMasters et al. (1954) studied the effect of initial moisture contents up to 40% w.b. and drying-air temperatures up to 150°F (65.6°C) on niacin, pantothenic acid, riboflavin, biotin, and pyridoxine contents of corn. Only pyridoxine content is

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lowered by drying 40% w.b. corn at drying-air temperatures of 120°F (48.9°C) to 150°F (65.6°C). Varietal and cultural differences produced larger changes in pyridozine content than drying treatments.

Glutamic acid decarboxylase activity (GADA) as determined by Linko (1961) was reported to provide a quick, reliable estimate of storage deterioration and protein denaturation caused by high-temperature drying (Bautista and Linko, 1962). The GADA test gives an indication of the enzymatic activity of corn. It involves the measurement of the quantity of carbon dioxide evolved from a mixture of 30g of ground corn and 15ml of a dilute solution of buffered glutamic acid maintained at 86°F (30°C) for 30 minutes. Linko and Sogn (1960) showed that the correlation coefficient between the log of the "GADA's" and germination is significant at the 5% level. One sample takes 45 minutes for analysis, and ten samples in series only require 90 minutes (Bautista and Linko, 1962). Mulhbäuer et al. (1976) developed a method of correlating readings on a Hunter model D25D3 M/L colormeter with lysine content as effected by thermal damage. However, the method must be further developed in order to take into account the effects of variations in maturity, frost damage and microbial effects.

2.1.2 Physical Indices

Tuite and Foster (1963) reported that corn dried at drying-air temperatures above 140°F (60°C) absorbs less water at relative humidities of 70-80% than corn dried at lower temperatures. The ability to absorb moisture decreases with increasing drying-air temperatures, and the effect is permanent. Air flow rates, batch versus continuous flow, and initial moisture content do not have a significant effect.

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Holaday (1964) developed a method of indirectly measuring moisture distribution within the corn kernel by determining the electrical capacitance and d.c. resistance of the corn. Capacitance and d.c. resistance were linearly related for corn that had not been heat damaged. A similar plot for heat damaged kernels will produce points not on the linear regression line. This method was reported as being an accurate index of heat damage to grain.

Other physical indices which are indicative of heat damage include percent heat damaged kernels, test weight (bulk density), percent stress cracked kernels, and susceptability to breakage. All except the last two are included in the present United States grain standards. Heat damage refers to a discoloration of the kernel due to high temperature. For corn, grain temperatures above 180°F (82.2°C) will cause visible damage; however, drying at kernal temperatures above 140°F (60°C) may result in hidden damage such as loss of fermentable carbohydrates or reduced wet- or dry-milling efficiency (Liebenow, 1972). Test weight usually increases during the drying process; however, other factors which affect test weight include the degree of kernel damage, initial and final moisture contents and the grain variety (Hall and Hill, 1972). Stress cracks are fissures or fault lines in the endosperm of the corn kernal. Their severity is catagorized as singles--one stress crack--, multiple--two or more parallel stress cracks--and checked--two or more stress cracks which intersect. Even mild drying will produce singles but as the drying severity increases, the percent of multiples and checks increase (Thompson and Foster, 1963). Unfortunately, stress cracks are difficult to measure with any degree of precision and, thus, may never be included in the grain standards (Gygax et al., 1974)

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drying severity. A method for measuring friability through the use of the Stein breakage tester was developed by McGinty (1970). Thompson and Foster (1963) and Katic (1975) determined that the amount of breakage as measured by the methods of McGinty (1970) is directly related to the severity of drying. Katic (1975) also found that drying in two passes with a moisture reduction of about 4% on the second pass reduced breakage. A storage period should be planned before the second pass in order to allow for stress relaxation in the grain. Stephens and Foster (1976) successfully related the measurement of the susceptability of corn to breakage determined with a Stein breakage tester to the susceptability of corn to breakage in a specific handling system, if gain moisture and temperature are the same in the tester as they are during handling.

2.2 Seed Viability As A Quality Index

Corn that is viable does not exhibit decreased processing yields, increased friability or reduced nutritional value (Baird et al. 1950, and MacMasters et al. 1959). The converse is usually but not always true--viability and not processing yield may be low because of freezing of moist grain, mechanical damage inflicted upon the embryo during harvest, invasion of microorganisms in the field or in storage, natural aging of the seeds and other reasons (Freeman, 1973).

2.2.1 Effect of Heat On Viability

After investigating the injurious effects of high-temperature on the viability of corn and other seeds, Robbins and Petsch (1932) concluded that the principle factors which decrease viability are the degree and time of application of the heat, the water content of the tissue, and the

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presence of liquifying or coagulating agents. Watson and Hirata (1962) reported that the drying air temperature which produced a significant drop in viability decreased with increasing initial moisture of the grain and with increasing drying air humidities and flow rates. Increased drying air humidities and flow rates have the automatic effect of increasing drying air temperatures. Viability was destroyed when corn at 32% w.b. was dried at a drying-air temperature of 140°F (60°C), but 160°F (71.1°C) was the lowest temperature that destroyed the viability of corn at 21% w.b. moisture content.

2.2.2 A Quick Indicator Of Viability

It was desirable to develop a quick test for viability, since corn which has dead germ is difficult to process and yields oil of lower quality (MacMasters et al. 1959). Baird et al. (1950), MacMasters et al. (1959) and Moore (1962) suggest the TZ (2, 3, 5 -- triphenyl-tetrazolium chloride) test (Lakon, 1949) as a means of measuring viability. Corn that reaches temperatures above 140°F (60°C) during drying shows a definite decrease in viability as determined by the TZ test (MacMasters et al. 1954).

Problems have arisen with the use of TZ test. MacMasters et al. (1954) and Schenk et al. (1957) found that dead kernels can give positive TZ tests because of fungus activity. MacMasters et al. (1954) reported no correlation of TZ-determined viability with overall processing results. Watson and Hirata (1962) found that drying conditions which destroy viability are less severe than those which adversely affect wet-milling quality. MacLeod (1950) and Bishop (1957) found germination much more sensitive to heat damage than several enzyme systems, including dehydrogenase which is responsible for the tetrazolium reaction. The TZ test greatly over-estimates germination of grain dried in certain narrow ranges of air temperature and grain moisture.

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2.2.3 Viability As Determined By Germination

Germination of a seed is accomplished by simply exposing the seed to favorable moisture and temperature conditions. Seeds which germinate are considered viable; however, all viable seeds will not germinate because some may be dormant and, if exposed to a cyclic temperature-moisture treatment, may germinate. Fortunately, dormancy is not a predominant factor in the case of corn; thus, the germination test is the simplest, most dependable method of measuring viability of corn. Unfortunately, the test requires a five to seven day lapse-time before results are obtained (Copeland, 1973).

2.3 Germination

The germination process is complex and not clearly understood. Theoretical biologists have not yet developed adequate laws to relate the molecular activities of cells to their macroscopic growth or death behavior. Thus, it is not surprising that attempts to explain germination or thermal death (the effect of temperature on reduced germination levels) have met with limited success. A moderate amount of success has been achieved in explaining the effect of temperature on the death rate of multicellular organisms (Rosenberg et al. 1973). These methods can be applied to the thermal death rate of the corn germ.

2.3.1 The Germination Process

Mayer and Shain (1974) define seed germination as "that series of steps normally occuring prior to the emergence of the radicle from the seedcoat." A germinating seed needs only water and oxygen in order to initiate a broad complexity of metabolic activities which fall into one

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of three general categories: 1) Breakdown of materials in the seed, 2) Transport of these materials from one portion of the seed to another, and 3) Synthesis of new materials from the breakdown products. The metabolic changes which occur in the early stages of germination are the result of the activity of various enzyme systems, which are either present in the dry seed or quickly become active as the seed imbibes water (Mayer and Poljakoff-Mayer, 1963). The complexity of changes which occur during germination include: the activation of proteolytic enzymes, synthesis and activation of proteins and other enzymes, activation or synthesis of a number of growth substances, and changes in membrane permeability.

The proteolytic enzyme system of barley includes eight different peptidoses and as many as three proteolytic systems--those in the aleurone layer, starchy endosperm, and the scutellum (Mayer and Shain, 1974). This proteolytic system is markedly similar to that of corn (Chen and Varner, 1973). Proteolysis in the aleurone occurs after the onset of germination but supplies the necessary nutrients for subsequent growth. The breakdown of lipids also occurs relatively late with respect to the onset of germination. These two systems can, therefore, be eliminated, and germination would not be blocked.

In comparison, synthesis and activation of proteins and enzymes occur relatively early in the germination process. RNA systhesis occurs early while DNA replication occurs relatively late, possibly because sufficient DNA is produced during seed formation to permit the initiation of germination. Some of the protein activation mechanisms which occur are insufficiently clear. Present technology limits the determination of the time of development of protein systhesis and protein activation such that it is not possible to determine which of the two processes regulates germination (Mayer and Shain, 1974.)

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Hormones and growth promoting substances, particularily gibberellins, have been studied widely. An interesting example is the production of gibberellic acid (GA) in the embryo of corn and its diffusion to the aleurone layer to induce hydrolase systhesis to include α-amlyase (Chen and Varner, 1973). Other growth regulators have been shown to affect germination, but the mechanism by which they do so is not yet clear.

Present knowledge of seed germination is rather limited so that the physiological and biochemical changes which occur during germination are not adequately understood (Mayer and Shain, 1974). With this limited knowledge, the specific cause of thermal death cannot be isolated.

2.3.2 Thermal Death of the Seed

Studies conducted on the effect of heat on seed viability have been carried out from the viewpoint of storage. Ching et al. (1959) found that increasing the moisture content from 5% to 10% causes a greater reduction in viability than increasing the storage temperature from 68°F (20°C) to 104°F (40°C). Roberts (1960) expressed all known wheat viability data in a simple mathematical relationship:

$$\text{Log } p_{1/2} = k_v - c_1 M - c_2 T$$

where $p_{1/2}$ = half viability period in days

T = temperature, °C

M = moisture, % w.b.

k_v = constant

c_i = constants

For wheat $k_v = 4.22$, $c_1 = 0.108$, and $c_2 = 0.050$. Temperatures ranged up to 140°F (40°C). No generalized model for thermal death of seeds at high temperatures has been developed.

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2.3.3 Thermal Death Models

Rosenberg et al. (1971) presented evidence that protein denaturation as described by the activated complex theory equation is the cause of thermal death in unicellular organisms. Rosenberg et al. (1973) reported that the thermal death rate of multicellular organisms is described by the product of the activated complex equation and a power law of time. They further speculated that the proteins encountered in the vital functions of multicellular organisms denature most rapidly, and thus, may be rate limiting in the thermal death of multicellular organisms. The specific mathematical relationships will be developed in Chapter III.

2.4 The Effect of High-Temperature Drying on Corn Quality

High temperature drying affects the processing characteristics of corn by changing the water-binding characteristics of the starch. Indications are that this is caused by protein denaturation which changes the organization of the protein molecule markedly, altering its water activity and reducing the ability of sulfurous acid to break the disulfide bond in zein.

There has been some controversy over whether or not high temperature drying is detrimental to the nutritive value of corn. More recent investigations have concluded that there may be a benefit in starch gelatinization in the case of the ruminant, and that only very severe heating of corn will decrease its nutritive value. Lysine, the limiting amino acid in corn, is subject to sugar amine condensation at high temperatures and low moisture contents. There is a trend in the use of in vitro (artificial environment) instead of in vivo (animal digestive environment)

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analysis for amino acids. Procedures for lysine have been developed so that preliminary testing may be performed using in vitro analysis.

2.4.1 Processing Characteristics

Brekke et al. (1972) using a fluidized-bed dryer reported the effect of high-temperature drying on the dry milling quality of corn. Quality as determined by yield and fat content of the prime product mix decreases with increasing drying air temperature. Cold paste viscosity, determined by the Brabender amylograph, was also adversely affected. Drying air temperature up to 104°F (60°C) produced good quality corn. Limitations on drying-air temperatures are different for other drying configurations.

Peplinski and Pfeifer (1970) found that steaming of corn grits alters their properties as measured by water-absorption index (WAI) and paste viscosity (measured on a Brabender amylograph viscograph). Increases in temper moisture level, in retention time and in temperature, increases WAI and starch gelatinization. Moisture contents ranged from 15% to 25%; autoclave steam temperature ranged from 212°F (100°C) to 266°F (136.66°); and retention times ranged from 2.5 to 45 minutes.

Starch wet milled from badly damaged corn comes mainly from the floury endosperm and has a high protein content because of pieces of protein that adhere to the starch granules. The horny endosperm resists grinding into pieces small enough to pass through the fiber removal screen and is passed into the feed by-product at one-sixth the monetary value (Watson and Sanders, 1961.) Improper drying affects protein and starch creating numerous wet-milling difficulties such as: difficult and incomplete grinding with starch loss to the by-product feeds; poor separation of starch and protein resulting in low starch recovery and poor

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quality starch; difficulty in drying the corn gluten fractions; poor germ separation; low yield of oil; and poor color and high fatty-acid content of the oil (MacMasters et al. 1959).

In the wet-milling process, shelled corn is steeped in 0.2% sulfurous acid for 40 hours at 115°F to 130°F (46.1 to 54.4°C). The sulfurous acid softens the hull and loosens the protein starch complex for later separations. Nitrogenous material and minerals are dissolved during the steeping operation (Seeley, 1958). Cox et al. (1944) observed that the action of sulfurous acid is to disintegrate the protein matrix surrounding the starch granules, thus releasing them. He observed the absence of this process in corn that was heated excessively. Watson and Sanders (1961), examining thin sections of horny endosperm during steeping, observed that more starch was retained by heat-treated sections and concluded that the cause was denaturation of the protein matrix which contained the starch. The reason that the sulfurous acid steep is effective is that sulfurous acid disrupts the disulfide bonds in zein and, thus, breaks the protein network binding the starch (Wall, 1964). Disulfide bonds are covalent bonds between cysteinyl residues (Jones, 1964). They provide permanent constraints and limit possible conformations of the protein molecule. Chemical modification of these bonds can be distinctly different from protein denaturation (Tanford, 1968). Frater et al. (1960) showed that reducing the number of disulfide bonds in dough reduces the resistance of the dough to mixing and stretching. Further study of the effect of heat on the subsequent action of sulfurous acid on disulfide bonds in protein is necessary.

McGuire and Earle (1958) noted that change in protein solubility is also related to decreased wet-milling quality. An investigation of the

solubility of zein in water, 0.01N potassium hydroxide, trichloroacetic acid and Duponal-C showed a decreasing trend in solubility with increasing drying temperatures from 120°F to 200°F (48.9°C to 93.3°C). Solubility of protein in water and potassium hydroxide showed the best promise but gave no indication that any drying-air temperature is critical; however, Tanford (1968) observed that the transition from native to denatured states is a "steep" transition which occurs within a narrow range of temperatures. Holaday (1964) reported the influence of initial moisture content on protein denaturation to be marked.

Varying drying-air temperature limitations have been reported for corn which is to be wet-milled. Cox et al. (1944) reported difficulty in processing corn dried at 180°F (82.2°C) to 200°F (93.3°C). Thompson (1967) reported that a drying-air temperature of 200°F (93.3°C) can be used in a concurrent dryer without affecting wet-milling quality. He observed that most of the decrease in wet-milling quality occured during the initial stage of drying, when both grain temperature and moisture content are high. MacMasters et al. (1959) present extensive data showing that drying-air temperatures of 180°F (83.2°C) or higher damaged corn for use in starch production. Initial moisture of the corn and drying air relative humidity were reported as being relatively unimportant. Watson and Hirata (1962) reported the same findings but noted that 150°F (71.1°C) at 40% relative humidity also reduces wet-milling quality. The initial moisture level did not influence milling quality but did affect viability. At 15% relative humidity 200°F (93.3°C) drying-air temperatures could be used. Foster (1965) found that starch yield decreases with increasing drying-air temperature up to 290°F (143.3°C).

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have been developed. Microscopic tests were developed by Cox et al. (1944), Wagoner (1948), Watson and Hirata (1954), and Watson and Sanders (1961). Abbreviated milling tests were developed by Watson et al. (1955) and Freeman and Watson (1969). Freeman (1971), while recognizing the usefulness of microscopic abbreviated tests, suggested that the best test is either a pilot plant test (Anderson, 1967) or a simulated wet-milling process of laboratory scale such as those developed by Lakon (1949), Wolf et al. (1954), Watson (1964), and Anderson (1963). All but one test (Freeman and Watson, 1969) require a lapsed time of two days and all require substantial work time. Consequently, none are suited for routine evaluations of samples on a daily basis. Their primary use is to assist in investigating production problems of significant magnitude (Freeman, 1971).

2.4.2 Nutritive Characteristics

Heat processing affects proteins, carbohydrates, lipids, vitamins and minerals. Denaturation of proteins enhances digestibility by proteases, while reaction of reducing sugars and other compounds with amino acids degrades the biological value of proteins. Short-term heating of proteins tends to improve the nutritive value of many products, while high-temperature, long-term heating tends to reduce the nutritive value of most products. Carbohydrates, while not of primary concern in food products, have been investigated with respect to the toxic effects of their degradative reaction products (Lang, 1970); however, starch gelatinization has possible beneficial effects in feed corn (Hale, 1973). Fats also have been investigated with respect to their degradation products (Lund, 1973). The water-soluble vitamins are less heat stable than the fat-soluble vitamins and trace minerals (Schoeder, 1971). Feed corn is of importance both as an energy

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source and as a protein source. Its protein content averages just under 10% and must be taken into account when it is used as a constituent of mixed feeds, in order that they may be nutritionally balanced in the most economical feed mix and in order to conserve protein sources for food use (Lund, 1973).

Investigations of the effects of high-temperature drying on the nutritional quality of corn have produced mixed results--some investigators conclude that there were no detrimental effects, while others concluded that, indeed, there were detrimental effects and, also, possible beneficial effects. Heusden and MacMasters (1967) emphasized the importance of investigating the effect of grain temperature on quality rather than that of drying-air temperature.

Chow and Draper (1969), noting frequent outbreaks of vitamin E deficiency in monogastric animals, investigated the effects of high-temperature drying on vitamin E and fatty acid content. No effect was discernable. Jensen et al. (1960) reported no effect of drying-air temperature on riboflavin, miacin, or carotene; however, pantothenic acid levels decreased as drying-air temperatures were increased from 140°F (60°C) to 220°F (104.4°C). Lang (1970) listed that heat labile vitamins and heat stable vitamins. Heat labile vitamins include: ascorbic acid, vitamin B_2, pantothenic acid, and thiamine; heat stable vitamins include: vitamin A, biotin, choline, cobalamin, vitamin E, folic acids, inositol, vitamin K, niacin, pyridoxines, and riboflavin.

Adams et al. (1943) found that kiln drying reduces the fermentable carbohydrate content of corn and attributes this effect to the possible formation of unfermentable dextrine. Hale (1973) presented data which suggested that high-temperature gelatinization may improve starch digestion by

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the ruminant. Jensen et al. (1960) found no effect on the performance of swine fed roasted corn as an energy source; however, Hathaway et al. (1952) reported that mature ear corn dried from 27% to 14% at drying-air temperatures greater than 140°F (60°C) is of significantly lower energy value as an energy source for rates as compared to the energy value of product dried at lower temperatures.

High drying-air temperatures destroy certain amino acids. Mulhbäuer and Christ (1974) determined lysine to be the most heat labile amino acid in whole kernel corn as compared to cystine and methionine. Small decreases in lysine were observed at 176°F (80°C) while cystine and methionine showed comparable decreases at temperatures up to 284°F (140°C). Lysine was reduced by more than one-third in 30 minutes at a temperature of 284°F (140°C) while equivalent reductions in cystine and methionine required temperatures in excess of 320°F (160°C). Liquid ion exchange chromatography was used for the amino acid determinations. Lysine has been found to be most heat labile owing to its very reactive epsilon-amine group (Lang, 1970). Lysine is already deficient in corn protein (Kies and Fox, 1972) so that any additional loss through thermal damage will reduce the overall nutritive value of corn as a protein source. Wall et al. (1975) reported a slight decrease in the amount of nutritionally available lysine in product which had been dried with a drying-air temperature of 289.4°F (143°C). The maximum product temperature reached was 219.2°F (104°C) and the method of assessing nutritionally available lysine was the methyl acrylate method.

Hathaway et al. (1952) reported that the nutritive value of the protein of mature ear corn dried from a moisture of 27% to 14% at temperatures from 160°F (71.1°C) to 240°F (115.6°C) is adversely affected as evidenced by reductions of 18% to 32% in weight gains of rats. Corn was their source of

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protein for the eight-week feeding trial. Sullivan et al. (1973) compared protein utilization of rats fed infrared roasted corn. They used roasting times ranging from 30 to 40 seconds to produce product temperatures of 176, 212, 284, and 320°F (80, 100, 120, 140 and 160°C). Protein utilization, as measured by average-daily-gain, was significantly depressed by corn heated to 320°F (160°C). Jensen (1960) observed no difference in feed efficiency and rate of gain for swine of different ages fed corn dried at drying-air temperatures of 140°F (60°C), 180°F (82.2°C) and 220°F (104.4°C). Emerick et al. (1961) found that corn dried from 21 to 10 or 12 percent moisture at drying-air temperatures as high as 250°F (121.1°C) and 350°F (176.6°C) caused no difference in weight gains or feed efficiency for checks and rats, respectively. Mild scorching and over-drying occurred at these temperatures but had no effect on weight gains or feed efficiencies. Costa et al. (1973a) used infrared roasting to produce temperatures of 179.6, 219.2, 260.6 and 287.6°F (82, 140, 127 and 140°C). There was no significant effect of temperature on protein efficiency for growing swine, as measured by average-daily-gain; however, significantly higher gain to feed ratios were experienced at 179.6°F (82°C) and 287.6°F (142°C).

High temperature treatments have other beneficial effects. Johnson et al. (1958) found higher dry matter digestibility for flaked, steamed, corn then for cracked corn, or steamed, dried and cracked corn. Costa et al. (1973b) reported that growing swine prefer corn infrared roasted at 212°F (100°C) as compared to corn roasted at 176, 248, 284, and 320°F (80, 120, 140 and 160°C) and corn dried at 176°F (80°C). Jensen et al. (1960) also reported a similar observation when swine preferred corn dried at 220°F (104.4°C) over that dried at 140°F (60°C) and 180°F (82.2°C). Sullivan et al. (1976) reported increased feed efficiency for ruminants depending on the feed ration. High temperature drying has another potential effect on the nutritive value of

corn and other products in that naturally occuring growth inhibitors are deactivated or are destroyed. Wheat, rye, and buckwheat (and to a lesser extent, rice, oats, and maize) contain trypsin inhibitors. Cooking destroys the inhibitors in rice, wheat, and oats but not in other cereals (Bender, 1972). Mann et al. (1967) found that heating peanut meal at 212°F (100°C) for two hours at 20 percent moisture produces 80% reduction in levels of aflatoxin B_1 and B_2. Neucere et al. (1972) reported that moist heat at a temperature of 230°F (110°C) for one hour will destroy trypsin inhibitors and aflatoxin without damage to amino acids. Woodham and Dawson (1968) observed similar results for trypsin inhibitors.

2.4.3 Heat Damage to Amino Acids

The view that the nutritive value of vegetable proteins and animal proteins of inferior quality is directly related to the number of lysine, epsilon-amine groups has been well-established (Boyne et al. 1961; Martinez et al. 1961; Kakade and Liener, 1966; Blom et al. 1967 and Boctor et al. 1968). Protein in ordinary dent corn is deficient in lysine to the point that lysine is the limiting essential amino acid. Corn is also deficient in methionine and tryptophan but contains an over abundance of glutamic acid and leucine (Mertz et al. 1964).

The importance of lysine in corn stems from the fact that it is the growth limiting amino acid and, also, that it tends to be the most heat labile amino acid in most food systems. Block et al. (1946) reported that in certain food systems lysine appears to be the only amino acid which is damaged during heat processing. Exposures of wheat flour, egg, yeast and lactalbumin to temperatures of 392°F (200°C) for 15 to 20 minutes reduced biological values as determined by protein efficiency ration (PER). The addition of lysine restored the initial values. Halevy and Guggenheim (1963)

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found the same result using a mixture of wheat gluten and glucose. Experiments by Carpenter et al. (1962) established that damage to amino acids is most severe at 4-14 percent moisture content. Dry materials are relatively resistant to heat (Miller), 1956), and boiling in excess water usually has no effect (Bender, 1972). Pomeranz et al. (1963) reported that more than half of the protein of wheat, when fed as the sole source of protein cannot be utilized by the animal organism for tissue growth becuase of lack of lysine. Neucere et al. (1972) found that dry and wet heat treatments at 248°F (120°C) for one hour have no effect on available lysine (AVL), but that both wet and dry heat at 266°F (130°C) for one hour cause reductions of AVL in peanut meal. Blom et al. (1967) reported that the biological availability of lysine may be reduced by heat treatments at 284°to 302°F (140° to 150°C). Available lysine is reduced by severe heating in ground nut cotyledons, but there is little change in the level of available methionine assessed using Streptococcus zymogenes (Anatharaman and Carpenter, 1969). Boyne et al. (1961), Carpenter and March (1961), Kakade and Liener (1966), and Boctor and Harper (1968) observed a correlation between available lysine content and the biological value of protein.

The low natural levels of lysine in corn and the possibility that these levels may be further reduced by high-temperature drying have implications in the efficient utilization of corn as a food or feed protein source. If the release of certain essential amino acids is delayed during digestion, or if certain essential amino acids are lacking and are not present at the site of protein synthesis at the same time, those that cannot be used for protein sythesis are oxidized (Melvick et al. 1946 and Cook et al. 1951). In addition to the need for all amino acids to be present at the same time, energy must also be present, and if not available in sufficient quantity, part of the amino acids will be oxidized and the nutritive value of the protein, lost (Bender,

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1972). Register and Peterson (1958) found that growth is depressed when sucrose is substituted for starch as an energy source. The sustained energy release of starch parrellels the slow release of amino acids during digestion.

Processing damage to lysine and other amino acids may include any of the following mechanisms: 1) reactions between amino acids and reducing substances (in the case of lysine, the terminal amine groups); 2) reaction between amino acids and carbonyl groups (Bjarnason and Carpenter, 1969); 3) protein - protein interaction (carbon-nitrogen linking); and 4) destruction by oxidation (Lea, 1958, Ellis, 1959; Lea et al. 1960; Finley and Friedman, 1972; Bender, 1972). Hodge (1953) summarized the browning reactions in model systems of carbonyls with amino compounds to include seven different types of reactions. These will be described more extensively in Chapter III.

The type of damage inflicted depends upon conditions. Lea et al. (1960) showed that at temperatures below 212°F (100°C) lysine was lost by reaction with autoxidizing fat, while at higher temperatures, 239°F to 266°F (115°C to 130°C), the loss is independent of the presence of fat. It has been clearly established that temperature, time of heating, the presence of moisture, and the presence of substances such as reducing agents control the damage done to proteins (Bender, 1972). If the relative humidity of the atmosphere is as high as 70%, or the moisture content is above a certain limit, the Maillard reactions may take place at temperatures as low as 86°F to 104°F (30°C to 40°C). The reducing pentoses and hexoses play a part in these reactions (Blom et al. 1967). Evans et al. (1948) found autoclaving causes two types of inactivation of lysine--one, the reaction of lysine with sucrose and the other, the reaction of lysine with protein to render it unavailable to enzymatic digestion in vivo. Hanks et al. (1948) reported the reaction of methionine with sucrose and glucose to form a linkage not

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hydrolyzed by enzymes in vivo. Evans and Butts (1948) reported cystine, methionine, and histidine inactivation to be caused by a reaction with sucrose to form an enzyme-resistant linkage. Osner and Johnson (1968) suggested that temperatures above 212°F (100°C) for more than one hour can diminish the availability of lysine, arginine, methionine, cystine, leucine, tryptophan and histidine. Reducing and nonreducing sugars (to include sucrose, raffinose, and trehalose) react with lysine in proteins to render it unavailable (El-Nockinsky and Frampton, 1967). In reaction with reducing sugars, after the formation of a Schiff's base, several further products can result from Browning and Maillard reactions (Hodge et al., 1972).

Hodge et al. (1972) reported that the characteristic browned cereal aromas occur largely due to the thermal degradation of the Amandori compounds of amino compounds. These compounds result from the Maillard reactions. A number of investigators have also shown that CO_2 and volatile carbonyl compounds are produced when cereal products undergo browning as a result of the Maillard reactions (Wiseblatt and Kohn, 1960; Linko et al. 1963 and Lea, 1958). Corn kernels gradually become brown during oven-dry moisture determinations at 217.4°F (103°C). The greatest amount of browning within the kernel takes place in the region surrounding the embryo where most of the sucrose and reducing sugars are located (Motz, 1969), suggesting the possible importance of the Maillard browning reactions. On the basis of similarities between products formed during browning in model systems and browning in corn, it appears that the Maillard reactions or very similar reactions occur in corn (Hart, 1972).

2.5 Determination of Available Lysine

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amino acid content but also upon the physiological availability of the essential amino acids (Finley and Friedman, 1972). The chemical analysis of protein which is preceded by acid hydrolysis does not yield information concerning the availability of the amino acids to a living organism. Lysine which has become unavailable is set free by hydrolysis and, although it is determined by chemical methods, is not accessible to proteolytic enzymes (Blom et al. 1967). At the same time, biological values such as net protein utilization (NPU), biological value (BV), and gross protein value (GPV) and protein efficiency ratio (PER) measure only the limiting amino acid and give no information about the other amino acids, unless multiple assays are carried out with various combinations of supplementary amino acids (Bender, 1954). Only direct measurement of the availability of amino acids provides the required information (Bender, 1972). Since direct methods have been applied, it has become clear that in some foods several amino acids may be damaged at the same time (Ford, 1962).

When considering the nutritive value of any product, three basic principles must be taken into account: 1) Changes in the nutritive value during porcessing are of little value unless the product comprises a significant proportion of dietary intake; 2) Inadequate assessments of the nutritive value of proteins can lead to false conclusions. Methods such as biological value (BV), gross protein value (GPV), net protein utilization (NPU), and protein efficiency ratio (PER) will reveal changes which are produced only by the limiting amino acid; and 3) The sulphur amino acids tend to be limiting (Bender, 1972).

Grau and Carroll (1958) and Bender (1972) believe that in the future, protein sources will be evaluated on the basis of their proportions of available amino acids. Ideally, these methods should be chemical methods,

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but at present, bioassay is the only method available. The few exceptions include the various chemical methods available for the determination of available lysine.

Costs of amino acids are dependent upon the protein source and will be of primary importance in the future. Estimates of protein quality must, therefore, be based upon the ability of the protein to supply the necessary amino acid needs of the animal. These needs, in themselves, are not yet precisely defined, because there are no precise standards for their determination. The ruminant is even more complex than the monogastric, because rumen microorganisms utilize ingested food and, in turn, are digested and metabolized by the host (Grau and Carroll, 1958).

Lysine has been studied widely and a number of tests for its availability which give very comparable results have been developed. There are three chemical determinations for available lysine content: 1 - fluoro - 2,4 - dinitrobenzene (FDNB), developed by Carpenter (1960); 2, 4, 6 - trinitrobenzenesulfonic acid (TNBS), developed for cereal products by Kakade and Leiner, (1969); and methyl acrylate, developed by Finley and Friedman (1972).

All of the above tests modify the lysine epsilon-amine groups and are specific for lysine only. The compounds are first allowed to react with the product. The compounds are allowed to react with the lysyl side chain under mild conditions. These mild conditions are comparable to the physiological conditions during digestion (Kotaki and Satake, 1964) and, thus, only the ϵ - amino groups of lysine which are nutritionally available tend to react. Lysyl side chains which are in the chemically or physically protected portions of protein do not react with the compounds and are not available physiologically. Once the reaction has gone to completion, the pH is lowered drastically to stop any further reaction and hydrolysis is

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used to free either the reacted radicals in the case of the TNBS and the FDNB methods or the unreacted radicals in the case of the methyl acrylate methods. The respective radicals are analyzed spectrophotometrically or by ion exchange chromatography (Finley and Friedman, 1972).

Several workers have compared the TNBS and FDNB methods with pure proteins and found that they agree quite well with biological determinations of available lysine (Finley and Friedman, 1972); however, in products with high carbohydrate content, colored products formed during hydrolysis tend to interfere with accurate spectrophotometry. Also, sample size (the larger the sample of either pure protein or carbohydrate containing material, the smaller the amount of available lysine detected), filtration, and lactose content -- in the case of milk (Posati et al. 1972) -- have an effect on the determination (Blom et al. 1960). If these are standardized, concurrence with data procured by more established methods can be observed.

In comparing the three methods, the TNBS analysis requires two hours, while the FDNB analysis requires 16 hours (Kakade and Liener, 1969). The methyl acrylate method requires about an intermediate amount of time and an amino acid analyzer, but is well-suited for high-carbohydrate content products (Finley and Friedman, 1972). The TNBS method requires that blanks and samples be run in triplicate (Posati et al. 1972).

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III. THEORY

The mechanisms of chemical reactions in biological systems such as whole kernel corn are complex. It has been the practice of individuals working in the applied areas of food and feed processing to approximate the very complex reactions which occur during thermal processing by simple reaction kinetics. First order reaction kinetics have been used in describing nutritive degradation during heat processing or in describing thermal death of microorganisms during commercial food sterilization.

The objective in assuming a simplistic model is to reduce the prohibitive number of experiments and associated costs required in order to develop data which will discriminate between a potentially large number of complex reaction systems. The results of a simplistic investigation yield insight into the complexity of a more thorough investigation and will give information which may be of as much use, practically, as that obtained from a more comprehensive investigation (Labuza, 1972).

The general approach taken during this investigation has been, first, to search the range of variables for areas where there are reactions occurring; then, to cover those areas with a limited number of experiments; and finally, to use the limited data as quantitative evidence in order to demonstrate that the particular process behaves according to one of a few simplistic reaction mechanisms. Although the limited amount of data will not produce conclusive evidence for one reaction mechanism, the results will provide a general index for process design and a basis from which to make a definitive statement on the feasibility of conducting more thorough investigations.

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Two chemical attributes of corn were studied--thermal death, as measured by germination (AOSA, 1965) and available lysine, as measured by the TNBS method (Kakade and Liener, 1969). Work in the area of biophysics and statistical mechanics has produced models for the thermal death rate of multicellular organisms which can be applied to the corn germ (Rosenberg et al. 1973 and Skurnick, 1974). Hart (1972) has implicated the Maillard reactions, reactions between amino acids and reducing sugars, as producing decreased lysine availability. Although there is strong quantitative evidence, conclusive proof of either mechanism has not been produced.

3.1 The Thermal Death, Protein Denaturation and The Power Law

There are three possible general mechanisms of thermal death: 1) There may be an increased rate of loss of heat sensitive structural and functional units such as cells, enzymes, and nucleo proteins; 2) The rate of utilization or destruction of some limiting non-replaceable metabolite, catalyst, or co-factor is increased by normal pathways at higher temperatures; and, 3) There may be an increasing rate of accumulation of some deleterious factor at the higher temperatures. The activation energies for the reactions involved in substrate utilization or in formation of metabolic by products are small, whereas the activation energies for protein or nucleoprotein denaturative processes and processes involving important biological constituents as described in mechanisms of the first type are markedly higher (Strehler, 1961).

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3.1.1 Protein Denaturation (Structural Changes)

Tanford (1968) defined protein denaturation as "a major change from the original native structure without alteration of amino acid sequence." Disruption of bonds (hydrogen and disulfide linkages) responsible for the secondary, tertiary, and quaternary structures of protein occurs during denaturation; the compact configuration of polypeptide chain unfolds into flexible chains showing random modes of coiling. During denaturation, some reactive groups of $-NH_2$, -COOH, -OH and -SH are liberated; enzyme inactivation may result from this type of denaturation. In the case of food proteins, denaturation increases susceptibility to proteolysis, and the unfolding of the coiled peptide chains brings to the surface many reactive groups (including amino acids) which were formerly masked from enzymatic proteolysis (Lang, 1970).

Proteins are made up of more than 20 different amino acid residues held together by a variety of chemical bonds and other forces. Covalent bonds are responsible for the skeletal structure of the protein molecule and are the shortest bonds exhibiting the highest energies (30 - 100 Kcal./mol.). Covalent bonds form intraresidue linkages, peptide bonds, and disulfide bonds between cysteine residues. Ionic bonds (10 - 20 Kcal/mol.) are the strongest polar bonds but are far less energetic than covalent bonds. Ionic bonds are formed between the acidic and basic polar sidechains of lysine, arginine, aspartic acid, and glutamic acid residues; they can also be formed from interaction with the free terminal amine and carboxyl groups at the ends of polypeptide chains. The hydrogen bond (a polar bond) is the next strongest bond with an energy level of 2-10 Kcal/mole. The presence of the α- helix in proteins is a result of polar bonding caused by hydrogen between amide and carbonyl groups of peptides three residues apart.

Van der Waals forces of mutual induction of dipole movements in electrically apolar groups and of repulsion between apolar groups in close proximity are less energetic, but equally important bonding forces. Also present is coulomb repulsion between charged groups of like sign (Jones, 1964).

3.1.2 Protein Denaturation (An Activation Process)

Denaturation is accompanied by a change in free energy which results from the destruction of secondary bonding. Changes in the secondary structure alter the vibrational frequencies of bonded groups by increasing their vibrational freedom and alter the vibrational frequencies in the structural backbone through extra freedom resulting from unfolding. Major increases in free energy occur with changes in secondary bonding -- this is especially true of hydrogen bonding (Joly, 1965).

The kinetics of protein denaturation can be developed in terms of activated complex theory. Gibbs' function defines the free energy for systems in which the state can be specified by temperature, pressure and variables of composition. Let

$$G = H - TS \tag{3.1}$$

where

G = energy of the system

H = enthalpy of the system

T = temperature, absolute

S = entropy of the system

The entropy is interpreted as an indication of the randomness of the protein molecule. With greater randomness there is increased entropy. When a protein molecule goes from a folded to an unfolded structure

(denaturation), the change in terms of free energy is given by

$$\Delta G = H_{unf} - H_{fold} - T_{unf} S_{unf} + T_{fold} S_{fold} \quad (3.2)$$

at constant temperature

$$\Delta G = \Delta H - T\Delta S \quad (3.3)$$

where

ΔG = free energy of the system

ΔH = enthalpy of activation

ΔS = entropy of activation

(Moore, 1972).

There are three fundamental assumptions in activated complex theory: 1) The reacting molecules must traverse certain states of potential energy higher than the average levels of either reactant or product; 2) Molecules at the high potential energy levels are in statistical equilibrium with the reactants; and 3) The rate of reaction is proportional to the concentration of molecules at the high potential energy state (Glasstone et al. 1941). It is possible to define a reaction coordinate along which movement corresponds to the transformation from reactant through transition state (activated complex) to product.

Native protein may be imagined as an assembly of helical peptide fragments held in a rigid configuration by disulfide bonds and side chain hydrogen bonds. When these bonds are broken, the protein molecule is considered to be in an activated state. In the activated state the protein molecule is unstable, and one of the bond vibrations or a special combination of vibrations will lead to decay of the activated state into denatured protein. In other words, one of the vibrational degrees of freedom in the activated complex has a potential energy maximum rather than a minimum and is thus unstable. The partition function for this

unstable degree of freedom, Q_u, multiplied by the velocity of motion along the reaction coordinate, v^*, is equal to KkT/h.

$$Q_u v^* = KkT/h \tag{3.4}$$

where

Q_u = partition function

v^* = velocity of motion along the reaction coordinate

K = transmission coefficient

k = Boltzman's constant

h = Plank's constant

T = temperature, degrees absolute

(Glasstone et al. 1941)

The reaction rate, k^*, is given by

$$k^* = C^* v^* \tag{3.5}$$

where

C^* = concentration of the forward-moving transition state species

$$C^* = K\, C_N \tag{3.6}$$

where

K = equilibrium constant for reaction

C_N = concentration of native protein

In terms of partition functions

$$C^* = \frac{Q_{trans}}{Q_N} * \exp\left(-\frac{\epsilon_{o\,trans} - \epsilon_{o\,reag}}{kT}\right) * C_N \tag{3.7}$$

where

Q_{trans} = partition function for the transition state

Q_N = partition function for native protein

$\epsilon_{o\,trans}$ = energy level of the transition state

$\epsilon_{o\,reag}$ = energy level of native protein

Factoring the partition function for the transition state into two terms -- one for the unstable degrees of freedom and one for other degrees of freedom

$$Q_{trans} = Q_u * Q^* \tag{3.8}$$

where

Q_u = partion function for unstable degrees of freedom

Q^* = partion function for other degrees of freedom

The reaction rate then can be simplified

$$k^* = \nu^* \frac{Q_u}{Q_{reag}} \frac{Q^*}{} \exp\left(- \frac{\epsilon_{o\ trans} - \epsilon_{o\ reag}}{kT}\right) C_N \tag{3.9}$$

$$= \frac{K\ kT}{h} \cdot \frac{Q^*}{Q_{reag}} \exp\left(- \frac{\epsilon_{o\ trans} - \epsilon_{o\ reag}}{kT}\right) C_N \tag{3.10}$$

Defining the equilibrium constant

$$K^* = \frac{Q^*}{Q_{reag}} \exp\left(- \frac{\epsilon_{o\ trans} - \epsilon_{o\ reag}}{kT}\right) \tag{3.11}$$

it follows to define quantities ΔG, ΔH, and ΔS which are the free energy, enthalpy, and entropy of activation. They are defined as the usual standard partial molar quantities of reaction.

$$\Delta G^* = RT \ln K^* \tag{3.12}$$

$$\Delta H^* = RT^2 \frac{\partial \ln K^*}{\partial T}_p \tag{3.13}$$

$$\Delta S^* = - \frac{\partial G^*}{\partial T}_p \tag{3.14}$$

where

p = pressure

The rate constant is then

$$k^* = \frac{KkT}{h} K^*$$

$$= \frac{Kkt}{h} e^{-\Delta G^*/RT}$$

$$= \frac{Kkt}{h} e^{-\Delta H^*/RT} e^{\Delta S^*/R} \tag{3.15}$$

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$$\frac{dC_N}{dt} = -k^* C_N \tag{3.16}$$

(Leffler and Grunwald, 1963)

Native protein may be imagined as an assembly of helical peptide fragments held in a rigid configuration by disulfide bonds and side chain hydrogen bonds. When the hydrogen bonds are broken, rapid disorganization occurs. The conceptualization of protein denaturation as an activation process visualizes the native molecule as being in an activated state if all side-chain hydrogen bonds responsible for the stabilization of the native molecule are broken. If it is assumed that the probabilities of the existence of hydrogen bonds are mutually independent, and that X_{ij}, X_{rs}, and X_{zm} are the probabilities that single, cooperative and double hydrogen bonds exist, respectively, the concentration of molecules in which all side-chain hydrogen bonds are broken is

$$C_N^* = C_N \prod(1 - X_{ij}) \prod(1 - X_{rs}) \prod(1 - X_{zm}) \tag{3.17}$$

where

C_N^* = concentration of molecules in which all side-chain hydrogen bonds are broken (activated state)

C_N = concentration of native protein

X_{ij} = probabilities that single hydrogen bonds exist

X_{rs} = probabilities that cooperative hydrogen bonds exist

X_{zm} = probabilities that double hydrogen bonds exist

Taking the products over all different kinds of hydrogen bonds, the first-order rate constant, k*, is

$$k^* = \frac{kT}{h} \prod(1 - X_{ij}) \prod(1 - X_{rs}) \prod(1 - X_{zm}) \tag{3.18}$$

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Denaturation with large ΔH (such as the ΔH's found in thermal death of organisms) involves the rupture of a large number of weak non-cooperative hydrogen bonds. Then, with largely singly hydrogen bonding involved

$$X_{ij} = \frac{K_{ij}}{1 + K_{ij}} \tag{3.19}$$

and

$$K^* = \frac{kT}{h} \pi \left(\frac{1}{1 + K_{ij}} \right) \tag{3.20}$$

where

K_{ij} = the hydrogen bond equilibrium constant

$K_{ij} = \frac{\text{concentration fraction with hydrogen-bonded i and j groups}}{\text{concentration fraction of molecules with i and j groups not hydrogen-bonded}}$

Then the equilibrium constant for the activated complex is

$$K^* = \frac{C_N^*}{C_N} = \frac{C_N \pi (1 - X_{ij})}{C_N} \tag{3.21}$$

$$= \pi \left(\frac{1}{1 + K_{ij}} \right)$$

The standard changes in free energy, enthalpy and the entropy of activation for the activation process are then

$$\Delta G^* = RT \ln (1 + K_{ij}) \tag{3.22}$$

$$\Delta H^* = - \frac{K_{ij}}{1 + K_{ij}} H_{ij} \tag{3.23}$$

$$\Delta S^* = -R \ln (1 - K_{ij}) - \frac{1}{T} \frac{K_{ij}}{1 + K_{ij}} H_{ij} \tag{3.24}$$

If all H_{ij}'s and K_{ij}'s are assumed equal as a first approximation

$$\Delta G^* = nRT \ln \left(1 + K_{ij} \right) \tag{3.25}$$

$$\Delta H^* = \frac{- n K_{ij}}{1 + K_{ij}} \quad H_{ij} \tag{3.26}$$

$$\Delta S^* = nR \ln \left(1 + K_{ij} \right) - \frac{n K_{ij}}{1 + K_{ij}} \quad \frac{H_{ij}}{T} \tag{3.27}$$

where

n = the number of ruptured hydrogen bonds (Joly, 1965)

In the case of proteins the activation entropy and the activation enthalpy of protein denaturation are related by the simple linear equation (Rosenberg et al., 1971)

$$\Delta S^* = a \Delta H^* + b \tag{3.28}$$

where

$a = 1/Tc = 1/329^{o}K$

$b = - 64.9$ cal/mol ^{o}K

Eg (3.15) then becomes

$$k = K \frac{kT}{h} e^{-64.9/R} * e^{H^*/RTc} * e^{-\Delta H^*/RT} \tag{3.29}$$

This form makes parameter estimation less difficult by eliminating one of the parameters, ΔS^*, and by requiring only the estimation of two parameters -- the transmission coefficient, K, and the activation enthalpy, ΔH^*.

3.2 Thermal Death of Multicellular Organisms

The description of thermally caused deaths of multicellular organisms through the application of the thermodynamics of rate processes is a relatively unexplored field. Unlike unicellular organisms, multicellular

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poikilothermic organisms, such as the corn germ, do not show simple exponential thermal death kinetics as a function of time. Instead of the simple exponential survivorship curve as exhibited by unicellular organisms, multicellular organisms exhibit characteristic sigmoidal curves (See Figure 3.1) which have both temperature and time dependent terms in the rate function. At lower temperatures such as T(1) there is a definite "lag" or a time period when there is little thermal death. With time, the survivorship curve becomes more like a first order reaction plot. As temperatures increase -- T(2) through T(5) -- the survivorship model becomes more closely identified with a first order plot.

Rosenberg et al. (1973) developed an analytic function which suitably described the typical sigmoidal survivorship curves and met certain other requisites to include: 1) The function must have no more than two constants; 2) One constant must be temperature dependent, its logarithm plotted against the reciprocal temperature should yield an Arrhenius plot; and 3) One should be able to test both the differential and integral form of the function, depending upon the nature of the data. Such a function is that the death rate, $\mu(t)$, increases as a power law of time.

$$\mu(t) = \frac{1}{N(t)} \frac{dN(t)}{dt} = A_D t^n \tag{3.30}$$

Integrated over time

$$\frac{N(t)}{N_o} = \exp\left[(A_D t^{n+1}) / (n+1) \right] \tag{3.31}$$

where

$\mu(t)$ = the thermal death rate as a function of time

t = time

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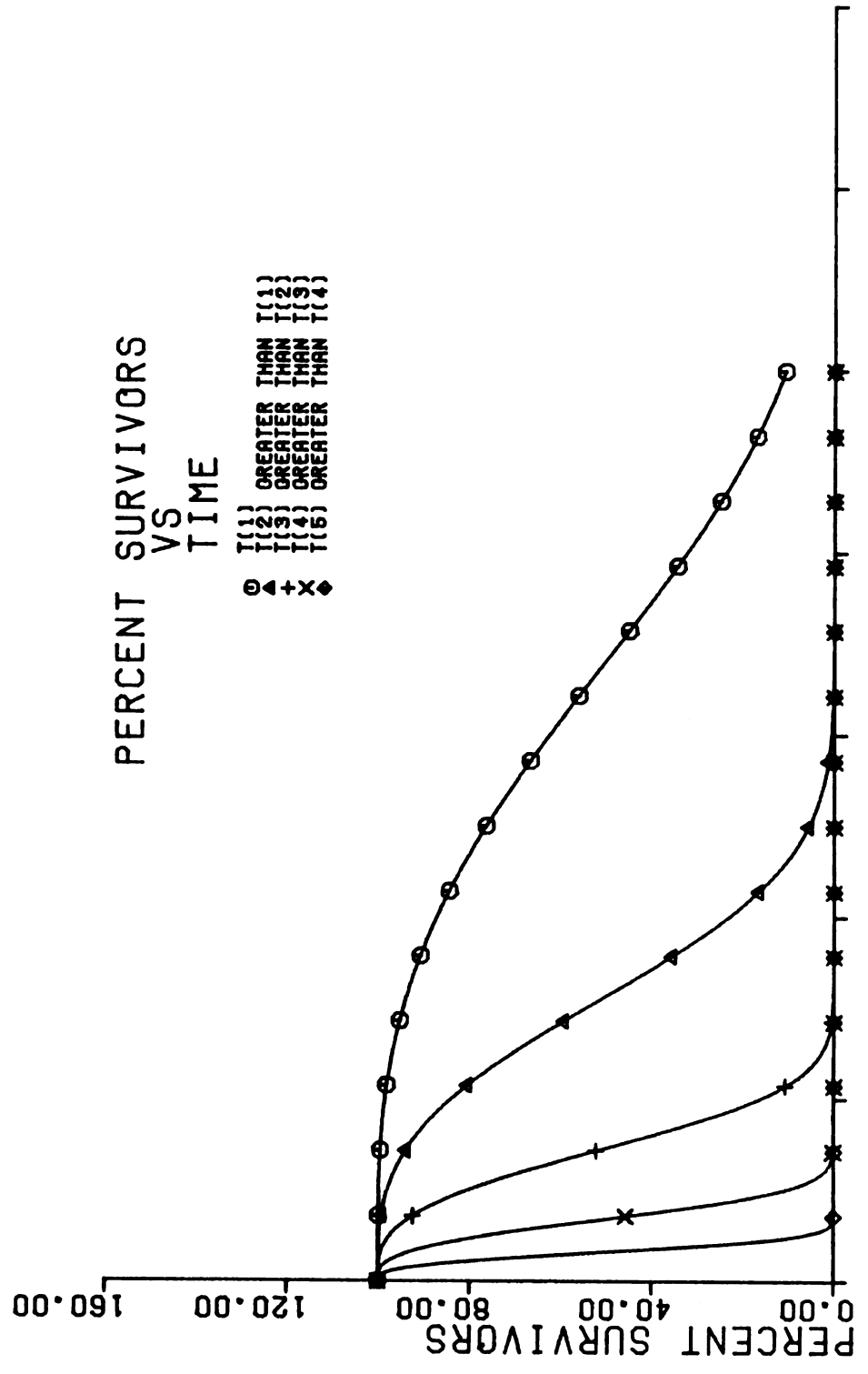


Figure 3.1 Thermal Death of Multicellular Organisms

N_o = the initial population

$N(t)$ = the population as a function of time

A_D = temperature dependent rate-constant (defined by Eq. 3.29)

n = power law constant

Statistics of extremes show that under rather general circumstances order statistics for the first event can take on only one of three possible (asymptotic) forms one of these being the power law (Gumbel, 1958). An abstract representation of a multicellular organism may be a chain consisting of a very large number of links. The chain is assumed to break (the organism perishes) when the first link breaks, regardless of which link breaks frist. If the failure of a link is described by a sequential process, the transformation of a link from one state to another is equivalent to deterioration. Assuming that the link must go through α units of deterioration and that the time spent in each stage of deterioration is independent of the time spent in other stages, let the time spent in each stage of deterioration be described by some probability density function $f_j(t)$. Then, the cummulative distribution function, $F_j(t)$, gives the probability that the transformation from the j to the j + 1 state takes place in a time interval of length t. Assuming the probability of completion of a transformation from one stage to another is independent of the time spent in that stage, the failure mechanism is composed of stages which, individually show no aging characteristics (independent of time). Expressed mathematically

$$\frac{1}{1 - F_j(t)} \quad \frac{d}{dt} \quad F_j(t) = \rho_j \tag{3.32}$$

where

$F_j(t)$ = probability that in the transformation from stage j is accomplished in a time interval of t.

ρ_j = the probability of an immediate transformation

From which it follows by integration that

$$F_j(t) = 1 - e^{-\rho_j t} \tag{3.33}$$

and differentiating

$$f_j(t) = \quad_j e^{-\rho_j t} \tag{3.34}$$

where

$f_j(t)$ = corresponding probability density function for each stage of deterioration

The time for the failure of a link, T_α, is the sum of the time spent in all stages of deterioration.

$$T_\alpha = \sum_{j=1}^{\alpha} t_j \tag{3.35}$$

The distribution in time for the link failures and, thus, the death rate of the population can be found by Laplace transforms. Since

$$E\left(e^{-sT_\alpha}\right) = D\left(e^{-s\sum_{j=1}^{\alpha} t_j}\right) = E\left(e^{-st_1} \cdot e^{-st_2} \cdots e^{-st}\right) \tag{3.36}$$

with the "t_j's" mutually independent it follows that the set $\{e^{-st_j}\}$ is also mutually independent. Then

$$E\left(e^{-sT_\alpha}\right) = E\left(e^{-st_1}\right) \cdot E\left(e^{-st_2}\right) \cdots E\left(e^{-st_\alpha}\right) \tag{3.37}$$

Since

$$E\left(e^{-st_j}\right) = \int_0^\infty e^{-st} f_j(t)dt = \mathcal{L}\{f_j(t)\} \tag{3.38}$$

where

$f_j(t)$ = the probability density for completion

Letting f(t) be the probability density function for the completion of all stages of deterioration, combining Equations 3.37 and 3.38 gives

$$\mathcal{L}\{f(t)\} = \prod_{j=1}^{\alpha} \mathcal{L}\{f_j(t)\} = \left[\mathcal{L}\{f_j(t)\}\right]^\alpha \tag{3.39}$$

which only applies if the time spent in each stage is identically distributed. Thus, Equation 3.34 becomes

$$f_j(t) = \rho e^{-\rho t} \tag{3.40}$$

for

$$j = 1, 2, \ldots \alpha \ .$$

Thus

$$\mathcal{L}\{f_j(t)\} = \int_0^\infty e^{-st} \rho e^{-\rho t} \, dt$$

$$= (\rho/(\rho + s) \qquad (3.41)$$

and

$$\mathcal{L}\{f(t)\} = (\rho/(\rho + s) \qquad (3.42)$$

Taking the inverse transform gives the distribution in terms of T_α the time of thermal death for each organism.

$$f(t) = \rho (\rho t)^{\alpha - 1} e^{-\rho t} \ / \ (\alpha - 1) \ ! \qquad (3.43)$$

The probability that a link fails by time t is given by integrating the probability density function so that

$$F(t) = \int_0^t f(u) \, du \qquad (3.44)$$

which becomes

$$F(t) = \frac{1}{(\alpha - 1)!} \gamma (\alpha , \rho t) \qquad (3.45)$$

a function of the incomplete gamma function defined as

$$\gamma (\alpha, \rho t) = \int_0^{\rho t} e^{-x} \, x^{\alpha - 1} \, dx$$

This differs from $\Gamma (\alpha)$, the gamma function, since the upper limit is not infinity.

If ρt is small, the incomplete gamma function can be expanded as

$$F(t) = \frac{e^{-\rho t}}{(\alpha - 1)!} \sum_{S = 0}^{\infty} \frac{\Gamma (\alpha)}{(\alpha + S + 1)} (\rho t)^{\alpha + S} \qquad (3.46)$$

$$\simeq \frac{(\rho t)^\alpha}{\alpha !} \qquad (3.47)$$

It is apparent that $F(o) = 0$ and that $F(\epsilon) > 0$ for each $\epsilon > 0$. Similarly

$$\lim_{(\rho t) \to 0} \frac{F(\tau \rho t)}{F(\rho t)} = \tau^{\alpha} \tag{3.48}$$

for $\tau > 0$

Thus by Gnedenko's criterion (Gnedenko, 1943), there are constants a_n and b_n such that $F(a_n t + b_n)$ belongs to a domain of attraction of the limited distribtuion $\Psi_{\alpha}^{(k)}(t)$. Thus, the decline of a cohort as described by the kinetics of chain breakage is described by the power law (Skurnick, 1974). Two other forms may be derived for ρt large and ρt of intermediate size. However, the case for ρt small gives the simplest analytical function and has met with the most success in being fit to experimental data (Rosenberg et al. 1973).

3.3 The Effect of Drying On Lysine Availability

The reactions taking place during high-temperature drying which have a direct effect upon the nutritional availability of lysine in corn are denaturation and nonenzymatic browning. Protein denaturation functions to unfold the protein molecule and to bring amino acids (including lysine) which were previously buried in the protein matrix to the surface. The nonenzymatic browning reaction has the reverse effect and involves the reaction of the lysyl residues with reducing sugars to include glucose and fructose. Only a small percentage of other amino acids to include arginine, histidine, tyrosine, and methionine are involved (Lea and Hannan 1950 a,b). Kinetic modeling of these two reactions involves assuming that the rate at which lysine becomes available is proportional to the rate of protein denaturation and that the nonenzymatic browning system can be represented by a simple kinetic rate equation.

3.3.1 The Effect of Protein Denaturation

Protein denaturation unfolds the coiled polypeptide chains bringing to the surface many amino acids which were formerly masked from enzymatic proteolysis during digestion. The effect of denaturation in increasing lysine availability can be described by a first order reaction. Assuming that the rate at which lysine is made available is proportional to the rate of protein denaturation, the rate is given by

$$\frac{dC_A}{dt} = k_1 C_L \tag{3.49}$$

where

C_A = concentration of available lysine

C_L = concentration of lysine masked from proteolysis by the protein matrix

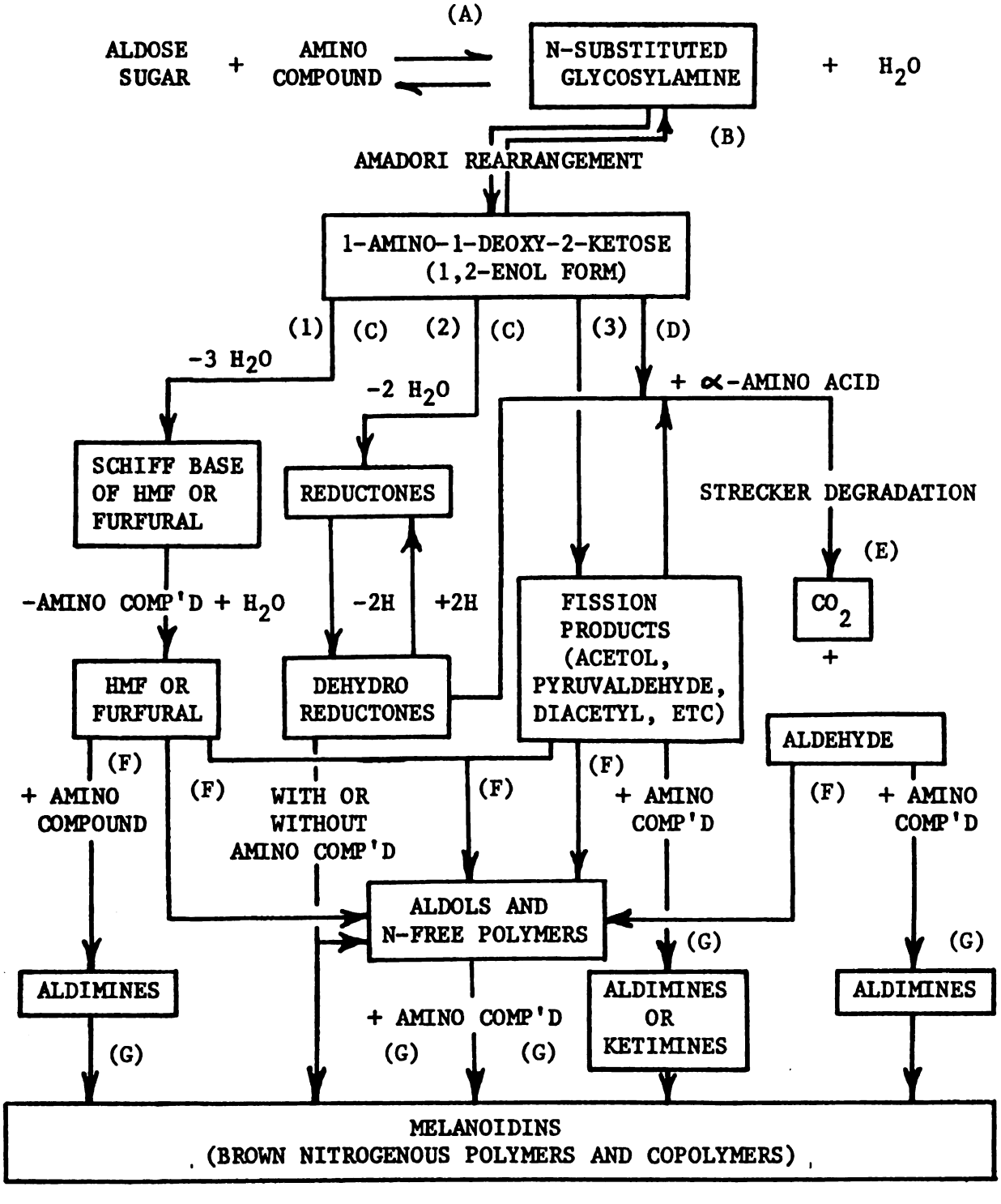
t = time

k_1 = first-order rate constant

This form follows directly from equation 3.16.

3.3.2 The Maillard Reactions

Hodge (1953) outlined an extensive system of reactions which are thought to be responsible for the degradation of protein in food systems (See Figure 3.2). Hart (1972) concluded that this system of reactions or a very similar reaction system is activated in corn during high temperature drying. The associated stoichiometry is very complex, and one would expect that, with changing temperature and the consequent shifts in equilibrium constants, the predominating reaction mechanisms will change. Reaction paths 1 and 2 (Figure 3.2) dominate at low temperatures. Schiff's



(1) ACID CONDITIONS
(2) BASIC CONDITIONS
(3) HIGH TEMPERATURE

Figure 3.2 Scheme of Nonenzymatic Browning Reactions (Labuza, 1975 and Hodge, 1953)

base of HMF or furfural is produced under acidic conditions, and reductones are produced under basic conditions. Reaction path 3 (Figure 3.2) is dominant at high product temperatures. In spite of the associated, complex stoichiometry good success has been achieved in the use of simple rate equations to describe nonenzymatic browning (Labuza, 1975). Two factors contribute strongly to this success. First, reactions B, C, D, E, F, and G can follow reaction A spontaneously, especially at low moisture levels (Hodge, 1953). And, second, the first two transformation, reactions A and B (See Figure 3.3), occur in series, and there is a possibility that one of the forward reactions is rate limiting. Thus, it is conceivable that after an initial reaction time the reactant concentrations, before the rate-limiting step, will be proportional to the reactant of interest (the preceding reactions are at or close to equilibrium). The product concentrations after the rate limiting reaction will be small (highly reactive product) in comparison to the reactant concentration and the reaction will become pseudo-first or second order.

The reactants involved in the reactions A and B, (Figure 3.3) beginning with the Schiff's base are reported as being very unstable (Hodge, 1953). If the concentration to Schiff's base is assumed to be very small, the rate limiting step is then one of the first two reversible reactions. Stoichiometrically the reaction is

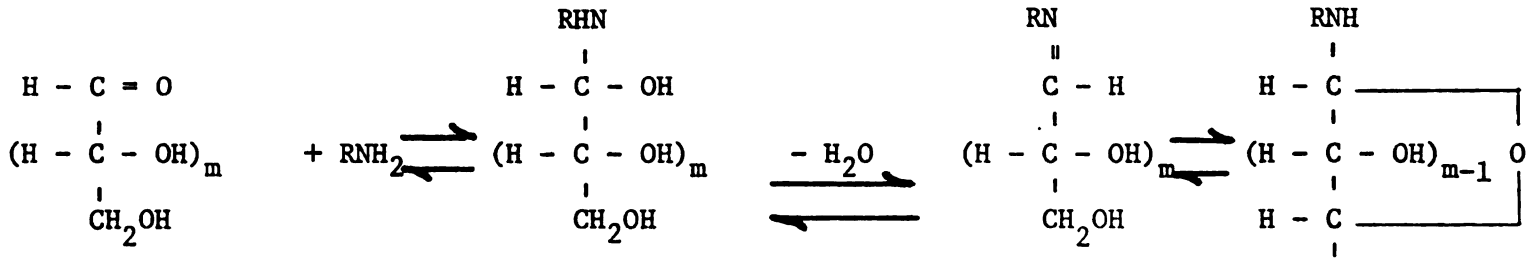
$$C + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P \underset{k_4}{\overset{k_3}{\rightleftharpoons}} S + W \qquad (3.50)$$

where

C = a reducing substance

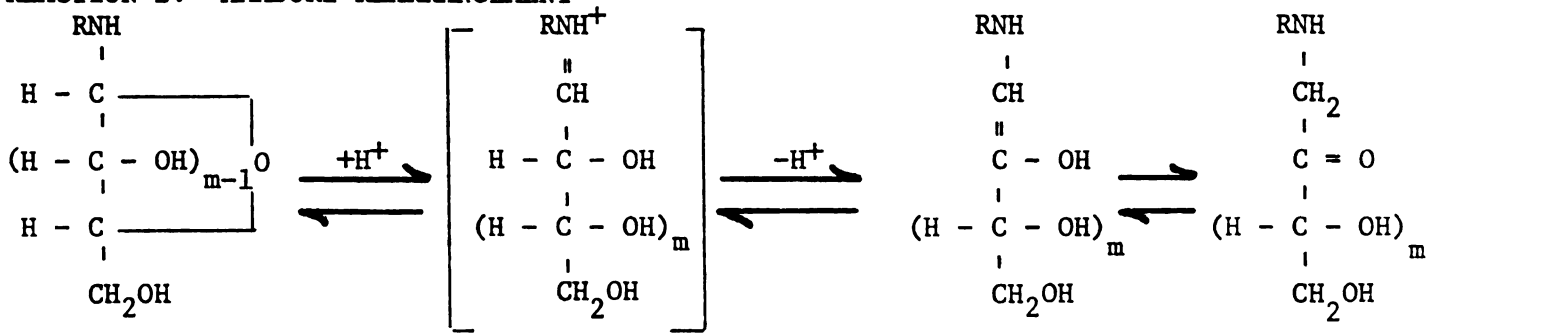
A = a lysine molecule

REACTION A: SUGAR-AMINE CONDENSATION



sugar | amine | addition product | Schiff's base | N-substituted glycosylamine

REACTION B: AMADORI REARRANGEMENT



N-substituted glycosylamine | cation of Schiff's base | (enol form) N-substituted 1-amino-1-deoxy-2-ketose | (keto form)

Figure 3.3: Initial stages of the browning mechanism -- sugar-amine condensation and amadori rearrangement (Hodge,1953)

P = an addition product

S = Schiff's base

W = a water molecule

Writing the associated differential equations we have

$$\frac{dC_A}{dt} = k_2 C_p - k_1 C_c C_A \qquad (3.51)$$

$$\frac{dC_p}{dt} = k_4 C_S C_W - (k_3 + k_2) C_p + k_1 C_c C_A \qquad (3.52)$$

where

k_1 through k_4 are rate constants

C_c = the concentration of the reducing substance

C_A = the concentration of available lysine

C_p = the concentration of addition product

C_S = the concentration of Schiff's base

C_W = the concentration of water

Unfortunately, the analytical solutions of consecutive reaction schemes such as reaction 3.50 involve complicated functions in which the arguments depend on the rate constants. Thus, these solutions are useful only when the ratios of the rate constants are known. Without these values an inordinate amount of mathematical manipulation is involved (Benson, 1960). Since numerical solutions are an approximation of analytical solutions, the same difficulties would arise in attempting to solve equation without some prior knowledge of the relative sizes of the reaction constants.

If it is assumed that Schiff's base is very unstable, then Equation 3.52 becomes

$$\frac{dC_p}{dt} = k_1 C_C C_A - (k_3 + k_2) C_p \tag{3.53}$$

If k_3 controls the rate of reaction, then after a certain amount of time the first reaction will go to equilibrium giving

$$K = \frac{k_1}{k_2} = \frac{C_p}{C_C C_A} \tag{3.54}$$

where K is the equilibrium constant for the first reaction. Equation 3.53 thus becomes

$$\frac{dC_p}{dt} = \frac{dC_A}{dt} = -k_3 C_p \tag{3.55}$$

which is a simple pseudo-first order equation. At this point there is no method by which to ascertain the amount of time which is required for the first reaction to go to equilibrium. If the first reaction is rate limiting, then the concentration of the addition product would become very small and Equation 3.51 would become

$$\frac{dC_A}{dt} = -k_1 C_C C_A \tag{3.56}$$

and the reaction system would be pseudo-second order.

3.3.3 The Reaction System in Corn

Combining the effect of protein denaturation and the nonenzymatic browning into simplistic form yields one of the following stoichiometric approximations

$$L \xrightarrow{k_1} A \xrightarrow{k_2} R \tag{3.57}$$

a consecutive, irreversible, first-order system of reactions

$$L \xrightarrow{k_1} 2A \xrightarrow{k_2} R \tag{3.58}$$

a consecutive, irreversible, first-order, second-order system of reactions

$$L \xrightarrow{k_1} A + C \xrightarrow{k_2} R \qquad (3.59)$$

an approximation to reaction (3.56).

Where

L = lysine masked by the protein matrix

A = available lysine

C = a reducing substance such as a carbohydrate

R = a reaction product

k_1 & k_2 = the associated constants

If reaction 3.55 is used, the associated rate equations for the three components are

$$\frac{dC_L}{dt} = K_1 C_L \qquad (3.60)$$

$$\frac{dC_A}{dt} = k_1 C_L - k_2 C_R \qquad (3.61)$$

The associated initial conditions are

$$C_L = C_{LO} \qquad (3.62)$$

$$C_A = C_{AO} \qquad (3.63)$$

Solution of Eg. (3.60) gives

$$C_A = C_{AO}^{-k_1 t} \qquad (3.64)$$

and solution of Eg. (3.61) gives

$$C_A = C_{LO}\, k_1 \left(\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right) - C_{AO} e^{-k_2 t} \qquad (3.65)$$

The family of curves of Figure 3.4 illustrates the model for available lysine for various k_1/k_2 ratios.

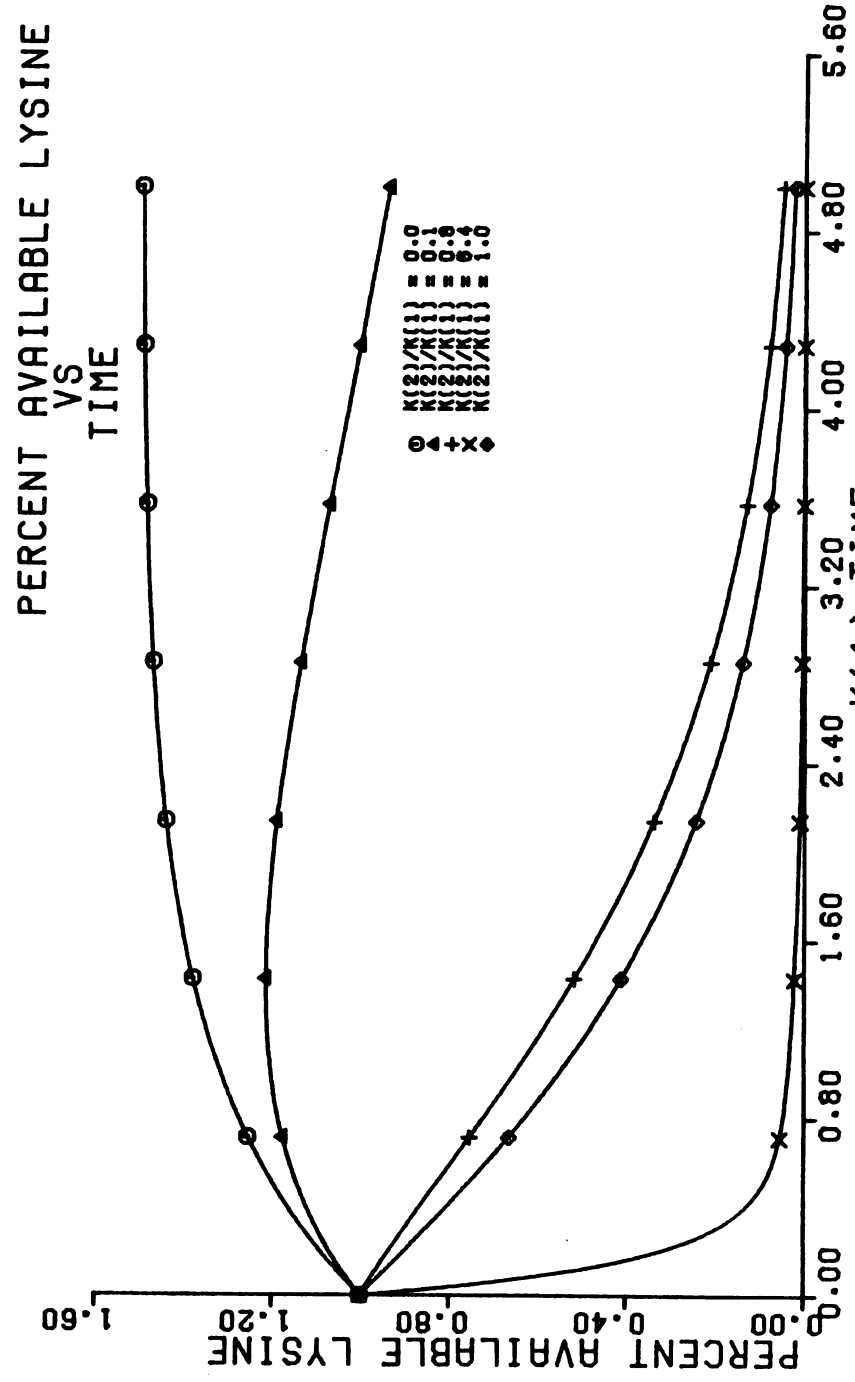


Figure 3.4 Consecutive First-Order Reaction Mechanisms for Lysine Availability as Affected by Heat.

If k, (see Equation 3.59) is sensitive to a temperature change at a different temperature than k_2 (see also Equation 3.57) or, more precisely, if the activation temperature is different for the two reactions, one will be more dominant depending on the temperature of the reactants. Also, if the activations energies are grossly different even though the activation temperatures are the same, different temperatures will produce different k_2/k_1 ratios and thus different plots according to Figure 3.4. One expects protein denaturation to occur at a relatively low temperature of approximately 140°F (60°C) having a relatively high activation energy of 80-120 k cal/mole (Labuza, 1972) and nonenzymatic browning to occur at relatively higher temperatures of approximately 220°F (104.4°C) (Wall et al., 1975) and relatively low activation energies of approximately 25-50 k cal/mole. Thus, with protein denaturation occuring (Labuza, 1972) at a relatively low temperature and being very sensitive to small temperature changes as compared to nonenzymatic browning, the regain above 140°F (60°C) and below 220°F (104.4°C) will produce plots characteristics of $k_2/k_1 = 0.0$ ($k_1 \neq 0$) and $k_2/k_1 = 0.1$. Regions above 220°F (104.4°C) will produce plots characteristic of $k_2/k_1 = 0.8$, 1.0 and 6.4.

3.4 The Complexity of Reaction Systems in Corn as Related to the Maillard Reaction

Food systems as related to the chemistry of degradative reactions during drying are complex and corn is no exception. Not only is the nonenzymatic browning system complex with many pathways to the end products, melanoids, but there are a number of reaction systems and physical mechanisms which can have a profound effect upon not only the reaction rate, but also the availability of reactants for the reaction system.

Water activity controls the reaction rate of many reactions, including the Maillard reaction (Labuza, 1975). The composition of the product before drying determines the total amount of each reactant present; and other reactions to include protein denaturation, sucrose carmelization, and rancidity reactions will furnish more reactants -- both free amino acids and reducing substances (Labuza, 1974 b, c).

3.4.1 The Effect of Water Activity on Reaction Rates

The water activity of a food is defined as the ratio of the water vapor pressure of the food to the vapor pressure of pure water. It is an index of the relative chemical activity of the water contained in the food. The chemical potential U_w, of water in food is controlled by temperature, pressure, and composition of the solution phase and is equal to its partial molar free energy $\bar{G}_w$ defined as follows

$$U_w = \bar{G}_w = \left(G_s / N_w \right)\Big|_{T,\, P,\, n_j} \tag{3.66}$$

where

G_s = free energy of the solution phase

N_w = the number of moles in water

T = temperature

P = pressure

n_j = number of moles of other constituents of the solution

(Bone, 1969).

The effect of water activity on the nonenzymatic browning reaction is one which is directly related to the involvement of water in the reaction mechanisms. Figure 3.5 shows the general effect of water activity,

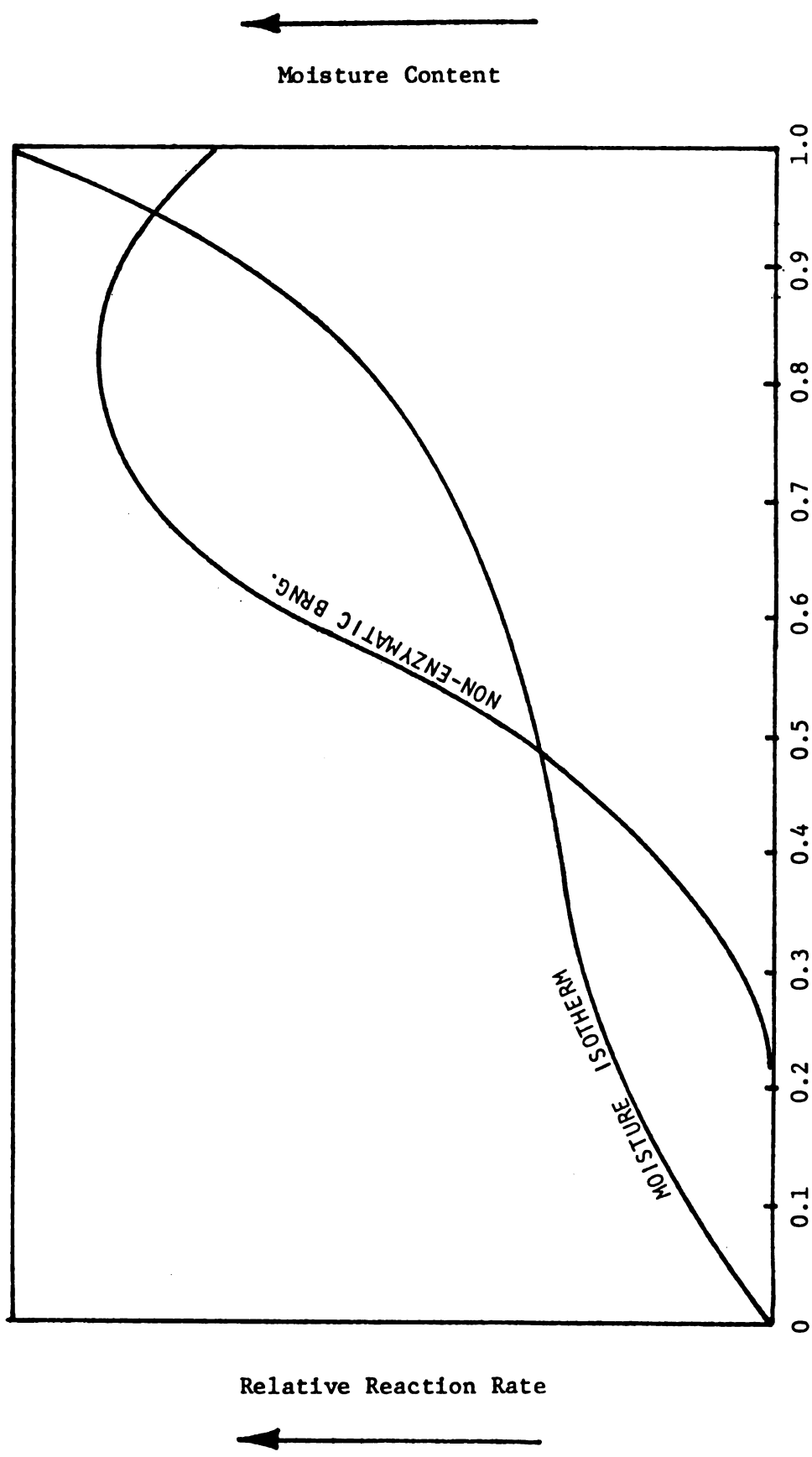


Figure 3.5 The Effect of Water Activity on Rates of Reaction (Labuza, 1975)

A_w, on many reactions, including the nonenzymatic browning reaction. The A_w of .3 corresponds to the monolayer level of concentration of water in the product. It is at this point that reactants are able to begin to move or diffuse in solution, contact, and react, and it is at this level that the reaction rate will start to increase from a very low rate. The reaction rate will peak at A_w .65 to .70 and, then, begin to decline (Labuza, 1974 a, 1975). In corn this A_w corresponds to a moisture content of less than 14% wb, depending on temperature.

3.4.2 The Chemical Composition of Corn

The chemical composition of corn will not only determine the rates of reaction during high-temperature drying, but also the end point to which the reaction will go (i.e. whether all of the reactants will react). The basic constituents of corn are shown in Table 3.1. Those of primary interest are protein and sugars which may become involved in the Maillard reaction. Table 3.2 shows the amino acid composition of corn protein. There is an average of approximately 3.7×10^{-5} gram moles lysine/grams corn. The carbohydrates of immediate importance are the reducing sugars glucose and fructose (See Table 3.3). There is an average of 1.56×10^{-5} gram mole fructose/ gram corn and an average of 1.41×10^{-5} gram moles glucose/gram corn. So there is approximately enough reducing sugar to react with the lysine.

However, there are two other complicating factors in the reaction system -- first, at temperatures above approximately 250°F (121.1°C) a carmelization reaction will cause sucrose to hydrolyze to glucose and fructose and other products, thus, providing as much as an average of

Moisture, % w.b.	16.2
Starch, %	71.5
Protein, %	9.91
Fat, %	4.78
Ash (oxide), %	1.42
Fiber (crude), %	2.66
Sugar, total, %	2.58
Total carotenoids, mg/kg	30.0

Table 3.1 Basic Constituents of Corn (Motz, 1969)

Amino Acid	Range	Average
Alanine	5.3 - 7.5	6.6
Arginine	8.5 -14.7	11.7
Aspartic Acid	3.2 - 5.5	4.0
Cyst(e)ine	1.8 - 3.0	2.4
Glutamic Acid	7.5 - 9.5	8.5
Glycine	2.7 - 4.7	3.8
Histidine	4.8 - 7.8	6.2
Isoleucine *	2.9 - 4.9	4.0
Lysine *	4.2 - 7.5	5.4
Leucine *	6.8 -11.0	9.3
Methionine *	2.6 - 3.3	3.0
Phenylalanine *	3.5 - 5.6	4.3
Proline	3.3 - 5.0	4.5
Serine	3.2 - 4.1	3.6
Threonine *	2.1 -10.8	6.5
Tryptophan *	0.72- 1.05	0.83
Tyrosine	2.0 - 3.2	2.5
Valine *	2.9 - 6.2	4.4
Amide	4.7 - 8.6	...

* essential amino acids

Table 3.2 Amino Acid Content of Protein Isolated from Maize Seeds
(Wolfe and Fowden, 1957).

Starch, %	71.5
Amylopectin, % total	73
Amylose, % total	27
Sugar, %	2.58
Raffinose, %	0.1 - 0.3
Sucrose, %	0.9 - 1.9
Glucose, %	0.2 - 0.5
Fructose, %	0.1 - 0.4

Table 3.3 Carbohydrate Content of Corn (Motz, 1969).

8.18×10^{-5} gram moles/gram corn of each reducing sugar to react with lysine; and second, cysteine tends to react preferentially with reducing substances to in effect protect lysine from destruction (Labuza, 1974 b). This would provide up to 2.3×10^{-5} gram moles/grams corn of amine substances to be reduced. These two reactions have not been studied in corn and were not considered in the stoichiometry of the previous section. Also, there are no acceptably accurate methods to measure the percent of cysteine and cystine in the product. Cysteine is a strongly reactive sulfur amino acid; whereas, cystine (approximately two cysteine residues) is not reactive (Simpson, 1975).

3.4.3 The Nonhomogeneity of Whole Kernel Corn

Another complicating factor, which potentially is a rate controlling mechanism, is the fact that the concentration of protein and sugars varies from portion to portion of the corn kernel. There is an abundance of protein in the endosperm and an abundance of sugars in the embryo (see Table 3.4). This can have two possible effects. First there may be an overabundance of one reactant in either or both of the locations, causing the reaction of lysine with reducing substances to go to completion in the germ or embryo and leaving some lysine in the available state in the endosperm. Second, there is the possibility that diffusion can be rate controlling.

3.5 The Nonhomogeneity of Corn with Respect to Transport Phenomena.

Corn is nonhomogeneous physically as well as chemically. The basic

DISTRIBUTION OF THE BASIC CONSTITUENTS OF YELLOW DENT AMONG THE FRACTIONS OF THE KERNEL

	Endosperm (%)	Embryo (%)	Pericarp (%)	Tip Cap (%)
Proportion of the part to the whole kernel	82	11.6	5.5	0.8
Protein	73.1	23.9	2.2	0.8
Oil	15.0	83.2	1.2	0.6
Sugar	28.2	70.0	1.1	0.7
Starch	98.0	1.3	0.6	0.1
Ash	18.2	78.5	2.5	0.8

Table 3.4 Distribution of the Basic Constituents of Yellow Dent Corn Among the Fractions of the Kernel (Motz, 1969).

components of corn which are physically different are starch, gluten, hull and germ. These components have different heat and moisture diffusivities and different adsorption and desorption isotherms. Thus, heat and mass transport become very complex. Even if the water vapor concentration within the kernel are uniform the moisture contents of different portions of the kernel would not be. Different portions of the kernel display different moisture isotherms. The germ has the lowest moisture content for a given A_w. Fortunately, under most heating and drying conditions significant temperature gradients only last for the first three to four minutes (Pabis and Henderson, 1962). Thus, lumped parameter systems are used to describe the temperature and moisture history of grain in current grain drying models (Bakker-Arkema et al. 1974).

3.5.1 Moisture Isotherms and Heats of Desorption of the Component Parts of the Corn Kernel.

There is a marked difference in the moisture isotherms of the component parts of corn. Since drying occurs largely on the desorption isotherms (Figure 3.6) it will be used in order to illustrate this point. The corn germ is the dryest portion of the kernel for any relative humidity. In addition, the germ is located at the tip cap of the kernel which is a very vapor permeable area. On the other hand starchy areas which are the wettest portions of the kernel at a given relative humidity, are well protected by the relatively vapor impermeable pericarp (Kumar, 1973). Thus, with the dryest portions of the kernel in a realtively unprotected area and the wettest portion of the kernel in a protected area, one would expect the possibility of a grain air space moisture gradient and a product moisture gradient. An investigation to ascertain the possible

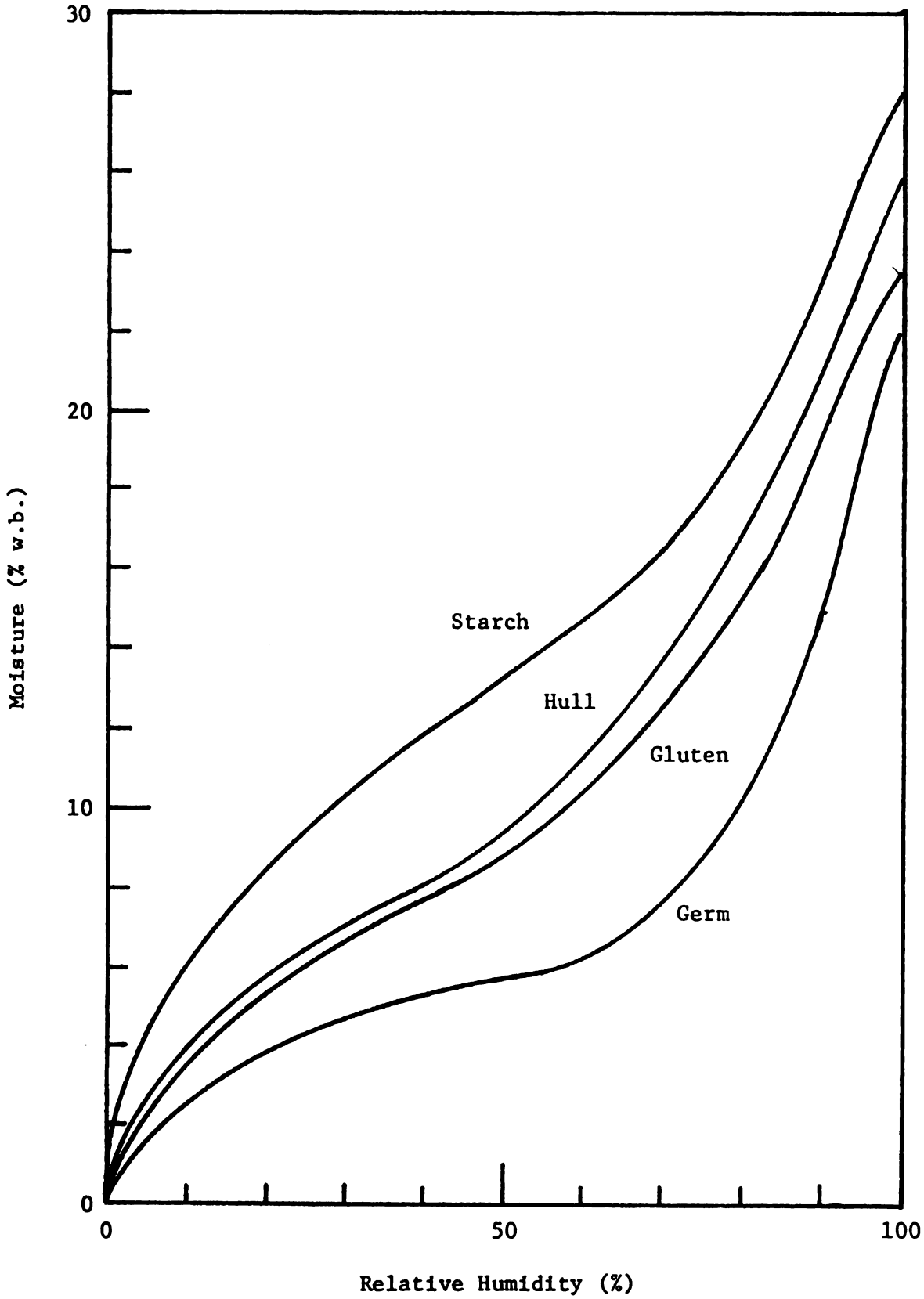


Figure 3.6 Desorption Isotherms of Corn Constituents at 50°C (122°F) (Chung and Pfost, 1967).

magnitude of these moisture gradients is needed before more grain quality simulation is performed because most rate constants in the degradation mechanisms of food systems are sensitive to moisture differences (Labuza, 1974 b).

3.5.2 Lumped Parameter Heat Transfer

The possibility of the existance of temperature gradients is more difficult to ascertain because of differences in net heats of desorption (Figure 3.7), the effect of which are confused with the effects of isotherm and permeability nonhomogeneity of corn. If all portions of the seed dry at the same rate, even though the isotherms and the grain air space humidities vary, the germ would most certainly be at the lowest temperature. However, with the complexity of permeability and diffusivity nonhomogeneity, only in-depth investigations to include simulation of internal heat and mass transfer will give indications of the possibility that temperature gradients do exist and of the drying conditions that tend to produce them. Pabis and Henderson (1962) have reported temperature gradients only during the first three to four minutes of drying. Thus, until further investigations are conducted, lump-parameter heat and mass transfer gives the most accurate indication of grain temperature. All existing grain drying models assume no grain temperature gradients (Bakker-Arkema et al. 1974).

Table 3.5 Net Heats of Desorption for Different Components of Corn for 4 to 20 Percent Moisture Content (w.b.) at 122°F (31°C) (Chung and Pfost, 1967).

Component	Net Heat of Desorption (Kcal./Kg. H_2O)
Whole Kernel	593-838
Starch	647-866
Hull	598-750
Gluten	592-739
Germ	589-679

IV. PROCEDURES

Laboratory investigations were conducted in an effort to define the effect of various temperature histories at different moisture contents on two chemical attributes of the product and to explore the difficulties which might be encountered in applying this knowledge to predict the effect of a drying treatment by a laboratory or field dryer.

Constant moisture heat treatments were given through the use of thermal-death-time (TDT) cans and either a hot water bath or a stream retort as a constant temperature heat source. The two chemical attributes studied were viability as measured by germination (AOSA, 1970) and available lysine as measured by the 2, 4, 6-trinitrobenzenesulfonic acid (TNBS) method (Kakade and Liener, 1969). Parameter estimation of proposed kinematic models was performed through the use of a generalized curve fitting program. A laboratory-scale concurrent dryer with counter-flow cooler was used in conjunction with a drying model and the proposed kinematic models in an attempt to predict the effect of a drying treatment on the product. And a thin-layer drying model with attached kinematic models was used to model a fluidized bed dryer described by Brekke et al. (1972).

4.1 Heat Treatments

Heat treatments of corn at constant moisture content and for various temperature-time combinations were accomplished through the use

of thermal-death-time (TDT) cans. Moisture contents of approximately 14, 16, 17, 20, 24, and 28 percent wet basis were used with temperatures ranging from 130°F (51°C) to 212°F (100°C) and for time periods up to 2 hours in studies of the effect of heat and moisture on viability as measured by germination. Moisture contents of approximately 9, 14, 16, 17 and 20 percent wet basis were used with temperatures ranging from 220°F (104.4°C) to 300°F (148.8°C) and for times of 10 minutes up to 60 minutes in the available lysine studies.

Single cross Garno corn from the 1973 harvest was picked and crib-stored approximately three months, then, shelled and stored at 40°F (4.4°C). The moisture content was 20% w.b. and, thus, the 24% and 28% samples were obtained through the controlled total moisture procedure of rewetting (Kumar, 1973) and stored for more than one month at 40°F (4.4°C) sealed in TDT cans before receiving the respective heat treatments. The 14%, 16%, 17% samples were dried at approximately 80°F and at the equilibrium humidity of a saturated sodium chloride solution. The 9% sample was dried at ambient room conditions. The 20% sample was neither rewetted nor dryed. All samples were sealed in TDT cans and stored at 40°F (4.4°C) before receiving the respective heat treatment.

A copper-constantan thermocouple was placed through the dented portion of the kernel into the germ of one kernel in 1/3 of the TDT cans in order to record temperature histories. Temperature histories were recorded on paper tape at time intervals of 10 seconds. The recorded data were used to estimate the temperature history of the product, especially during heating and cooling. Temperature gradients were ignored during the heating and cooling phases of the heat treatment, and a lumped-system transient heat transfer parameter was estimated

from the data (see section 3.5.1).

The only energy terms considered in a lumped-system are convective heat transfer from ambient (the water bath or the retort) and the energy stored in the object (TDT can and corn). The energy balance can then be written as

$$\dot{q}_c = \dot{E}_s \tag{4.1}$$

where

$\dot{q}_c$ = the rate of convective heat transfer to the object

$\dot{E}_s$ = the rate of energy storage within the object

The appropriate energy transfers can be written as

$$\dot{q}_c = h_c a \, (T_\infty - T) \tag{4.2}$$

$$\dot{E}_s = \rho_c \, V \, c \, \frac{dT}{dt} \tag{4.3}$$

where

h_c = convective heat transfer coefficient

a = convective heat transfer area

T_∞ = ambient temperature

T = average object temperature

c = average object specific heat

ρ_c = average object density

t = time

Substituting Equations (4.12) and (4.13) into (4.11) gives

$$\frac{dT}{dt} + \frac{ha}{\rho_c Vc} (T - T_\infty) = 0 \tag{4.4}$$

Upon solution with the initial condition $T = T_i$ at $t = 0$, the solution becomes

$$T - T = (T_i - T_\infty) \, e^{-(h_c a/\rho_c \, Vc) \, t} \tag{4.5}$$

The lumped heat transfer parameter is $ha/\rho_c Vc$. It is termed a lumped

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parameter because in parameter estimation only the value of the fraction can be estimated from temperature time data (Myers, 1971).

4.2 Viability Determination

The effect of heat at different moisture levels on viability was measured through germination tests. Germination was determined by the "rag doll" method in adherence to the requirements of the Association of Official Seed Analysts (1970). However, in determining viability, all seeds in which the radicle had emerged from the seedcoat were counted as being viable. Vigor was not evaluated. Only 50 kernel samples were used for viability studies.

The mean and pooled variance of germination tests of control samples at various times during the storage period were calculated by statistical methods as described by Himmelblau (1970) and discussed in reference to the computation of the variance of the available lysine test (see Section 4.3).

4.3 Available Lysine Determination

Available lysine as affected by heat at different moisture levels was determined by the procedure of Kakade and Liener (1969). However, some minor modifications were incorporated into the procedure for reason as will be stated later.

Approximately a 30 gram sample (the contents of one TDT can) was ground in a Thomas mill to pass through a 20 mesh screen. The sample was mixed thoroughly and a 50 mg aliquot placed in a pyrex, 125 ml, screw-top, erleneyer flask. To it was added 5 ml of 4% $NaHCO_3$, pH 8.5.

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The suspension was then placed in a constant temperature shaking bath at 104°F (40°C) for 10 minutes prior to the addition of 5 ml of a freshly prepared water solution of 1% TNBS. The reaction was allowed to proceed at 104°F (40°C) for 2 hours at which time 15 ml of concentrated HCl were added. The screw tops of the flask were then loosened slightly to prevent explosions or implosions and their contents autoclaved at 246°F (120°C) for 1 hour. After the hydrolyzate cooled to room temperature, 25 ml of distilled water was added. The contents of each flask were extracted twice with approximately 50 ml ethyl ether in order to remove picric acid which results from the reaction, TNP-N-terminal amino acids or peptides and picric acid which result from the reaction. Blanks were carried through the same procedure except that the concentrated HCl was added to the solution before the addition of the TNBS reagent. The procedure differs from that of Kakade and Liener (1969) in that the sample size and all reagents were 5 fold those used in their procedure. This alteration was necessary in order to improve sample measurement accuracy and to obtain a more homogeneous, representative sample.

In accordance with Posati et al. (1972) both blanks and samples were run in triplicate. All samples were read against all blanks at 346 mu. The amount of E-TNP-lysine (or the lysine equivalent) was calculated from the extension factor of 1.46 E + 04 M^{-1} cm^{-1} given by Kakade and Liener (1969).

The mean and variance of each determination was computed by first computing the mean and variance of all three samples read against each blank, and, then by computing the weighted average of the means and a pooled estimate of variance (Himmelblau, 1970). The overall mean was computed as

$\bar{x}$ =

where

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$$\bar{x} = \frac{1}{n_t} \sum_{i=1}^{m} X_i \, n_i \qquad (4.6)$$

where

$\bar{X}$ = overall mean

X_i = the mean of each determination

n_i = the number of samples read against one blank to determine the mean

n_t = the total number of sample-blank comparisons

m = the number of means averaged

The pooled estimate of variance was computed as

$$s_p^2 = \frac{\sum_{i=1}^{m_v} V_i \, S_i^2}{\sum_{i=1}^{m_v} V_i} \qquad (4.7)$$

where

s_p^2 = pooled estimate of variance

s_i^2 = the variance of each determination

V_i = the number of degrees of freedom associated with each S_i^2

m_v = the number of variances pooled

4.4 Variance of Heat Treatments

Replicating all heat treatments many times in order to estimate the variance of the heat treatments is impractical;however, variance reduction by pairing of samples (replicates) can be used to estimate

the variance of

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where

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where

the variance of individual heat treatments (Himmelblau , 1970).

If for each pair of determinations given the same moisture-temperature-time treatment

$$\bar{X}_i = (X_{i1} - X_{i2}) / 2 \qquad (4.8)$$

then the sum of the squares of the deviations for the i^{th} pair of determinations

$$(X_{i1} - \bar{X}_i)^2 + (X_{i2} - \bar{X}_i)^2 = \frac{(X_{i1} - X_{i2})^2}{2} = \frac{D_i^2}{2} \qquad (4.9)$$

where

X_{i1} = one determination for the i^{th} heat treatment

X_{i2} = the other determination from the i^{th} heat treatment

$\bar{X}_i$ = the average of the determinations at the i^{th} heat treatment

D_i = the difference in measurements

The variance, s_i^2, for a pair of determinations is

$$s_i^2 = \frac{1}{2-1} \quad \frac{(X_{i1} - X_{i2})^2}{2} = \frac{D_i^2}{2} \qquad (4.10)$$

And the pooled variance Sp^2 for m sets of measurements is

$$s_p^2 = \frac{\sum_{i=1}^{m} V_i S_i^2}{\sum_{i=1}^{K} V_i} = \frac{1}{K} \sum_{i=1}^{k} V_i \frac{D_i^2}{2} = \frac{1}{2K} \sum_{i=1}^{k} D_i^2 \qquad (4.20)$$

where

$dF = \sum_{i=1}^{m} V_i$ = the total number of degrees of freedom

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4.5 Laboratory Scale Concurrent Dryer

Anderson (1972) described a dryer composed of two deep beds in series, the first a concurrent flow drying bed and the second a counter-flow cooling bed. A laboratory scale of the concurrent dryer was built and is the second prototype mode. The first model (Carrano and Bickert, 1971) had a 0.3 m. x 0.3 m. cross-sectional area and contained the Anderson grain spreading mechanism; however, channeling of air led to non-uniform drying of the grain bed. A new prototype was built with a circular cross-section with an area of one square foot (0.0929 sq. m.) and a redesigned grain feed mechanism. The dryer is illustrated in Figure 4.1.

In the present dryer, the grain is carried to an air lock at the top of the dryer by a bucket elevator and enters the charging chamber. In the charging chamber, the grain is spread in uniform layers by a circular moving spreader which assures that the grain is exposed to drying air temperatures greater than 600°F (315.5°C) for no longer than one cycle of the spreader (20 seconds). The drying air is heated by an LP gas burner running at approximately 0.21 Kg. per sq. cm. gas pressure. In the drying chamber, grain and air move in the same direction. A water-cooled, copper-tubing cooling coil is used to prevent "popping" of those kernels of corn which contact the drying chamber wall just below the charging chamber. The drying air is exhausted at the end of the drying chamber; the grain passes through a second air lock into the cooling chamber. Here the grain is cooled (while losing a small amount of moisture) as the cooling air flows countercurrently to the descending grain column. A drying bed length of 0.61 m. and a cooling bed depth of 0.76 m. feet were used.

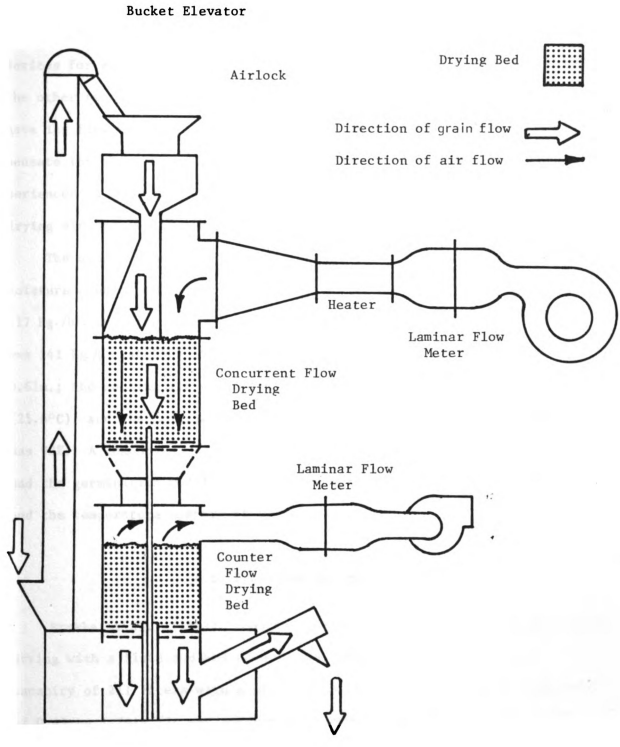

Figure 4.1 Concurrent Dryer with Counter Flow Cooler

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Design of the laboratory dryer posed considerable problems. The top airlock and charging chamber are complicated components and are crucial in producing corn which has comparable temperature-moisture histories as that dried in commercial sized dryers. The unloading devices for each bed consists of three perforated disks -- one stationary, the other two rotating. The second grain bed, the cooling bed, must have its flow rate adjusted to that of the drying bed in order to compensate for shrinkage of corn during drying. Good success was experienced in achieving uniform graim flow. Any channeling of the drying air was overcome by the rotating feeding and unloading components.

The single cross Garno corn was dryed from 19.2 to 15.6% w.b. moisture content in the laboratory dryer. The grain flow rate was 117 Kg./hr. measured at the exit moisture content; the airflow rate was 141 Kg./hr. at 500-515°F (260-268.3°C); the drying bed depth was 0.61m.; the cooling air flow rate was approximately 9 Kg./hr. at 78°F (25.6°C); and the cooling bed depth was 0.76 m. Initial germination was 92%. A concurrent drying model (Bakker-Arkema et al., 1974) and the germination models were used to simulate the drying process and the temperature history of the germ.

4.6 Fluidized Bed Dryer

Brekke et al. (1972) reported germination decreases after artificial drying with a fluidized bed dryer. The laboratory dryer had a bed capacity of 211 liters with a grain depth of 12-15 cm. The air flow rate of 0.45 cu.l./min./l. was sufficient to produce enough agitation so that each kernal received approximately the same drying treatment.

4.7 The Drying Models

Lykov (1966) developed the system of differential equations which describes the drying of capillary porous products such as corn based on the following physical mechanisms:

1) Capillary flow
2) Liquid diffusion
3) Surface diffusion
4) Vapor diffusion
5) Thermal diffusion
6) Hydrodynamic flow .

The rate of moisture, temperature and pressure change within the product is described by three coupled differential equations

$$\frac{\partial M}{\partial t} = \nabla^2 K_{11} M + \nabla^2 K_{12} \theta + \nabla^2 K_{13} P \qquad (4.21)$$

$$\frac{\partial T}{\partial t} = \nabla^2 K_{21} M + \nabla^2 K_{22} \theta + \nabla^2 K_{23} P \qquad (4.22)$$

$$\frac{\partial P}{\partial t} = \nabla^2 K_{31} M + \nabla^2 K_{32} \theta + \nabla^2 K_{33} P \qquad (4.23)$$

where

M = product moisture content

θ = product temperature

P = pressure

K_{11}, K_{22}, K_{33}=phenomenological coefficients

K_{ij} = coupling coefficients when i=j

The phenomenological coefficients are easily determinable; whereas, the coupling effects are not easily determined. Unfortunately, for corn

and other cereal grains few transfer coefficients are constant or known. Neglecting the effects of pressure, product temperature gradients and the coupling effects simplifies equation (4.21) to become

$$\frac{\partial M}{\partial t} = \nabla^2 K_{11} M \tag{4.24}$$

Equation (4.24) is termed a diffusion equation since moisture flow within a corn kernal usually takes place by diffusion in both the vapor and the liquid states. To date, various solutions to equation (4.24) have been proposed but none have been satisfactory because of inaccuracy and because of stability problems which have been encountered in some grain drying models. Thus, the most successful grain drying models have been based on empirical versions of equation (4.24) (Bakker-Arkema et al., 1974).

The concurrent flow corn drying model (Bakker-Arkema et al., 1974) uses the following empirical model

$$\frac{dM}{dt} = \frac{(Me - Mo)}{\sqrt{A^2 + 4Bt}} \exp\left[\frac{- A - \sqrt{A^2 + 4Bt}}{2B}\right] \tag{4.25}$$

where

$$A = 1.86178 + 0.0048843\Theta$$

$$B = 427.3640 \exp(- 0.03301\Theta).$$

(Thompson, 1967). The system of differential equations which represent the concurrent model includes equation (4.25) and is obtained by making heat and mass balances on an elemented volume of dryer ΔX deep. The rate of change in the specific humidity the air as it passes through the elemental volume is

$$\frac{dH}{dX} = \frac{G_p}{G_a} \frac{dM}{dX} \tag{4.26}$$

The rate of change in grain temperature is

$$\frac{d\theta}{dX} = \frac{ha}{G_p\ c_p + G_p\ c_w\ M} (T - \theta) - \frac{h_{f_g} + c_v\ (T - \theta)}{G_p\ c_p + G_p\ c_w\ M} G_a \frac{dH_a}{dX} \tag{4.27}$$

The corresponding rate of change in air temperature is

$$\frac{dT}{dX} = \frac{-h_c a\ (T - \theta)}{G_a\ c_a + G_p\ c_v\ H_a} \tag{4.28}$$

The implied assumptions are

1) No appreciable volume shrinkage during drying.
2) No temperature gradients within the grain kernel.
3) Particle-to-particle heat transfer is negligible.
4) Air and grain flow are plug flow.
5) Bin walls are adiabatic with negligible heat capacity.
6) Changes of air temperature and humidity with respect bed depth, x, are much greater than changes with respect to time.
7) The specific heats of air and product are constant for small changes in time.

The first assumption relating to volume shrinkage does not hold absolutely in real drying processes. Fortunately, in the case of the concurrent flow dryers, the decrease is not substantial because seldom are more than 6 to 8 points of moisture removed from the corn in on pass and the corresponding volume shrinkage is small (about 3 - 5%). Assumptions 2 through 6 apply to conditions which actually exist in practically all grain dryers (Bakker - Arkema et al., 1974).

The fluidized bed model is much less complex in that only the thin layer equation and one additional differential equation must be solved. However, the thin layer equation takes on a different form because the product temperature ranges from 90°F to 160°F in the fluidized bed dryer as compared to temperatures between 120°F and over 200°F in the concurrent dryer. The thin layer equation for the fluidized bed model is

$$\frac{dM}{dt} = a\,(M - Me)^b \qquad (4.29)$$

where a and b are parameters (Troeger and Hukill, 1971).

An energy balance on the grain gives

$$\frac{d\theta}{dt} = \frac{ha}{\rho_p c_p + \rho_p c_w M}\,(T - \theta) = \frac{h_{f_g} + c_v\,(T - \theta)}{c_p + c_w M} \qquad (4.30)$$

where ρ_p is the product density. The corresponding assumptions are

1) The product moisture content and temperature are uniform throughout the drying bed.
2) The air humidity and temperature do not change appreciably within the drying bed.
3) There are no temperature gradients within the grain kernel.
4) Air flow is plug flow.
5) The specific heats of air and product are constant for small changes in time.
6) The bin walls are adiabatic with negligible heat capacity.

Assumptions 1 and 2 imply high air velocities and rapid agitation. These conditions do, indeed, exist since the grain bed is less than 15 cm. thick and air velocities are in excess of 213 m./min. Thus, the residence time of the air within the drying bed is less than .05 seconds.

4.8 Parameter Estimation

Data from both the germination tests and the available lysine tests was plotted and stochiometric mechanisms proposed. All parameter estimation was done through the use of a general purpose program written by Dye and Nicely (1971).

The program provides statistical information so that the goodness of fit to a model can be estimated without any special constraints on the data collection procedure. Also, the program provides for proper weighing of individual data points.

One of two methods can be used in parameter estimation. One method is a matrix method (Wentworth, 1965) modified to include iteration steps (Pitha and Jones, 1966). This method provides an estimate of the variance-covariance matrix, estimates of standard errors of the parameters and multiple correlation coefficients. The second method (Powell, 1965) converges less rapidly in many cases and provides no statistical information upon convergence; however, initial parameter estimates need not be as good. The method of Powell (1965) was used in preliminary work to find good estimates and then the first method was used to converge more precisely and to give statistics for estimation of goodness of fit.

4.9 Numerical Solution of Differential Equations

Two basic numerical methods were used for the solution of differential equations during parameter estimation and modeling of the various drying processes studied -- the fourth-order Runge-Kutta method

(Carnahan et al., 1969) and the Adams-Moulton method (Hamming, 1971) with a Runge-Kutta starter. Step size was fixed during the Runge-Kutta solution. Whereas, step size was varied according to the estimate of the truncation error in the case of the Adams-Moulton method.

V. RESULTS

The models were successfully fit to the experimental data; however, the region in which nonenzymatic browning occurred was outside of the temperature moisture region of most drying processes. Laboratory drying could not be conducted in these temperature regions without causing severe damage to the product. Actual and modeled germination results were not in agreement. The most probable factor which might account for this difference is the existance of temperature gradients during the early stages of the drying process.

5.1 Convective Heat Transfer to TDT Cans

An averaged, lumped-parameter, convective-heat-transfer constant (see equation 4.5) of 0.027 hr^{-1} was estimated from the water-bath heating data (see table 5.1). This corresponds to the time needed for temperature gradients to disappear as measured by Pabis and Henderson (1962). Since temperature gradients disappear as the product reaches constant temperature, there is some indication that the heating rate in the can and thus, the temperature gradients were not much different from those encountered during a drying process.

A considerable amount of difficulty was experienced in attempting to measure temperature histories in TDT cans in the water bath because of large pressure differentials created during heating and cooling. The epoxy resin sealant would fail frequently allowing water vapor to escape in the latter stages of heating and allowing water to be drawn

Table 5.1 Calculated Lumped-Parameter Heat Transfer Time Constants of Corn in TDT cans.

Method of Heating or cooling	Maximum Temperature °C	Moisture Content % wb	Time Constant hrs.
water bath heating	54.4	28	.0267564
	60.0	24	.0252851
	65.5	20	.0301998
	65.5	16	.0265016
	76.7	20	.0379020
	76.7	14	.0152471
		average	.0269820
		standard deviation	.0073549
retort heating	121.1	20	.0210553
	126.7	20	.0216579
	126.7	14	.0134895
	132.2	20	.0163658
	143.3	20	.0141019
	148.9	20	.0186380
		average	.0175863
		standard deviation	.0034544
retort cooling	121.1	20	.0113020
	137.8	20	.0138783
	143.3	20	.0134794
	148.9	20	.0133751
		average	.0131000
		standard deviation	.0012100

into the can during cooling. Consequently, product was not germinated from cans which leaked to assure that the heat treatment was at as constant a moisture content as possible.

Retort heating was much quicker because of larger temperature gradients. The average time constant was 0.017 hr^{-1} for heating and 0.013 hr^{-1} for cooling. There were no problems with pressure gradients in the retort.

5.2 Effect of Heat and Moisture on Germination

The germination results show characteristic plots of the survivorship curves of Rosenberg et al. (1973). The general trend is that with increasing moisture the corn germ becomes more susceptible to thermal death until at 28% moisture thermal death rates are close to the simple, characteristic first-order death rates of single celled organisms. The data was successfully fit to the model and the model was attached to two corn drying models -- a concurrent model and a fluidized bed model. In both cases, the thermal death model greatly over-estimated thermal death when compared with experimental results. The success of the two drying models in modeling corn germ temperature is questioned because of the high-temperature, high-moisture, long-time-duration drying history of the corn as it is dried. The residence time distribution of the corn cannot be used to explain differences between experimental and predicted values.

5.2.1 Germination Data

The germination data (listed in Appendix A and plotted in Appendix B), although somewhat scattered, exhibits characteristics of the survivor-

ship curves of Rosenberg et al. (1973) (Figure 3.1). Both the first-order rate effect and the power law effect are evident, especially in Figures B.3, B.4, B.5, and B.6. The power law effect is manifested in a low death rate at initial times. At 20% moisture and 140°F (60°C) there is no significant decrease in viability until after 50 minutes. At the same moisture and 154°F (67.7°C), there is no signficant decrease in viability until after 10 minutes (see Figure B.4). The first-order rate effect can be seen most explicitly at 24% moisture and 140°F (60°C) from 20 minutes to 60 minutes (see Figure B.5). Other less explicity first-order tendencies are found in the treatment at 17% moisture and 160°F (71.1°C) (Figure B.3), at 20% moisture and 154°F (67.7°C) of (Figure B.4), and at 28% moisture and temperatures of 141°F and 145°F (Figure B.6).

5.2.2 Germination Test Variance

Results of germination tests performed on control samples with the overall mean and pooled variance are given in Table 5.2. All control samples were tested for germination approximately one month after their moisture contents had been adjusted and they had been enclosed in the TDT cans. Effects of the storage moisture or time on viability were not discernable for the period of time during which the control samples were stored; however, the effects of storage time at various moistures on the resistance of the germ to thermal death was not investigated.

5.2.3 The Effect of Heat Treatment Variance on Germination

It was not practical to replicate all of the heat treatments; however, variance reduction by pairing of replicated tests was used to

Table 5.2 Germination Tests -- mean, variance and pooled variance.

Moisture Content %	Germination %	Variance	Standard Deviation	df
14	91.0	15.6	3.95	5
16	92.0	0.0	0.00	0
17	92.5	40.5	6.36	1
20	91.5	60.5	7.78	1
24	94.0	18.0	4.25	1
28	92.5	11.0	3.32	3

overall average	92.0
pooled variance	19.17
standard deviation	4.38

estimate the variance of heat treatments through their effect on germination. Table 5.3 lists the specific test conditions replicated and the differences between each pair of replicates. The estimated standard deviation produced by the heat treatment and, thus, the confidence interval of the measurement is twice that of the control samples.

5.2.4 Parameter Values of the Germination Model

Parameter values for the germination model as estimated by the Runge-Kutta method and the Adams-Moulton method (see Section 4.9) are given in Table 5.4. Plots of the experimental data versus the model at various moisture contents, temperatures and times are given in Appendix C. Low temperature plots of the models are given in Appendix D and high temperature plots of the models are given in Appendix E. A complete analysis was performed using the Runge-Kutta numerical solution with fixed step size. But because of computer costs, only one of the Adam-Moulton predictor corrector solutions with variable step size was followed to convergence. Only 6 to 7 iterations were performed on 4 of the remaining 5 moisture levels.

The general trend in all three estimated parameters was that with increasing moisture content the parameter value increased until at the high moisture levels the increase in parameter values is smaller (Table 5.4). There are two possible causes for this trend. The most apparent, is the fact that with increasing moisture the viability of the corn germ is more sensitive to heat and, thus, the temperature and time ranges of the heat treatments tend to shift. A contributing factor is that the temperature range was changed with moisture content. Low moisture corn was heated for longer times and at higher temperatures than high moisture

Table 5.3 Variability In Heat Treatment Replication on Viability as Determined by Germination.

Moisture Content % w.b.	Temperature °C	Time Min.	Treatment Difference % Germination
17	71.1	20	2
17	71.1	15	8
17	71.1	10	16
17	76.7	5	4
17	82.2	4	0
20	60.0	80	8
20	72.2	7	12
20	77.2	6	2
20	77.2	5	36
20	77.2	4	4
24	65.6	5	4

Variance	85.4545
Standard Deviation	9.2442
Degrees of Freedom	11

Table 5.4 Germination Model

G = Germination, %

Table 5.4 Germination Model

$$\frac{dG}{dt} = A * G * t^n$$

$$A = K * \frac{k*T}{h} * \exp(S/R) * \exp(-H/R*T)$$

$$S = H/329\ k\ -\ 64.9\ \text{cal./mole}^{\circ}\text{K}$$

G = Germination, %

t = time, hours

T = Temperature, $^{\circ}$K

Moist. %wb	Method	$K * \frac{k}{h}$	Standard Deviation	H	Standard Deviation	n	Standard Deviation	Sum of Residuals Squared	df
14	RK	.456428E+09	.832E+09	.130684E+06	.433E+05	.649167	.778	.826268E+04	22
	PD	.346783E+09	--	.146190E+06	--	1.031890	--	.232965E+04	
16	RK	.221269E+10	.263E+10	.130242E+06	.346E+05	.550200	.627	.464242E+04	17
	PD	.216857E+10	.245E+10	.130732E+06	.311E+05	.542126	.506	.478521E+04	
17	RK	.244122E+10	.160E+10	.140436E+06	.202E+05	1.126450	.423	.411738E+04	31
	PD	.344660E+10	--	.134561E+06	--	1.215370	--	.224408E+04	
20	RK	.445386E+10	.928E+09	.201415E+06	.821E+04	2.044600	.172	.204076E+04	35
	PD	.553937E+10	--	.189364E+06	--	1.93430	--	.157689E+04	
24	RK	.185359E+12	.375E+11	.181064E+06	.167E+05	1.391760	.308	.657522E+03	20
	PD	.190885E+12	--	.180598E+06	--	1.446860	--	.643276E+03	
28	RK	.163097E+12	.259E+11	.116667E+06	.803E+04	0.0	--	.436060E+04	25

K = transmission coefficient

k = Bolzmann's constant, 1.3805E-23 J/$^{\circ}$K

h = Planck's constant, 6.6256E-34 J*s

RK = Fourth-order Runge-Kutta method

PD = Adams-Moulton predictor corrector method

R = universal gas constant, 1.987 cal/$^{\circ}$K mole

S = activation entropy, cal./mole $^{\circ}$K

H = activation enthalpy, cal./mole $^{\circ}$K

corn (see Appendix B). There is the possibility that this markedly influenced the final parameter value. Another possible cause is that some other parameter, not linearly related to moisture content, such as water activity may have a more linear effect on the sensitivity of corn germ viability to heat. For example, this may be related to the effect of different moisture levels on the activation and rate of protein denaturation. More investigations into the function of water in protein denaturation and enzyme deactivation may explain these observed trends in parameter values.

The standard deviations of the parameter estimates decrease as the number of data points increase. Most of the standard deviations are very large in comparison with the parameter values, and although these values are useful in preliminary work, more data is needed in order to ascertain more precise parameter values; however, it is encouraging that the standard deviation is small for the activation enthalpy and power factor at 20% moisture with only 35 data points. This indicates that the model does fit large numbers of data points, and it is also a good indication that the model is adequate for describing the thermal death of a corn germ.

A comparison of the parameter values obtained by the Runge-Kutta method and the Adams-Moulton method shows that the estimate of the frequency factor ($K_o * \frac{k}{h}$) is lower in the case of the Adams-Moulton method for 14% and 16% moisture and higher for moistures of 17% to 24%. The reverse is true for the activation enthalpy and with the exception of the 24% moisture level. The differences in power factor are mixed; however, the same general trend in parameter value is followed as related

to moisture for each method of numerical solution. In the range of moisture from 17% to 20%, the Runge-Kutta method gave parameter values which produce death rate estimates below those estimated using parameter values from the Adams-Moulton numerical solution. As will be seen in Section 5.2.6, this is the range of moisture in which the model with Runge-Kutta parameter values was tested and over-estimated death rates.

5.2.5 Comparison of Model and Experimental Data

The model (Equation 3.20) was used successfully to fit experimental data over the complete range of moisture and temperature investigated (Appendix C). The model fit data gathered for long-term, low-temperature data best; however, for short-term, high-temperature data, there was a tendency for the model to under-estimate initial viability and to over-estimate the lower viabilities. The probable reason for better estimates at low temperature is that with longer times, there was a tendency to collect more data, and thus, the model was fit best in the region of the most data points. The probable reasons for a poorer fit in the higher temperature range for each moisture content are the rapidity of thermal death at high temperatures (steep slopes) and the fact the mild heat treatments (short-time) tend to break the dormancy of seeds. Rapid thermal death requires more precise experimental control. The dormancy effect is not included in the derivation of the thermal death model and, thus, this effect alone will introduce error into high-temperature, short-time portion of the model. This tendency

would also be produced if the rate of thermal death were sensitive to the rate of heating. This has not been the case with single celled organisms.

5.2.6 Moisture and Temperature Effects on Corn Germ Survivorship

Graphs of the germination models of Table 5.4 are presented in Appendixes D and E. Long-time, low-temperature plots at each moisture content are presented in Appendix D while short-time, high-temperature plots at 14%-20% moisture are plotted in Appendix E. The general trend is that with increasing moisture the first order rate increases at a given temperature. Also, the distortion of the first order reaction rate is evident in all plots except at 28% where the effect was not present and the power law factor had to be forced to zero.

The high temperature plots of Appendix E demonstrate that at lower moistures, where the corn germ is most resistant to thermal damage, death of the germ occurs rapidly only at very high temperatures -- 175-180°F (79.4-82.2°C). This is consistent with observations of most investigators (Robbins and Petsch, 1932 and Watson and Hiraton, 1962).

5.2.7 The Germination Model as Attached to the Drying Models

The germination model failed to predict the experimentally measured decreases in germination when attached to the concurrent and fluidized bed drying models as described previously (see Section 4.5 and 4.6). Complete death occurred within 6 minutes of drying time in the fluidized

bed drying model (Figure 5.5) and within 36 seconds of drying time in the concurrent drying model (Figure 5.6). Possible reasons for these large discrepancies include the constant moisture method of determining the model parameters, the actual existence of a temperature gradients in the kernel during the early part of the drying process, the possible existence of moisture gradients and the residence time distribution of the grain in the dryer. The most probable cause is the actual existence of temperature gradients in the kernel during the early portions of the drying process; although, the validity of constant-moisture heat treatments cannot be proven.

There is little doubt that the heat treatment received in a TDT can differs from that received during drying in a number of respects. The air to grain ratio is very small in a TDT can as compared to a drying process. This has implications in a number of areas. The air in the can quickly becomes saturated so that there is no evaporative cooling taking place anywhere within the kernels. There is a limited amount of oxygen in the TDT can and a possible build-up of volatiles during the heat treatment which may influence the thermal death rate. On the positive side, the absence of moisture evaporation from the kernels reduces the time needed for the temperature gradients to disappear and the slight amount of moisture lost by the kernel places it on the desorption moisture isotherms.

The existence of temperature gradients has been observed by Pabis and Henderson (1962). These gradients are largest during the first 3 to 5 minutes of the drying process, and this is where the germination

Table 5.5 Fluidized Bed Dryer -- Drying Air Temperature 87.8°C

Moisture Content % d.b.	Grain Temperature °C	Germination %	Drying Time Hr.
25%	17.8	85.00	0.00
24%	68.3	80.50	0.05
24%	77.5	0.00	0.10

Table 5.6 Concurrent Dryer -- Drying Air Temperature 260°C

Moisture Content % d.b.	Grain Temperature °C	Germination %	Drying Time Hr.
19%	4.4	92.00	0.000
19%	75.6	91.90	0.005
19%	109.4	0.00	0.010

model failed in two markedly different drying processes. Two factors which tend to produce temperature gradients are the large air to kernel temperature gradients which exist at the beginning of a process and the differences in observed heats of desorption. One would expect the air to kernel temperature differences to be the dominant factors because much heating and little drying occurs in the initial parts of both drying processes.

Moisture gradients could be of the order of magnitude of 5 to 10% (see Figure 3.5), with the germ at the lowest moisture content. However, in the actual drying process, germ moisture may only be 2 or 3 points different than a given germ moisture during the TDT heat treatment at the same average kernel moisture content. This will not produce as severe a discrepancy as over-estimating germ temperature by $5^{o}F$ ($2.8^{o}C$) as can be seen from Table 5.7.

The grain residence-time distribution was suspected as being responsible for the presence of germinating seed in corn dried by the concurrent dryer. However, a plot of input versus output distribution of the grain (see Figure 5.1) indicated no marked departures of the output distribution from the input distribution. The comparable thermal death results with the fluidized bed model further ruled out this possibility. Thus, since germ death is most sensitive to relatively small temperature changes and since the drying models estimate average kernel temperature of $171.5^{o}F$ ($77.5^{o}C$) and $228.9^{o}F$ ($109.4^{o}C$) respectively for fluidized bed (see Table 5.5) and concurrent (see Table 5.6) dryers one would suspect these average temperatures as being inadequate especially when looking at the relative rates of thermal death of the germ in Table 5.7.

TABLE 5.7 DEATH RATE (%/MIN.) AT 1 MINUTE OF DRYING TIME

	Moisture Content % w.b.					
	14	16	17	20	24	28
TEMPERATURE (°C)						
57.2						0.01
60.0						0.05
62.8					0.01	0.22
65.6					0.05	0.93
68.3		0.01			0.51	3.83
71.1	0.01	0.05	0.01	0.30	4.46	15.47
73.9	0.04	0.25	0.06	0.31	37.45	61.17
76.7	0.16	1.15	0.03	3.18	304.22	236.56
79.4	0.73	5.08	1.49	30.65	2391.36	895.70
82.2	3.17	21.95	7.23	292.86		
85.0	13.44	92.53	34.11	2701.73		
87.8	55.74	381.81	157.18			
90.6	226.17	1541.87	707.58			
93.3	898.42					

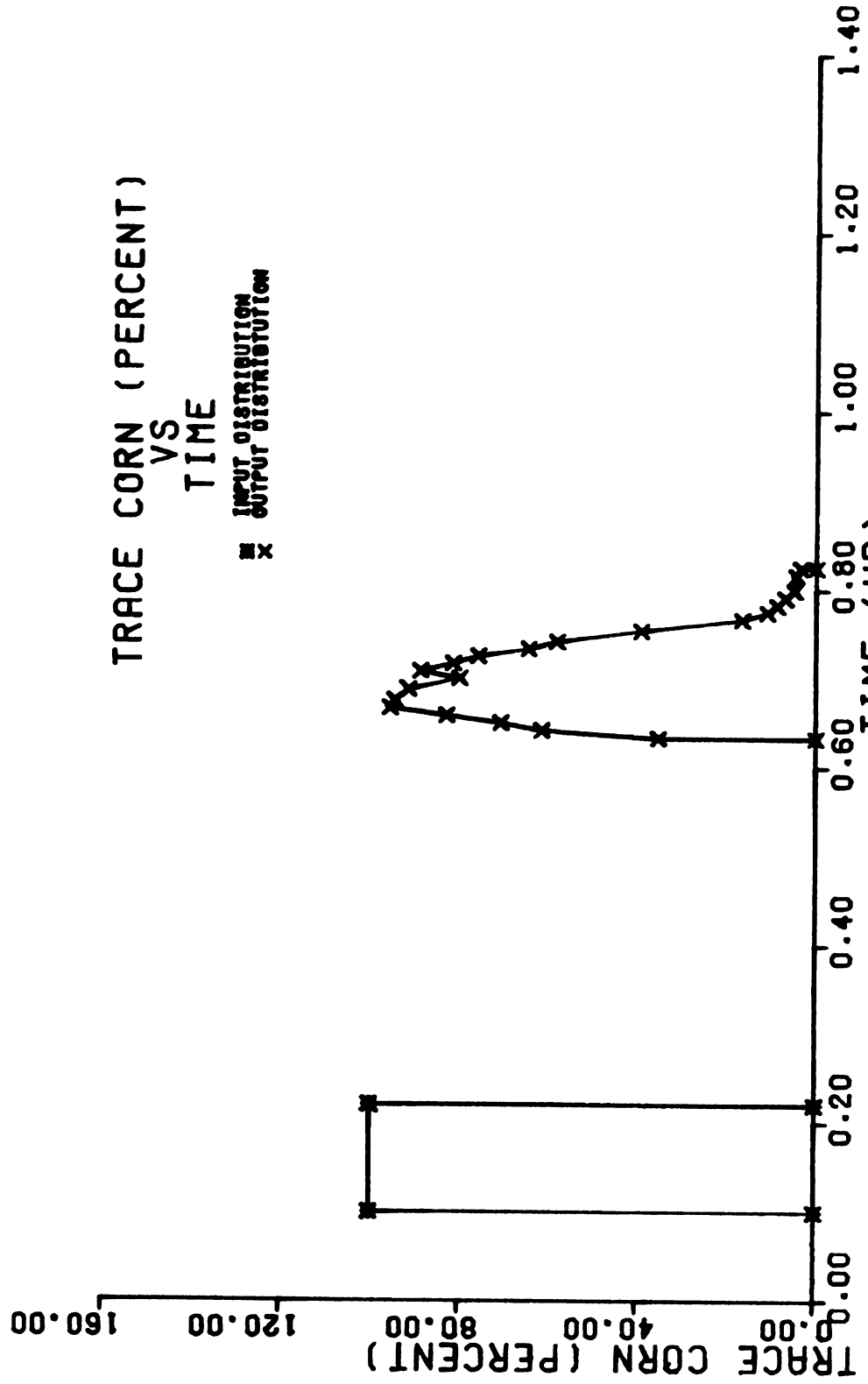

Figure 5.1 Residence Distribution of Corn in the Concurrent Dryer -- Bed Length of 2 Ft. (0.61 m.).

Complete death at 170°F (76.7°C) and 24% average moisture content occurs in less than 20 seconds in the case of the fluidized bed dryer and almost instantaneously 230°F (110°C) and 19% average moisture content in the case of the concurrent dryer. These rates are not extraordinarily high according to people associated with the grain industry and biochemists familiar with the thermal death of seed germ.

5.3 Effect of Heat on Lysine Availability

The available lysine data at 270°F (132.2°C) gives a plot characteristic of the consecutive first-order reaction mechanism (see Figure 3.4); however, data plotted at higher temperatures does not exhibit the initial increase in AVL attributed to protein denaturation. It is possible that the sampling rate is too low to detect increased lysine availability caused by protein denaturation at higher temperatures since the reaction is very temperature-sensitive. Significant decreases in AVL were only found when heating was severe enough to cause marked darkening of the kernels and when there was an associated "roasted" smell which has been reported in conjunction with other non-enzymatic browning reactions by previous investigators. The temperatures at which this occurred were beyond those of convective-air corn dryers.

5.3.1 Available Lysine Data

The available lysine data (Figures 5.2-5.5 and Appendix F), although scattered for long heat-treatment times, does exhibit the characteristics of the consecutive first-order reaction mechanism (see

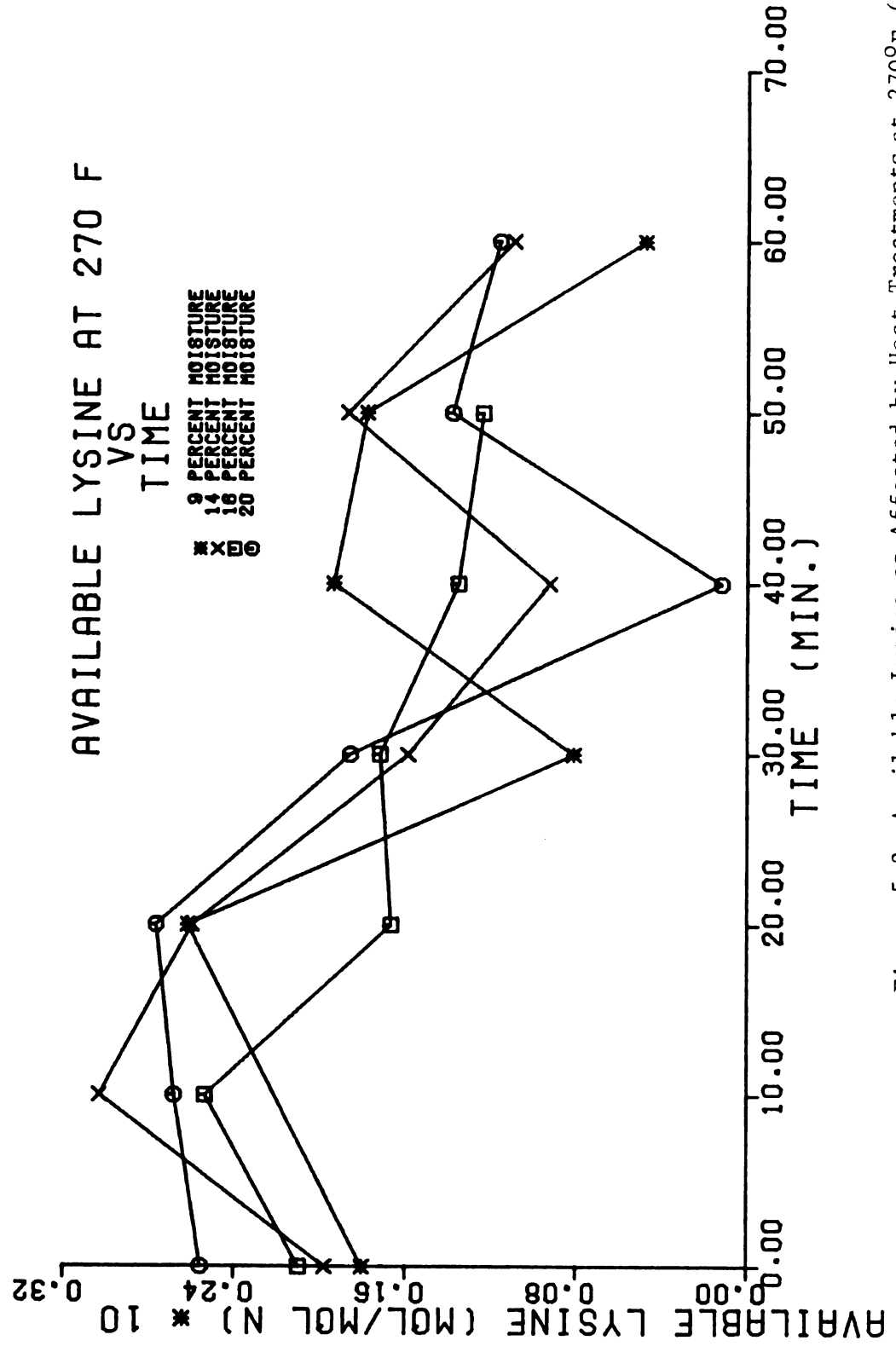

Figure 5.2 Available Lysine as Affected by Heat Treatments at 270°F (132.2°C) for Various Times at Various Moisture Contents.

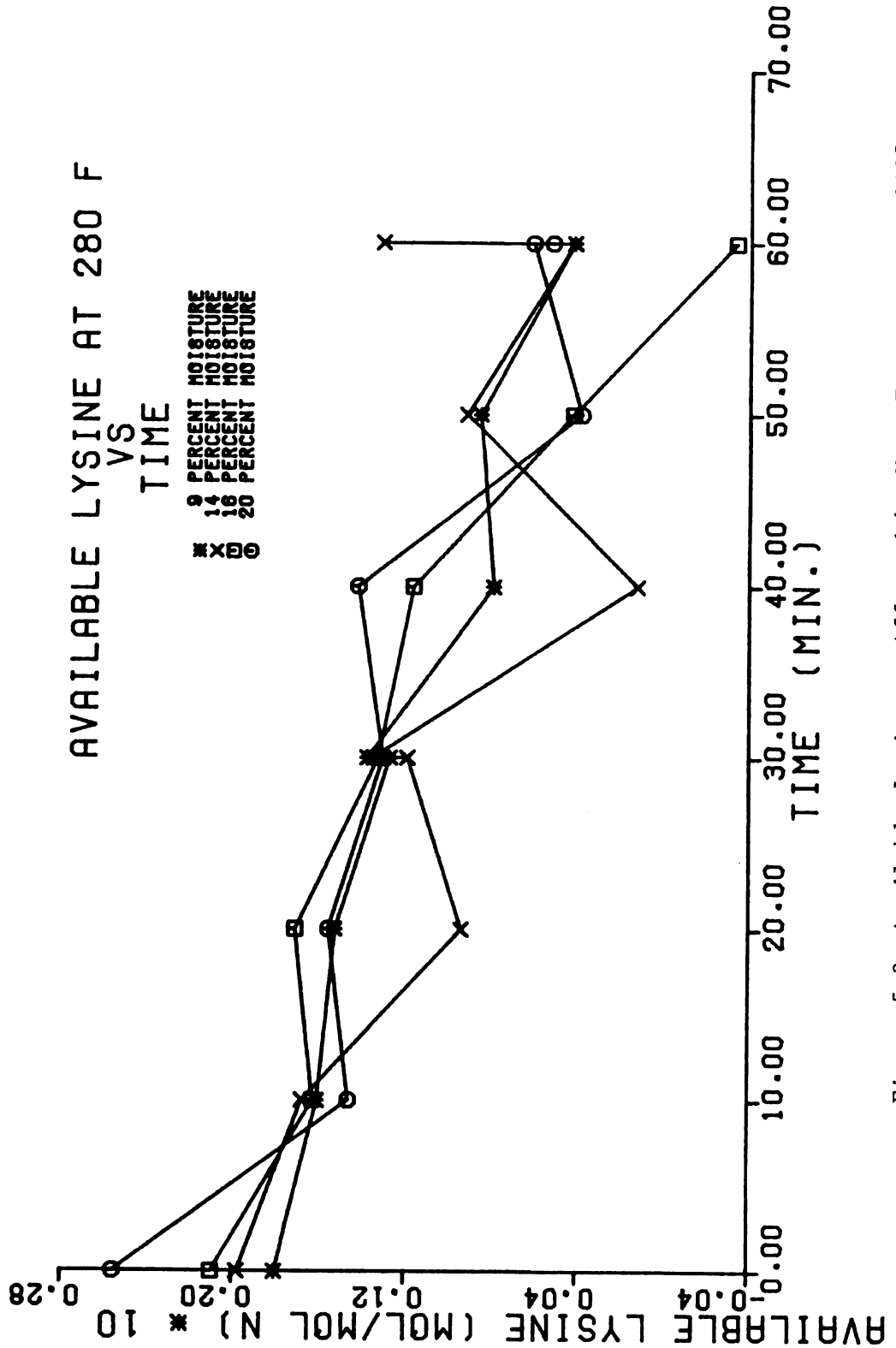

Figure 5.3 Available Lysine as Affected by Heat Treatments at 280°F (137.8°C) for Various Times at Various Moisture Contents.

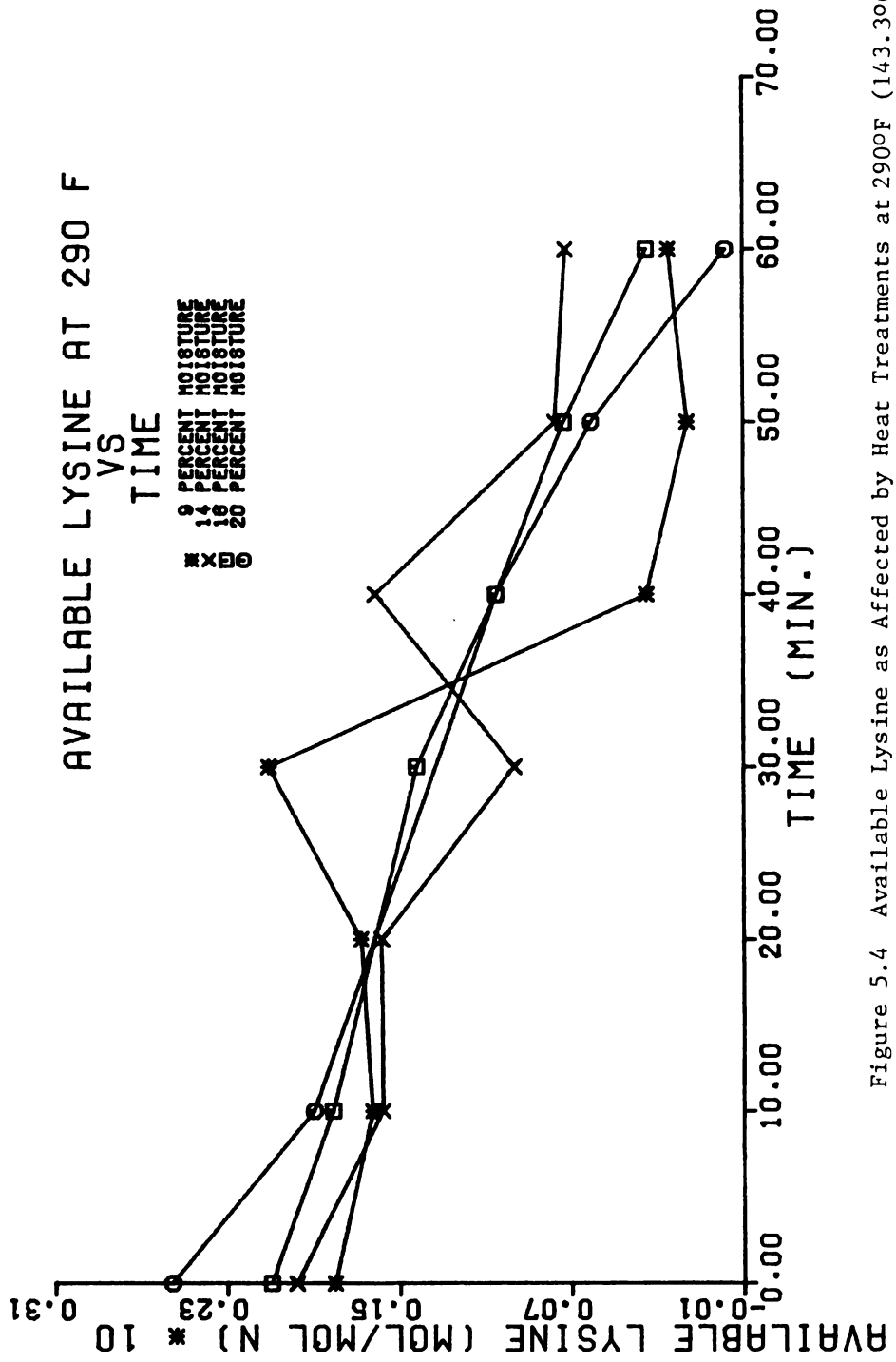

Figure 5.4 Available Lysine as Affected by Heat Treatments at 290°F (143.3°C) for Various Times at Various Moisture Contents.

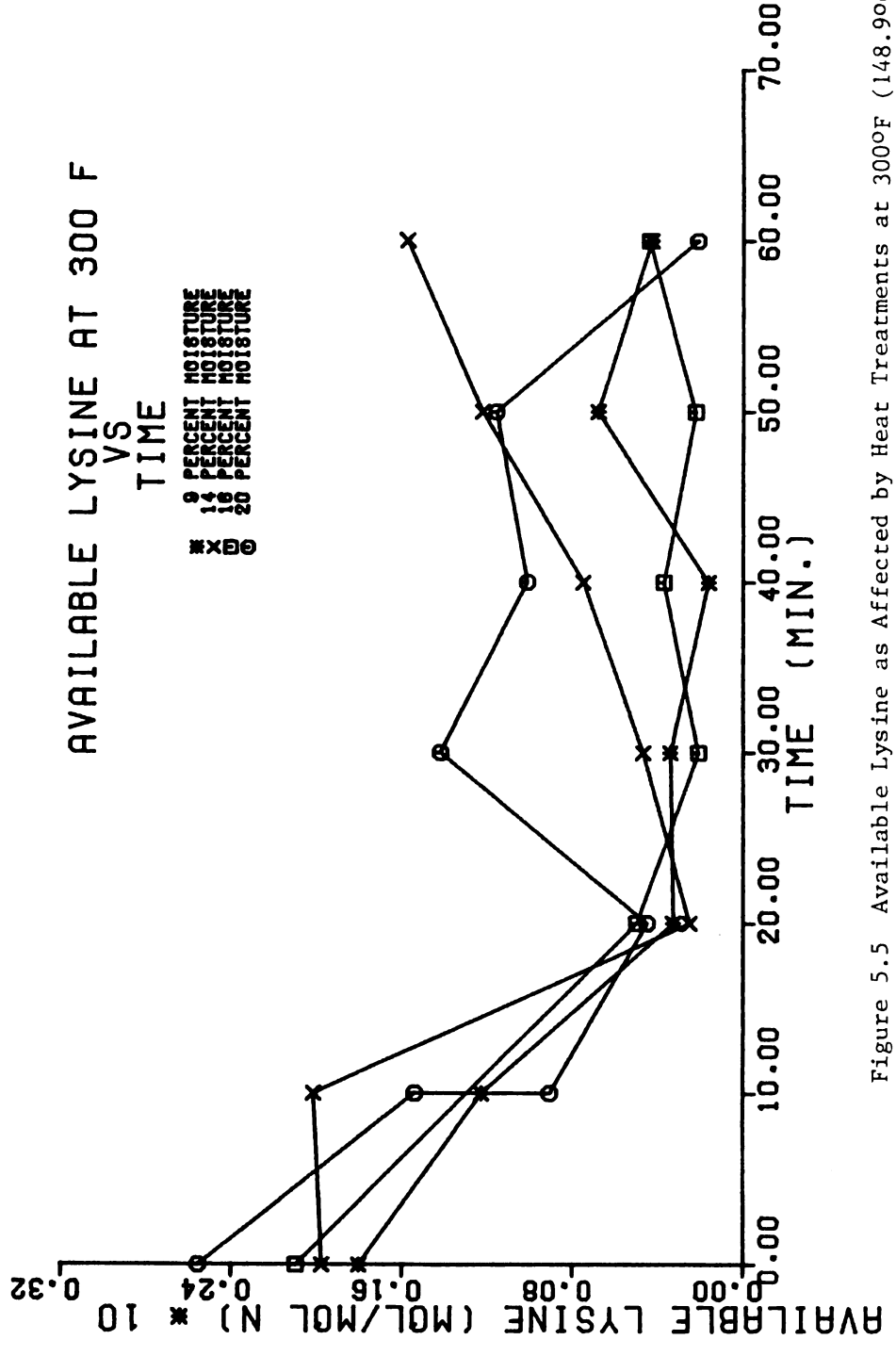

Figure 5.5 Available Lysine as Affected by Heat Treatments at 300°F (148.9°C) for Various Times at Various Moisture Contents.

Equation 3.31 and Figure 3.3). At 270°F (132.2°C) the percent initial increase in available lysine (AVL) is highest at 9% w.b. moisture content and decreases with increasing moisture content and time for the 10 and 20 minute heat treatments. This contrasts with the data reported by Mühlbauer and Christ (1974) in that they were not able to detect the initial increase in available lysine. In using ion exchange liquid chromatography they measured the total concentration of lysine -- that which was masked by the protein matrix and that which was nutritionally available (see equation 3.59). Whereas, the TNBS method tends to detect only the amount of lysine which is nutritionally available. Thus, the TNBS data is indicative of the effect of high temperature drying on the nutritional value of corn. Moisture content does not markedly effect the browning reaction in corn so that data at higher temperatures and longer heating times compare well with the findings of Mühlbauer and Christ (1974)

At higher temperatures, either the rate of decrease in AVL masks the effect of protein denaturation in increasing AVL or, more likely, the frequency at which data was developed during the process is not high enough to detect the initial, short-duration increase in AVL. The physical limitations of the method of investigation prevented the gathering of data at high sampling rates, especially during the first 10 minutes of the process. It took approximately 3 minutes for the product to reach processing temperature, leaving, at most, a 7-minute time interval for gathering data. Each data point was obtained by heating the product to temperature for a desired time, cooling the product at the end of the processing time in order to stop the process and, finally, performing a 3-hour procedure in order to analyze for AVL. Although the processing time was precisely controlled, the large number of chemical analyses

required and the time required for heat treatment and chemical analysis prohibited high sampling rates at each processing temperature.

As can be seen from the data as plotted in Figures 5.2 - 5.5, the time-temperature treatment at which there is a significant decrease in AVL is beyond that normally experienced by corn during drying. Corn seldom reaches temperatures above 200°F (93.3°C) for more than one hour and very seldom experiences temperatures as high as 260°F (126.6°C). Furthermore, only samples which showed physical evidence of severe heat damage (browning) and exhibited a strong, roasted-nut odor were found to contain less available lysine than the control samples. Thus, the feasibility of a more intensive investigation is very questionable when considering browning reactions that may occur during the drying process.

5.3.2 Available Lysine Analysis

The standard deviation of single determinations are of the same order of magnitude as the concentration reading and increase as temperature and heating time increase (see Figure 5.6 and appendix F.1). This makes multiple determinations on each sample mandatory which is in concurrence with the recommendation of Posati et al. (1972). This is a major disadvantage of the TNBS method; however, with only 3 blanks and 3 samples precision was increased adequately in order to obtain proper resolution to the first half-life reduction in AVL. Any parameter estimation performed using results from the test must take into consideration the relationship between the standard deviation of the TNBS method and the concentration determination.

It is interesting in comparing the analysis of the control samples that as moisture content decreases, the amount of AVL per mole of nitrogen

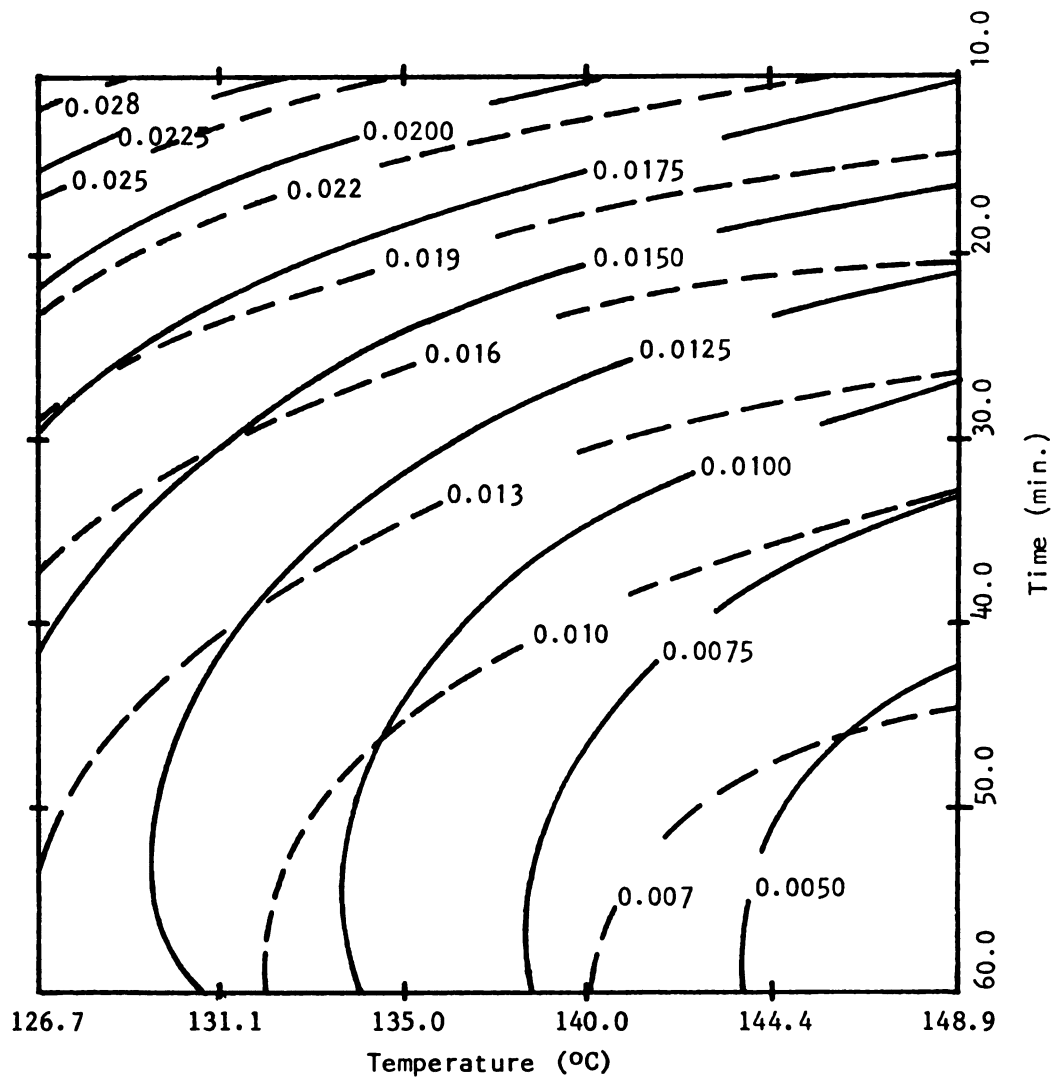

Figure 5.6 Available lysine and the Standard Deviation of a single TNBS Determination as Affected by Temperature and Duration of Heat Treatment at 9% Moisture.

detected also decreases. This is in concurrence with observations of Posati et al. (1972). As sample size increases, the amount of AVL detected by the TNBS method decreases. Thus, since there is more dry matter and, therefore, more proteinaceous material as moisture content decreases (the effective sample size is larger) it is expected that the amount of AVL detected will decrease. It is also interesting to note that the levels and the decrease in AVL reported by Wall et al. (1975) in corn dried at a maximum product temperature of 219.2°F (104°C) are almost identical to those of the control samples at high and low moisture. Wall et al. (1975) may be observing the same effect of decreased moisture content causing decreased AVL even though he used the methyl acrylate method. This is not unlikely since the reaction conditions for the methyl acrylate method and the TNBS method are comparable.

5.3.3 Heat Treatment Variance Effect on Available Lysine

Variance reduction by pairing of replicated tests was used to estimate the variance of heat treatments through its effect on available lysine reduction. The estimated standard deviation produced by heat treatment (see table 5.8) is of the same order of magnitude as that of the control-sample determination.

5.3.4 The Available Lysine Model

As mentioned previously, it was not practical to develop the data necessary for the estimation of parameters in the first of the two con-

Table 5.8 Variability In Heat Treatment Replication on Available Lysine Determinations.

Moisture	Temperature °C	Time (Min.)	AVL	(mol/mol N)	
9	137.8	30	.01374	.01270	
14	121.1	60	.01716	.01664	
14	126.7	60	.02205	.01279	.004763
14	137.8	60	.01308	.004195	
14	137.8	30	.01349	.01190	
17	137.8	60	.005196	.007437	

Pooled variance = .3393E-5

Standard Deviation = .5825E-3

Degrees of freedom = 7

secutive first-order reaction mechanisms of the available lysine model. Parameter values for the second reaction (sugar-amine condensation) are given in Table 5.9.

The rate constant is not markedly sensitive to temperature change except when the temperature is increased from 290°F to 300°F (143.3°C to 160°C). This may be evidence that the reaction system shifts markedly or, more likely, that another reaction (possibly the direct destruction of lysine) is activated at these extreme temperatures. Using the Arrhenius relationship for the data taken at 9% moisture shows that the AVL reaction is relatively insensitive to temperature changes in comparison to germination. The activation energy is only 18,000 cal. for AVL as compared to 130,000-200,000 cal. in the case of viability. Also, the reaction is relatively slow at normal drying product temperatures and is of little consequence unless product temperatures are reached which would produce visible, severe heat damage to the kernels.

Table 5.10 compares some calculated rates with rates published for soybeans. The rates predicted by the first order portion of the AVL model for corn are much higher, quite possibly, because of published data for soybeans was only fit to a simple first order model and did not take the effects of protein denaturation into account; however, since the reported rates are from soybeans, no definitive conclusions can be drawn.

A plot of model "B" (see Table 5.9) based only on the 9% moisture data is presented in Figure 5.7. In contrast to the germination model there is very little variation in reaction rate with variation in temperature. Also, the reaction is relatively slow as compared to the germination model and takes place at much higher temperatures which,

Table 5.9 Available Lysine Model

$$\frac{dC_A}{dt} = K * C_A$$

$$K = K_o * \exp(-E/RT)$$

Test No.	Moisture % wb	Temperature °C	Temperature K	K_1 hr^{-1}	Standard Deviation	Sum of Residuals Squared	Degrees of Freedom
1	9,14,16,&20	121.1	394.1	.24655	.389	.348260E-04	6
2	9,14,16,&20	126.7	399.7	1.4056	.190	.184277E-03	7
3	9,14,16,&20	132.2	405.2	4.4056	1.02	.892465E-03	20
4	9,14,16,&20	137.8	410.8	1.5338	.218	.243825E-03	26
5	9,14,16,&20	143.3	416.3	1.5314	.280	.259033E-03	20
6	9,14,16,&20	148.9	421.9	19.022	4.20	.300788E-01	22

A
K_o = .740207E+10 Standard Deviation = .143E+12 Degrees of Freedom = 4
E = 18012.4 Standard Deviation = 16700.

B
For 9% Moisture Only
K_o = .59933E+10 Standard Deviation = .310E+11 Degrees of Freedom = 28
E = 18012.4 Standard Deviation = 4110.
Sum of Residuals Squared = .686048E-03

For 14,16,20% Moisture -- Variances too high for parameter estimation

Table 5.10 Comparison of Predicted First-Order-Rate Constants of Corn With Published Data of Soybeans.

Temperature °C	Calculated Rate Corn	Reported Rate Soybeans
100.0	.145	.02*
115.0	.376	.046*
125.6	.704	.166*

* Labuza, 1972

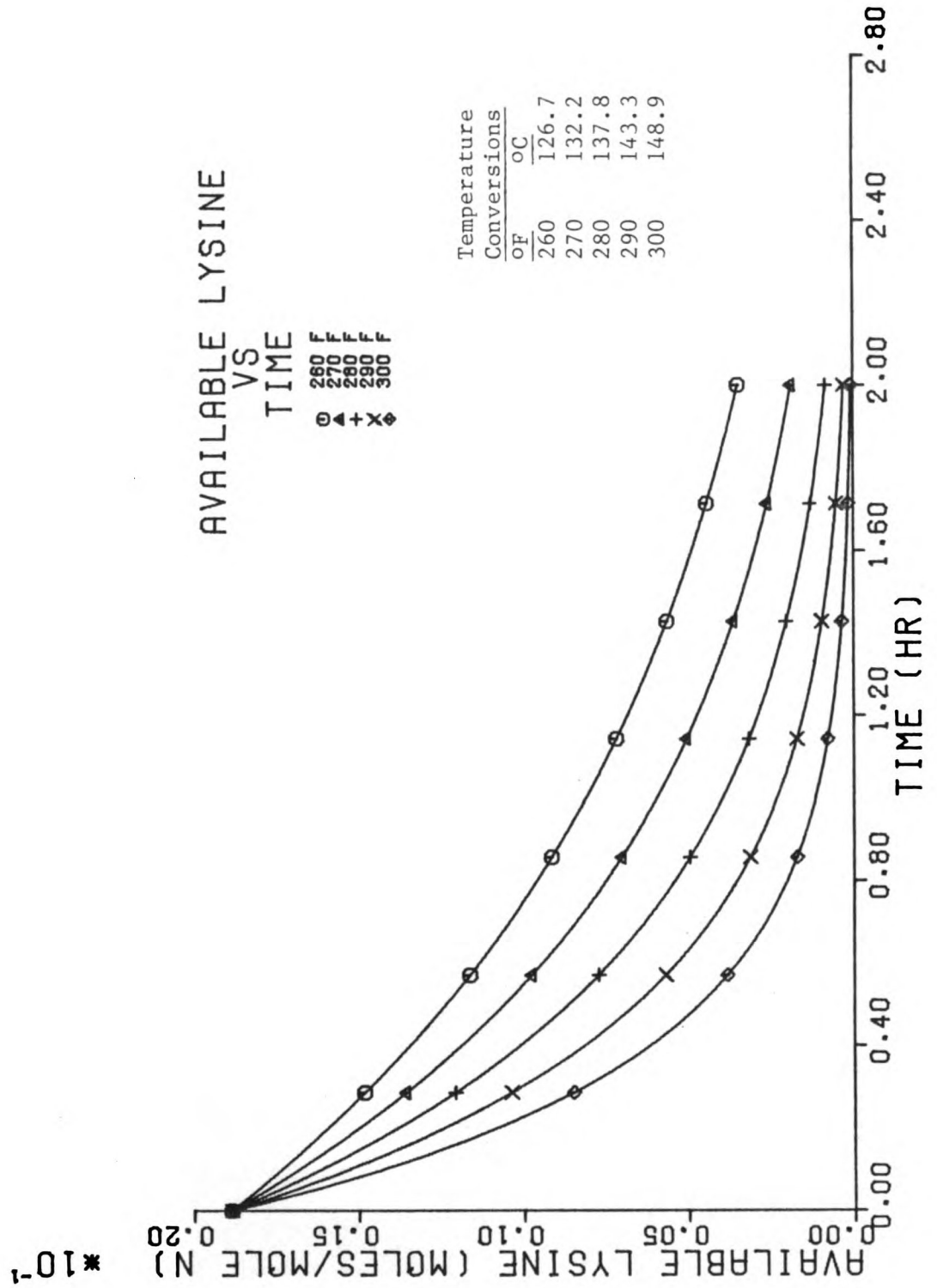

Figure 5.7 First Order Model for Available Lysine at 9% Moisture Content in Whole Kernel Corn

as mentioned previously, are above the product temperatures normally encountered in high-temperature drying.

5.3.5 Comparison of Model and Experimental Data

A comparison of the first order portion of the AVL models 3.6 with the experimental data is found in appendix G. For the most part, the first-order model was successful in describing the data; however, at 300°F (148.8°C) the data does not fit the first-order model. This suggests, as mentioned before, that the dominant mechanism may have shifted.

VI. CONCLUSIONS

This investigation was the first attempt to use TDT cans to give a known temperature-moisture heat treatment to corn and to develop corn quality models. While this method was useful, some limitations were encountered. The TDT heat treatment may be more severe than a drying treatment at the same average product temperature and moisture. The difference between these constant moisture heat treatments and drying treatments must be accounted for in order to use the TDT method of investigation to develop certain models which predict grain quality deterioration. The existence of temperature gradients is the most likely cause.

The survivorship model was successfully fit to the germination data. Since the survivorship model is markedly different than other chemical modes of deterioration and its range of temperature and moisture sensitivity is different than other quality indicators, germination is a questionable index of grain quality; however, there is a potential for the use of the model by seed scientists in predicting the effect of age, moisture, and temperature on seed viability and vigor during storage and drying.

The simple first or second order reaction models commonly used in food systems are not adequate for describing the effect of heat and moisture on lysine availability in whole corn. The effect of protein denaturation on increasing lysine availability will be of most interest with respect to the drying process. Sugar-amine condensation (The Maillard reaction) occurs in a temperature range outside of the

temperature range normally experienced by the product in high-temperature corn drying. This indicates that drying temperature limitations are not necessary to preserve the nutritional quality of corn protein. Corn must be severely heat damaged before nutritional quality is effected.

The disulfide bridge in protein is directly related to the physiochemical behavior of corn flour obtained by dry-milling. The disulfide bond is also key to the release of starch by the wet-milling process. Heat denatures the usually compact configuration of polypeptide chains into greatly entangled flexible chains showing random modes of coiling. The end result in the case of the dry milling process is that characteristics attributed to the normal "slippage" of the disulfide bond such as cold paste viscosity are greatly reduced. This is due to the disorganized nature of the polypeptide chains even though the disulfide bonds are left in tact. In the case of wet-milling, denaturation reduces the solubility of the protein, thus, greatly inhibiting the ability of the SO_2 steeping process to disrupt the disulfide bonds. A study of the effect of heat on the physiochemical properties of corn protein would be useful with regard to the dry-milling process while a study of the effect of heat on the ability of an SO_2 steep to break the disulfide bond would be useful in evaluating the wet-milling quality of corn.

VII. FUTURE WORK

This work has been extensive but not intensive in nature in that it dealt with a large number of aspects of the problem of predicting corn quality after drying. The investigation covered the measurement of two quality attributes, the construction of one model for the effect of heat and moisture on germination, and a more thorough understanding of the effect of heat and moisture on the nutritive value of corn as measured by one chemical attribute. Areas were covered which need a more intensive investigation if grain quality deterioration is to be predicted apriori in the design of any grain drying systems. They range from an investigation of a more complicated drying model, which includes a multi-thin layer model, to more direct methods of determining the nutritional and processing quality of corn.

Most importantly, a search for an index of thermal damage should concentrate on criteria which are directly related to the monetary value of the product as feed, food or raw product for wet or dry-milling, or as a nonfriable product in shipment. Any efforts to use one attribute for any combination of the above will not be successful because all chemical and physical properties deteriorate according to their own characteristic mechanisms and because the rates of deterioration are affected in different characteristic regions of temperature and moisture. This is very evident when comparing germination and available lysine. The former has a relatively low range of temperature sensitivity and a high range of moisture sensitivity as compared to the latter.

Of almost equal importance is the need for slightly more complex drying models. Although drying models give an adequate description of average product temperature and moisture during drying, there is a need for a study of moisture and temperature distributions within specific portions of the kernel (germ, floury endosperm, and horny endosperm) in order to accurately describe the effect of different drying treatments on physiochemical properties.

The value of the germination percentage of corn as a quality indicator is very limited with the exception of the seed industry. The value of using the survivorship model in predicting seed quality to include viability and vigor as effected by drying and storage should be investigated.

A more thorough investigation of the effects of heat on protein denaturation as related to the effect of the SO_2 steep used in the wet milling process is needed. The feasibility of chemically determining the extent of disulfide bonding after steeping should be investigated. A similar investigation of the role of disulfide bonding and protein denaturation on the quality of corn for dry-milling should also be conducted.

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APPENDICES

APPENDIX A

Thermal Effects on Germination

Table A.1 Thermal Effect on Germination

Test No.	Moisture Content	Temperature		Time	Germination
	% wb	°F	°C	min.	%
1	14	150	65.6	110	32
2	14	150	65.6	100	78
3	14	150	65.6	90	50
4	14	150	65.6	80	72
5	14	150	65.6	70	66
6	14	150	65.6	60	70
7	14	160	71.1	30	6
8	14	160	71.1	25	26
9	14	160	71.1	20	50
10	14	160	71.1	15	74
11	14	160	71.1	10	88
12	14	165	73.9	12	34
13	14	165	73.9	10	70
14	14	165	73.9	9	82
15	14	165	73.9	6	86
16	14	165	73.9	4	94
17	14	170	76.7	9	6
18	14	170	76.7	8	38
19	14	170	76.7	7	40
20	14	170	76.7	6	76
21	14	170	76.7	5	92
22	14	170	76.7	4	98
23	14	180	82.2	6	2
24	14	180	82.2	5	46
25	14	180	82.2	4	46
26	16	150	65.6	80	38
27	16	150	65.6	70	5
28	16	150	65.6	60	44
29	16	150	65.6	50	25
30	16	150	65.6	40	72
31	16	150	65.6	30	84
32	16	160	71.1	20	10
33	16	160	71.1	15	36
34	16	160	71.1	10	68

Table A.1 (cont.) Thermal Effect on Germination

Test No.	Moisture Content	Temperature		Time	Germination
	% wb	°F	°C	min.	%
35	16	165	73.9	9	2
36	16	165	73.9	8	40
37	16	165	73.9	7	52
38	16	165	73.9	6	40
39	16	165	73.9	5	74
40	16	170	76.7	8	2
41	16	170	76.7	7	4
42	16	170	76.7	6	32
43	16	170	76.7	5	54
44	16	170	76.7	4	86
45	16	180	82.2	4	50
46	17	150	65.6	60	32
47	17	150	65.6	50	40
48	17	150	65.6	40	42
49	17	150	65.6	30	70
50	17	150	65.6	20	84
51	17	150	65.6	10	96
52	17	151	66.1	60	10
53	17	151	66.1	50	30
54	17	151	66.1	40	46
55	17	151	66.1	30	74
56	17	151	66.1	20	82
57	17	151	66.1	10	94
58	17	160	71.1	25	8
59	17	160	71.1	20	6
60	17	160	71.1	20	4
61	17	160	71.1	15	42
62	17	160	71.1	15	50
63	17	160	71.1	10	88
64	17	160	71.1	10	72
65	17	160	71.1	5	92
66	17	165	73.9	8	22
67	17	165	73.9	7	42
68	17	165	73.9	6	66
69	17	165	73.9	5	88
70	17	165	73.9	4	92

Table A.1 (cont.) Thermal Effect on Germination

Test No.	Moisture Content	Temperature		Time	Germination
	% wb	°F	°C	min.	%
71	17	170	76.7	7	12
72	17	170	76.7	6	20
73	17	170	76.7	5	64
74	17	170	76.7	5	60
75	17	170	76.7	4	88
76	17	180	82.2	4½	14
77	17	180	82.2	4	26
78	17	180	82.2	4	26
79	17	186	85.6	4	14
80	20	140	60.0	130	32
81	20	140	60.0	120	30
82	20	140	60.0	110	42
83	20	140	60.0	100	44
84	20	140	60.0	90	48
85	20	140	60.0	80	72
86	20	140	60.0	80	64
87	20	140	60.0	70	78
88	20	140	60.0	60	78
89	20	140	60.0	50	78
90	20	140	60.0	40	88
91	20	140	60.0	30	90
92	20	154	67.8	20	2
93	20	154	67.8	15	6
94	20	154	67.8	12	76
95	20	154	67.8	10	88
96	20	154	67.8	8	84
97	20	154	67.8	7	90
98	20	154	67.8	6	94
99	20	154	67.8	5	94
100	20	162	72.2	8	6
101	20	162	72.2	7	16
102	20	162	72.2	7	4
103	20	162	72.2	6	44
104	20	162	72.2	5	84
105	20	162	72.2	4	90
106	20	162	72.2	3	100

Table A.1 (cont.) Thermal Effect on Germination

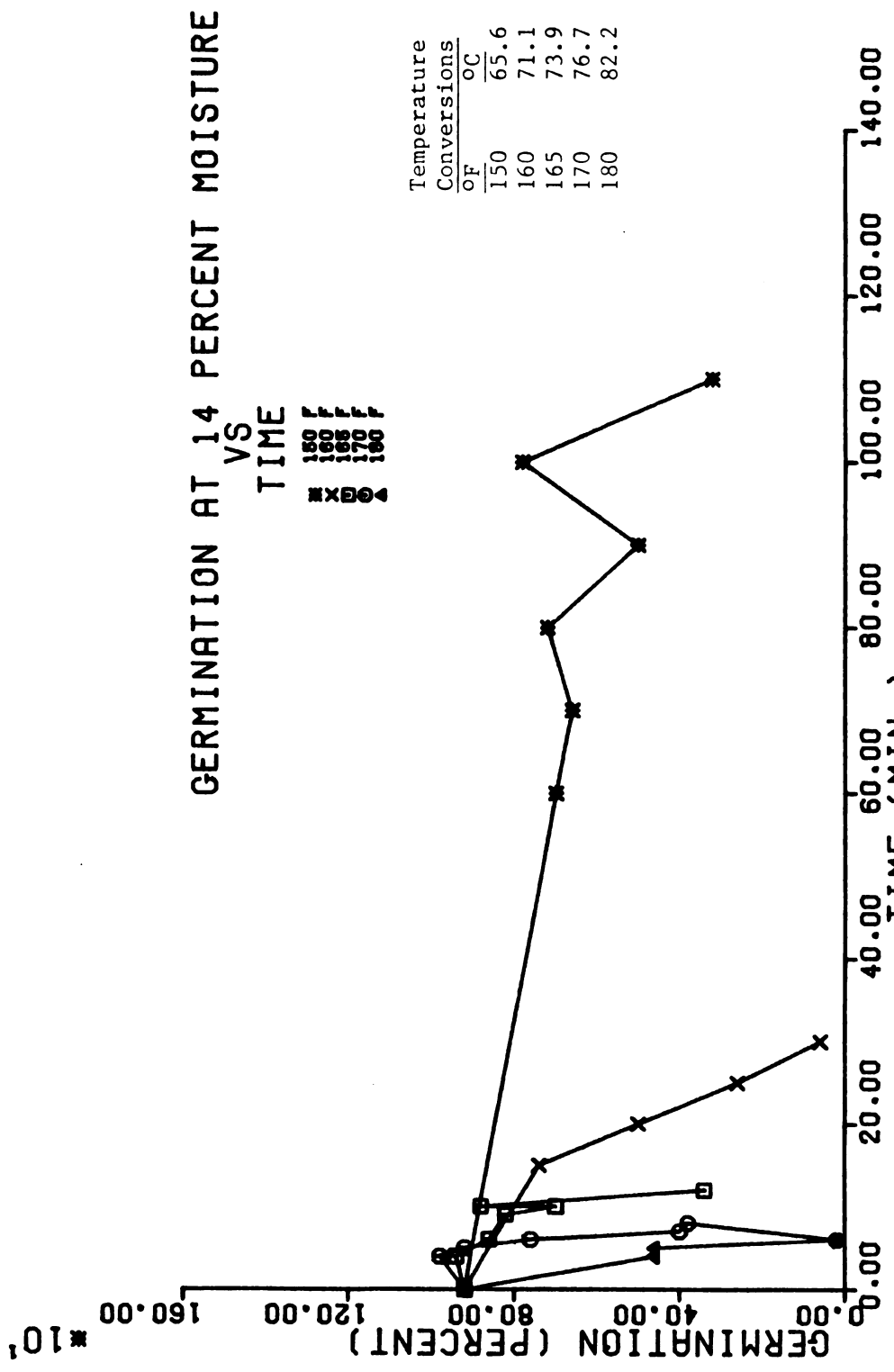
Test No.	Moisture Content	Temperature		Time	Germination
	% wb	°F	°C	min.	%
107	20	171	77.2	6	6
108	20	171	77.2	6	8
109	20	171	77.2	5	48
110	20	171	77.2	5	12
111	20	171	77.2	4½	14
112	20	171	77.2	4	76
113	20	171	77.2	4	80
114	20	171	77.2	3½	92
115	20	171	77.2	3	90
116	20	180	82.2	3½	20
117	20	180	82.2	3	68
118	24	130	54.4	90	82
119	24	130	54.4	80	72
120	24	130	54.4	70	94
121	24	130	54.4	60	90
122	24	130	54.4	50	82
123	24	130	54.4	40	88
124	24	140	60.0	60	2
125	24	140	60.0	50	4
126	24	140	60.0	40	16
127	24	140	60.0	30	46
128	24	140	60.0	20	70
129	24	140	60.0	15	86
130	24	150	65.6	9	12
131	24	150	65.6	8	22
132	24	150	65.6	7	46
133	24	150	65.6	6	80
134	24	150	65.6	5	90
135	24	150	65.6	5	94
136	24	150	65.6	4	90
137	24	160	71.1	5	6
138	24	160	71.1	4	74
139	24	170	76.7	4	2
140	24	170	76.7	3	58

Table A.1 (cont.) Thermal Effect on Germination

Test No.	Moisture Content	Temperature		Time	Germination
	% wb	°F	°C	min.	%
141	28	131	55.0	110	42
142	28	131	55.0	100	80
143	28	131	55.0	90	80
144	28	131	55.0	80	64
145	28	131	55.0	70	82
146	28	131	55.0	60	82
147	28	135	57.2	80	26
148	28	135	57.2	70	76
149	28	135	57.2	60	52
150	28	135	57.2	50	50
151	28	135	57.2	40	72
152	28	135	57.2	30	60
153	28	141	60.6	50	6
154	28	141	60.6	40	16
155	28	141	60.6	30	10
156	28	141	60.6	20	38
157	28	141	60.6	10	36
158	28	146	63.3	20	4
159	28	146	63.3	15	10
160	28	146	63.3	10	34
161	28	146	63.3	5	78
162	28	150	65.6	9	6
163	28	150	65.6	8	16
164	28	150	65.6	7	46
165	28	150	65.6	6	52
166	28	150	65.6	5	36
167	28	150	65.6	4	86

APPENDIX B

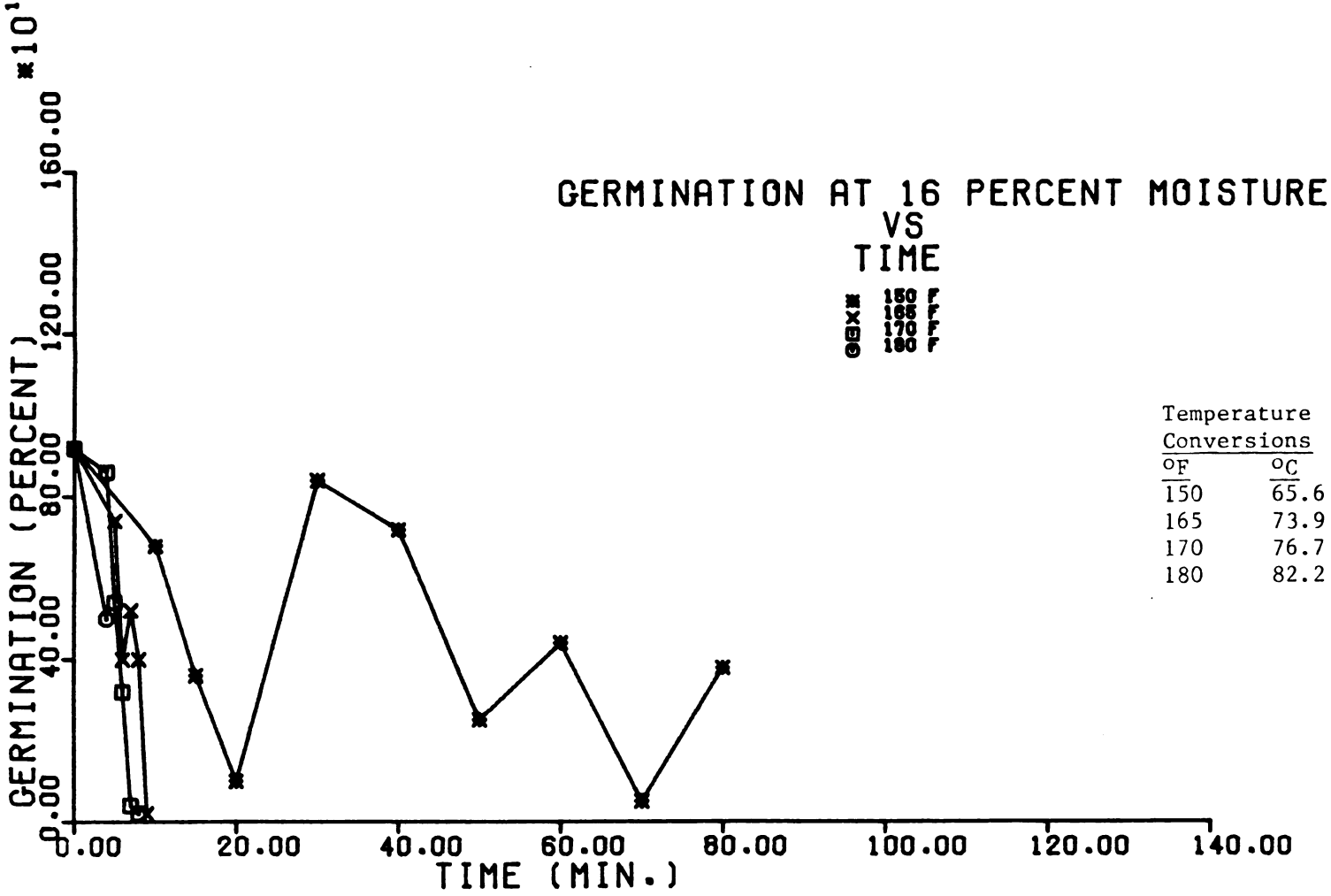
Germination Data Plots



Temperature Conversions

°F	°C
150	65.6
160	71.1
165	73.9
170	76.7
180	82.2

Figure B.1 Germination at 14% s.b. Moisture Content as Affected by Various Temperature-Time Heat Treatments.



Temperature Conversions

°F	°C
150	65.6
165	73.9
170	76.7
180	82.2

Figure B.2 Germination at 16% w.b. Moisture Content as Affected By Various Temperature-Time Heat Treatments.

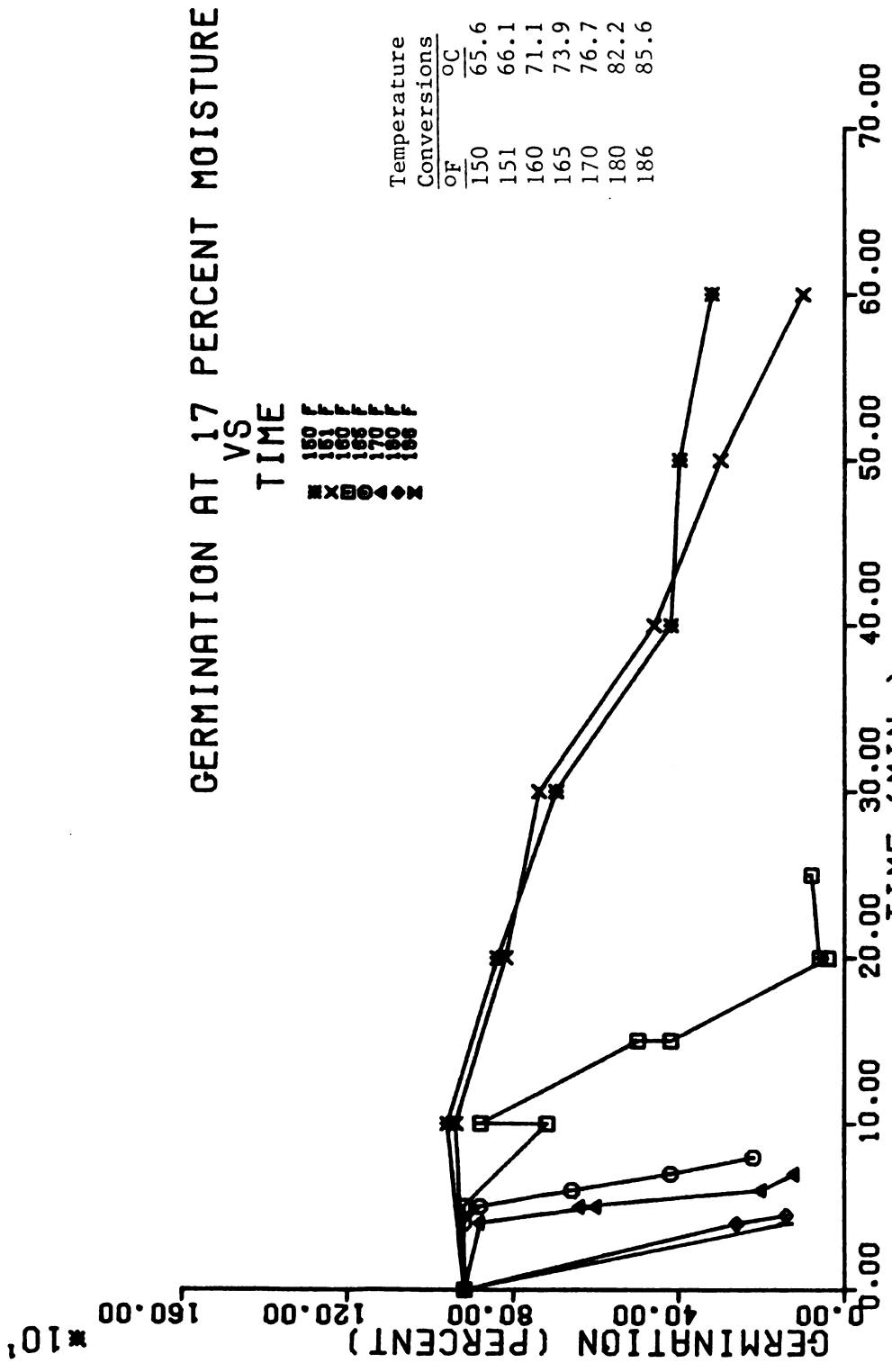


Figure B.3 Germination at 17% w.b. Moisture Content as Affected By Various Temperature-Time Heat Treatments.

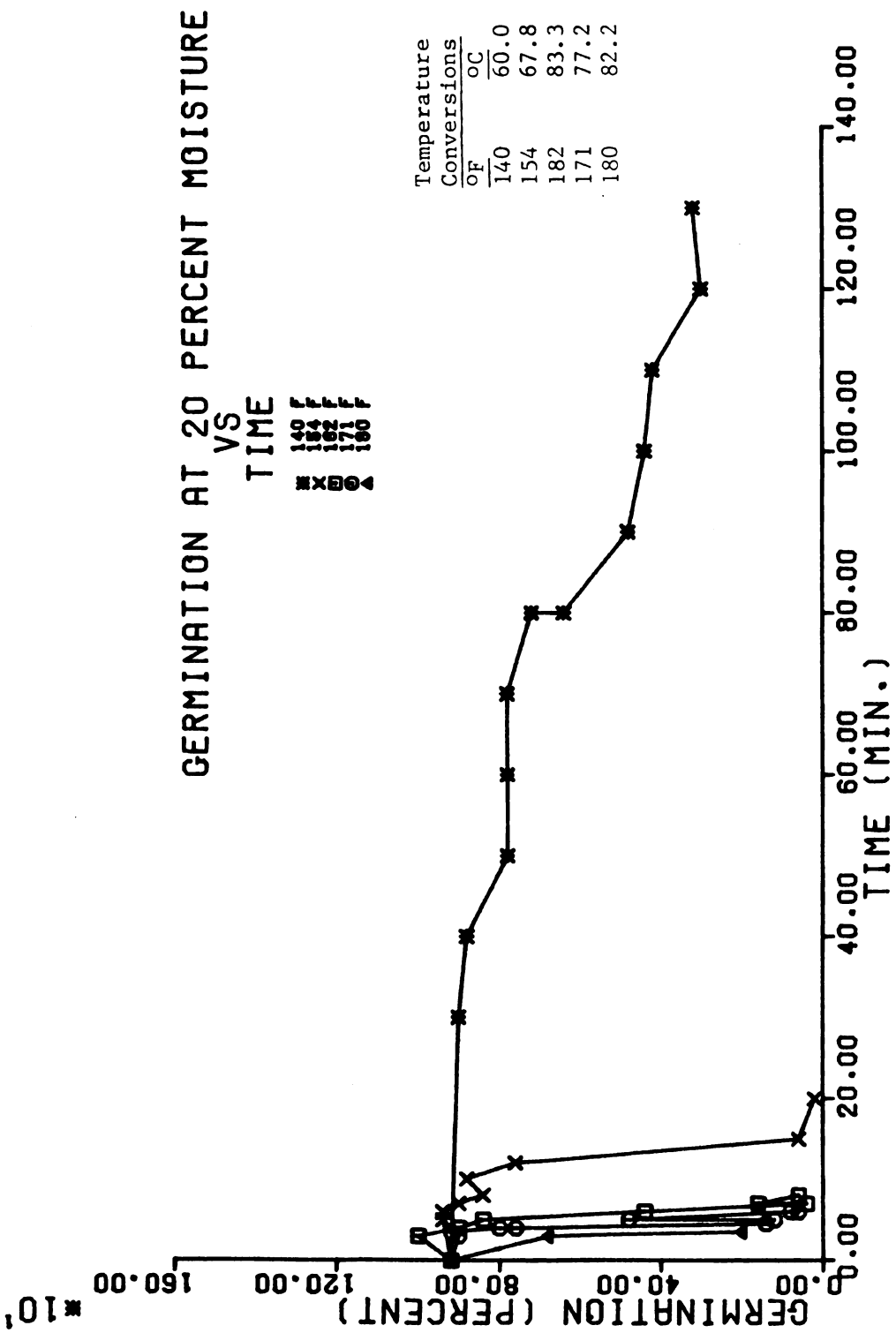
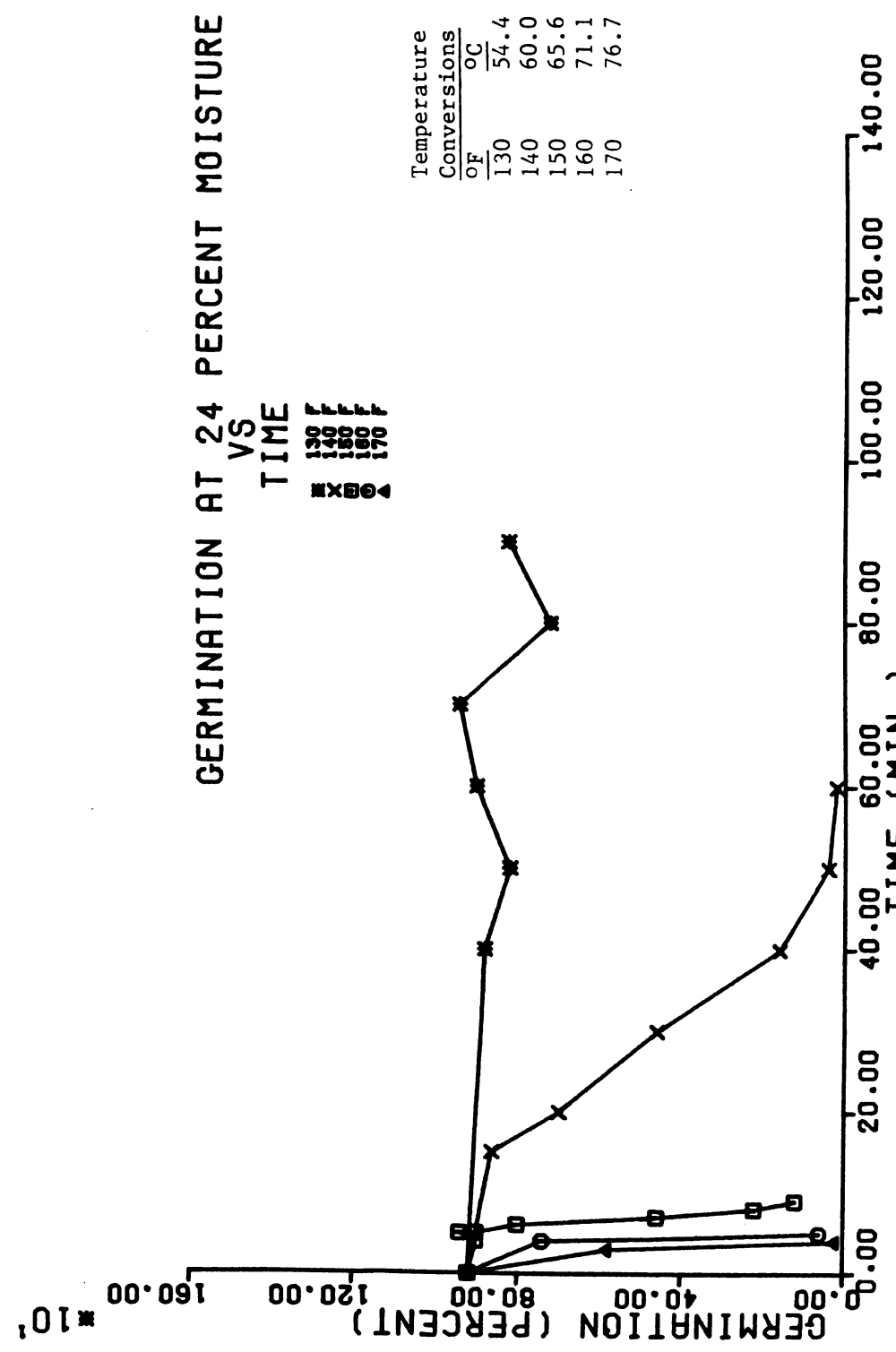
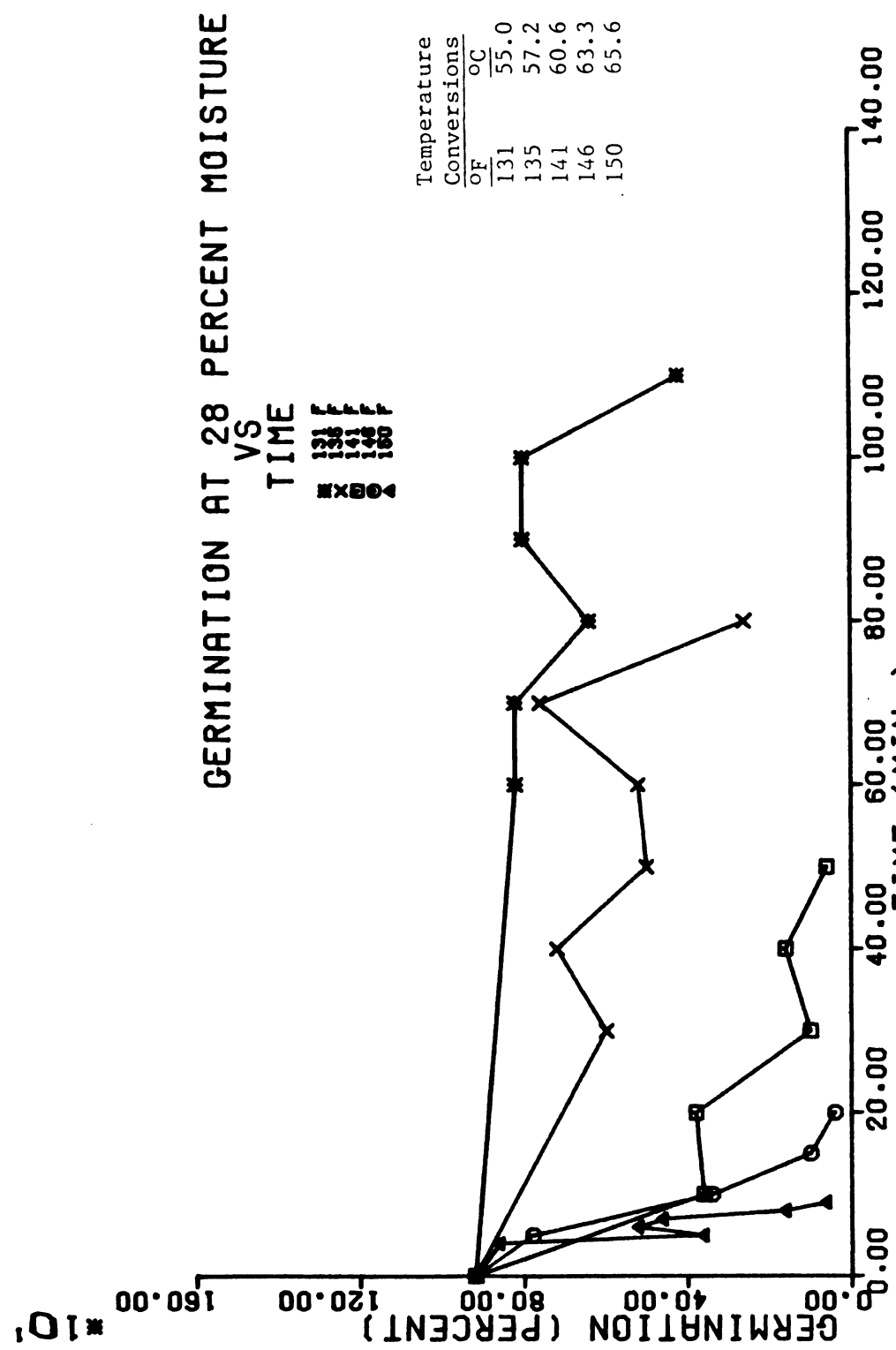


Figure B.4 Germination at 20% w.b. Moisture Content as Affected By Various Temperature-Time Heat Treatments.



Temperature Conversions	
°F	°C
130	54.4
140	60.0
150	65.6
160	71.1
170	76.7

Figure B.5 Germination at 24% w.b. Moisture Content as Affected By Various Temperature-Time Heat Treatments.



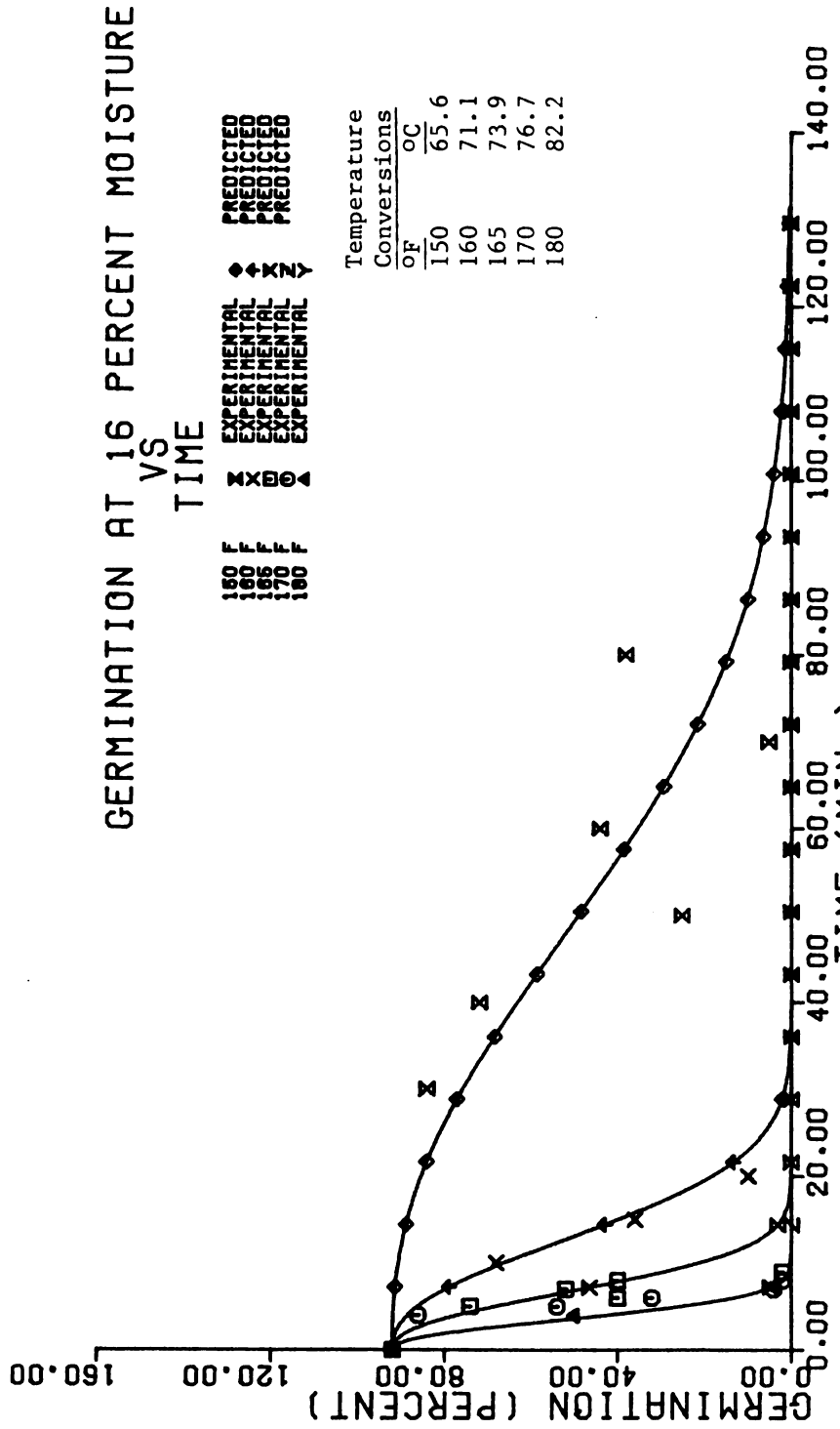
Temperature Conversions

°F	°C
131	55.0
135	57.2
141	60.6
146	63.3
150	65.6

Figure B.6 Germination at 28% w.b. Moisture Content as Affected By Various Temperature-Time Heat Treatments.

APPENDIX C

Germination Model and Data Plots



Temperature Conversions

°F	°C
150	65.6
160	71.1
165	73.9
170	76.7
180	82.2

Figure C.1 Comparison of Germination Model and Data at 16% w.b. Moisture Content.

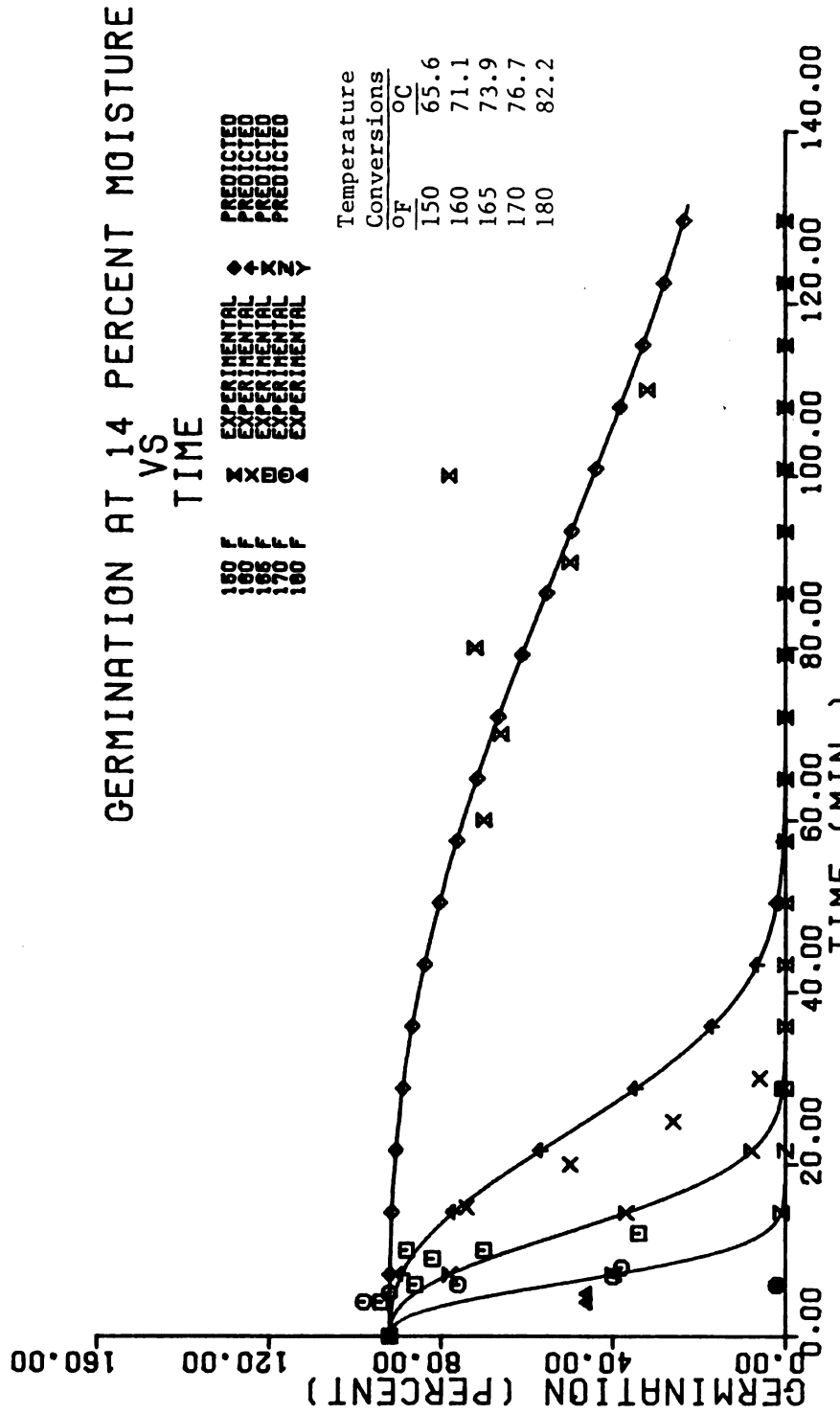
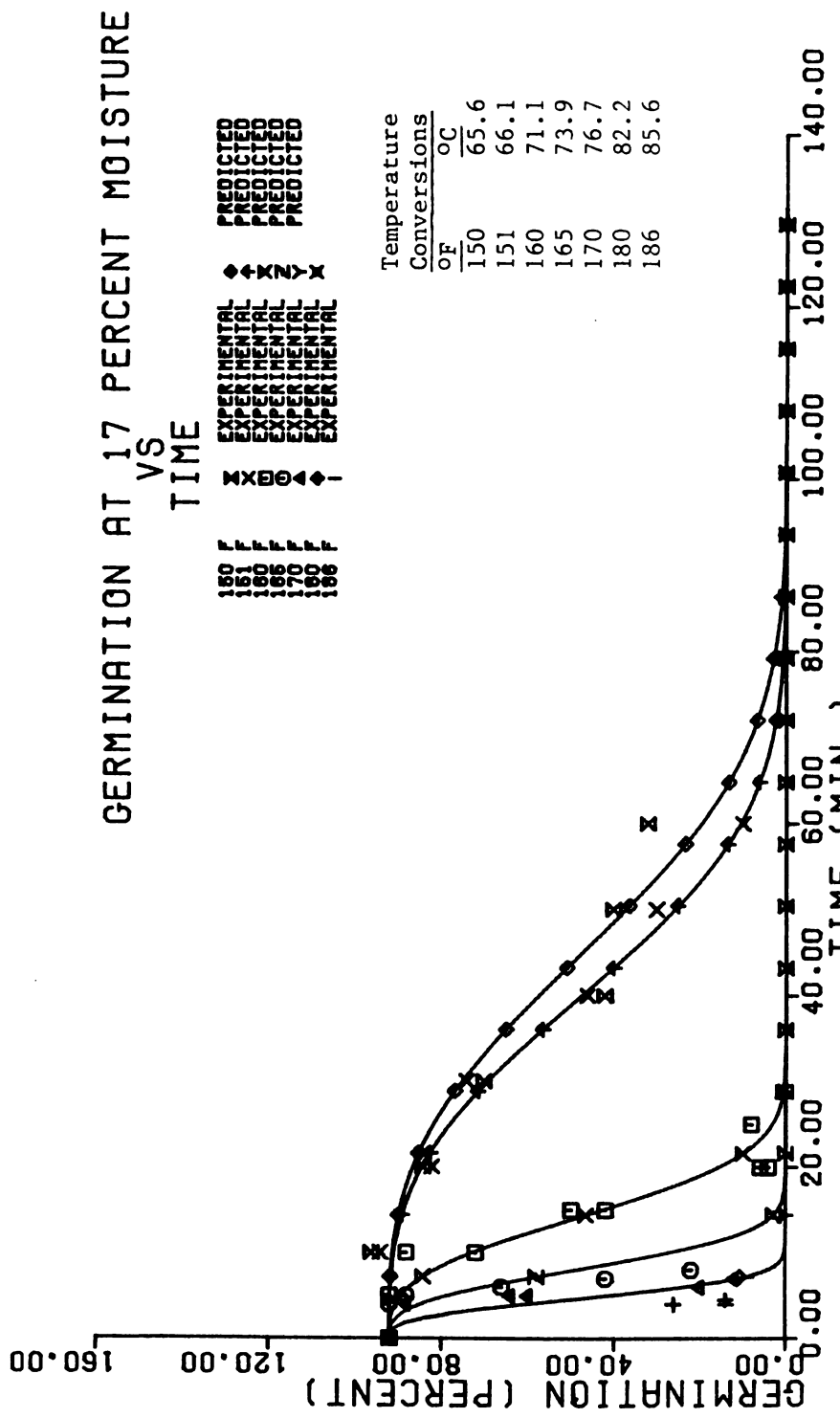


Figure C.2 Comparison of Germination Model and Data at 14% w.b. Moisture Content.



Temperature Conversions

°F	°C
150	65.6
151	66.1
160	71.1
165	73.9
170	76.7
180	82.2
186	85.6

Figure C.3 Comparison of Germination Model and Data at 17% w.b. Moisture Content.

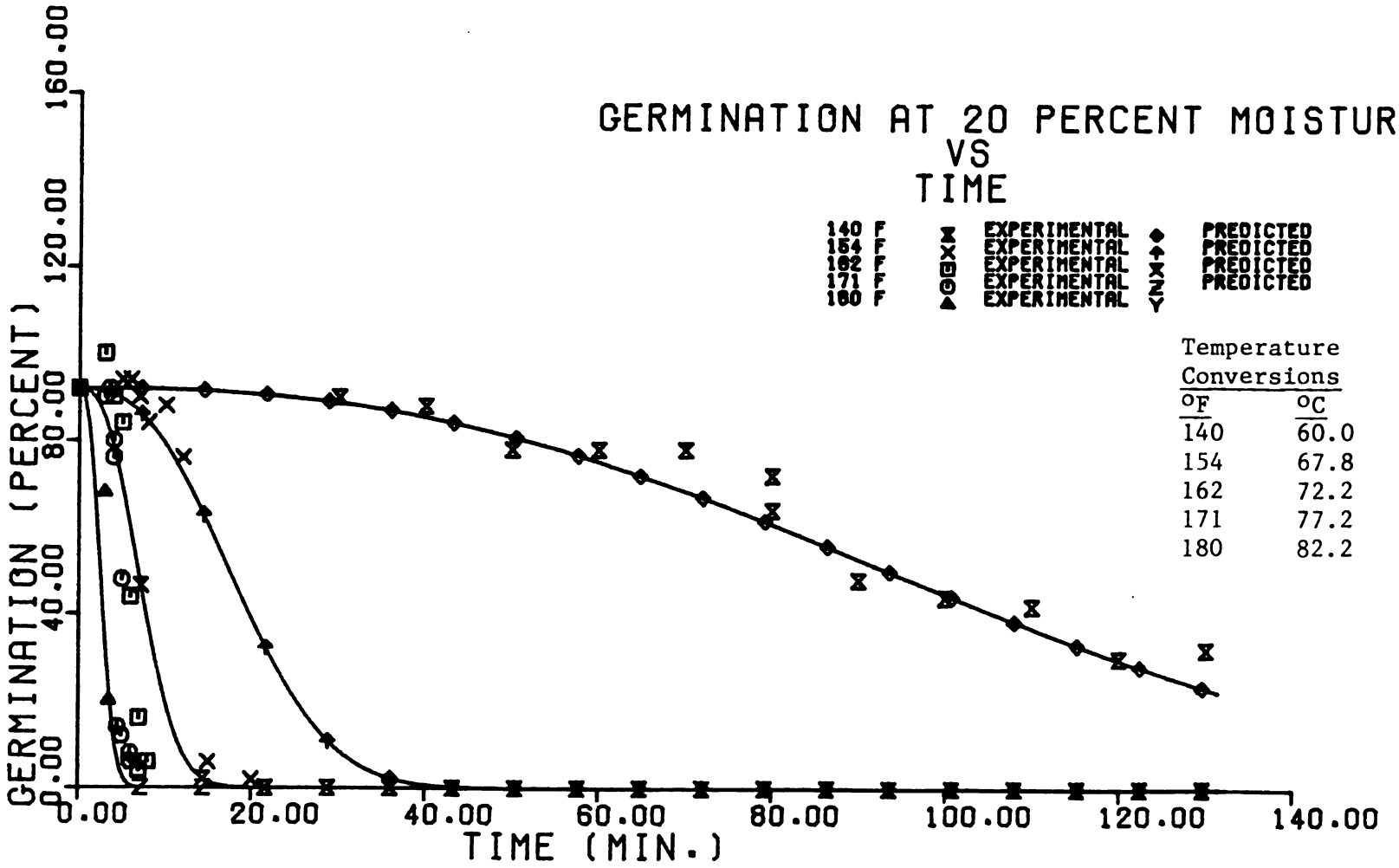


Figure C.4 Comparison of Germination Model and Data at 20% w.b. Moisture Content.

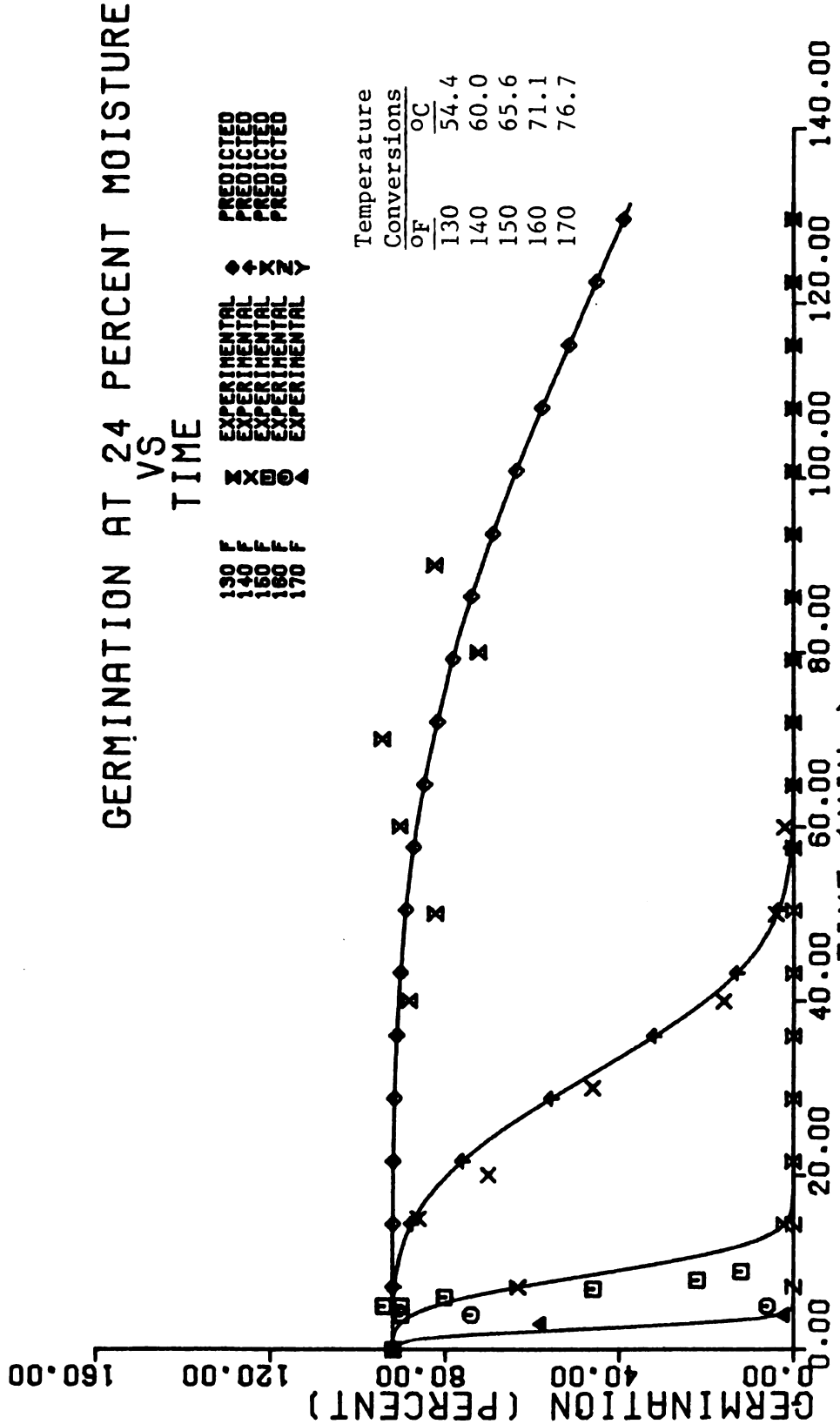


Figure C.5 Comparison of Germination Model and Data at 24% w.b. Moisture Content.

APPENDIX D

Germination Model--Low Temperature

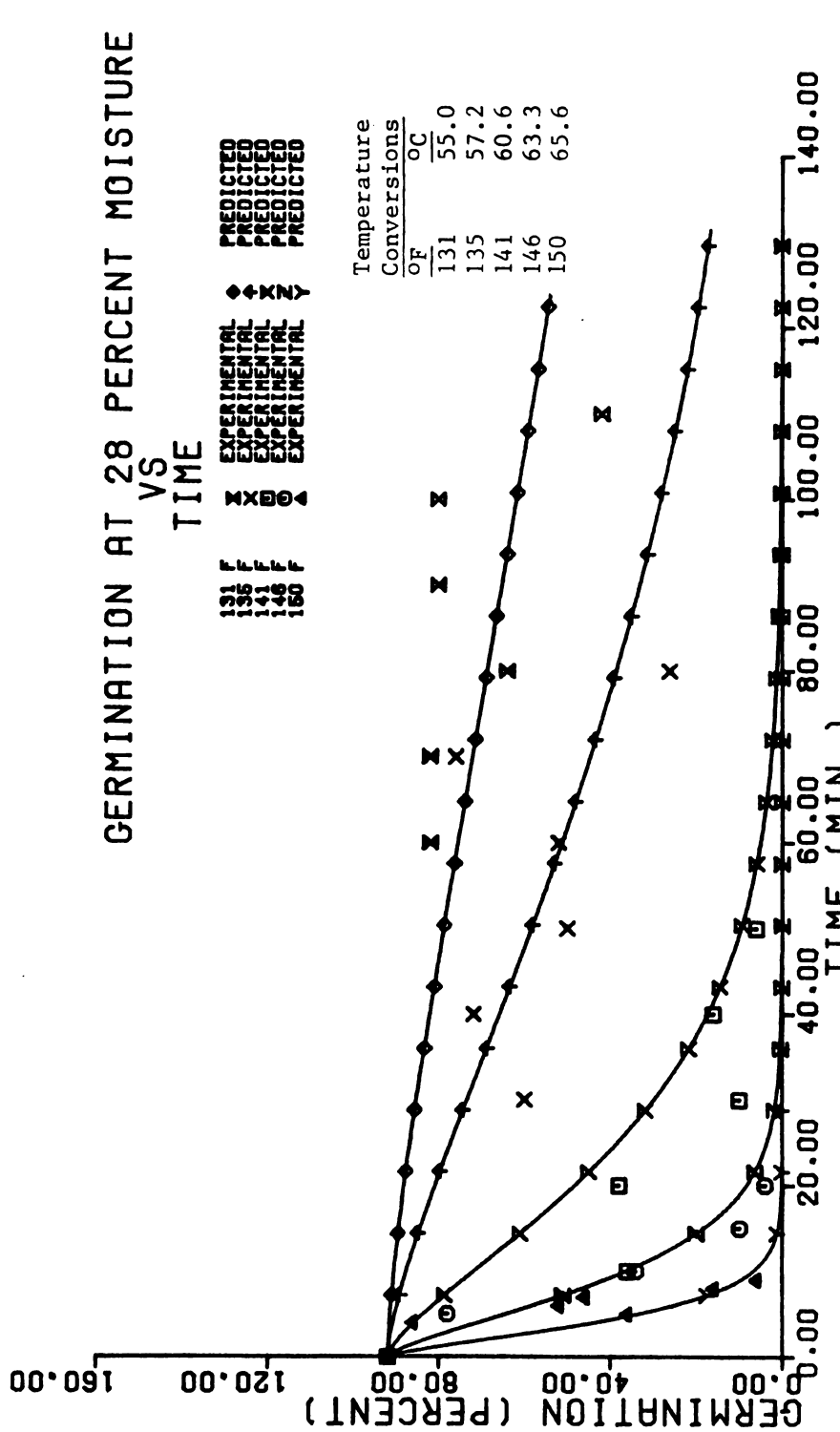
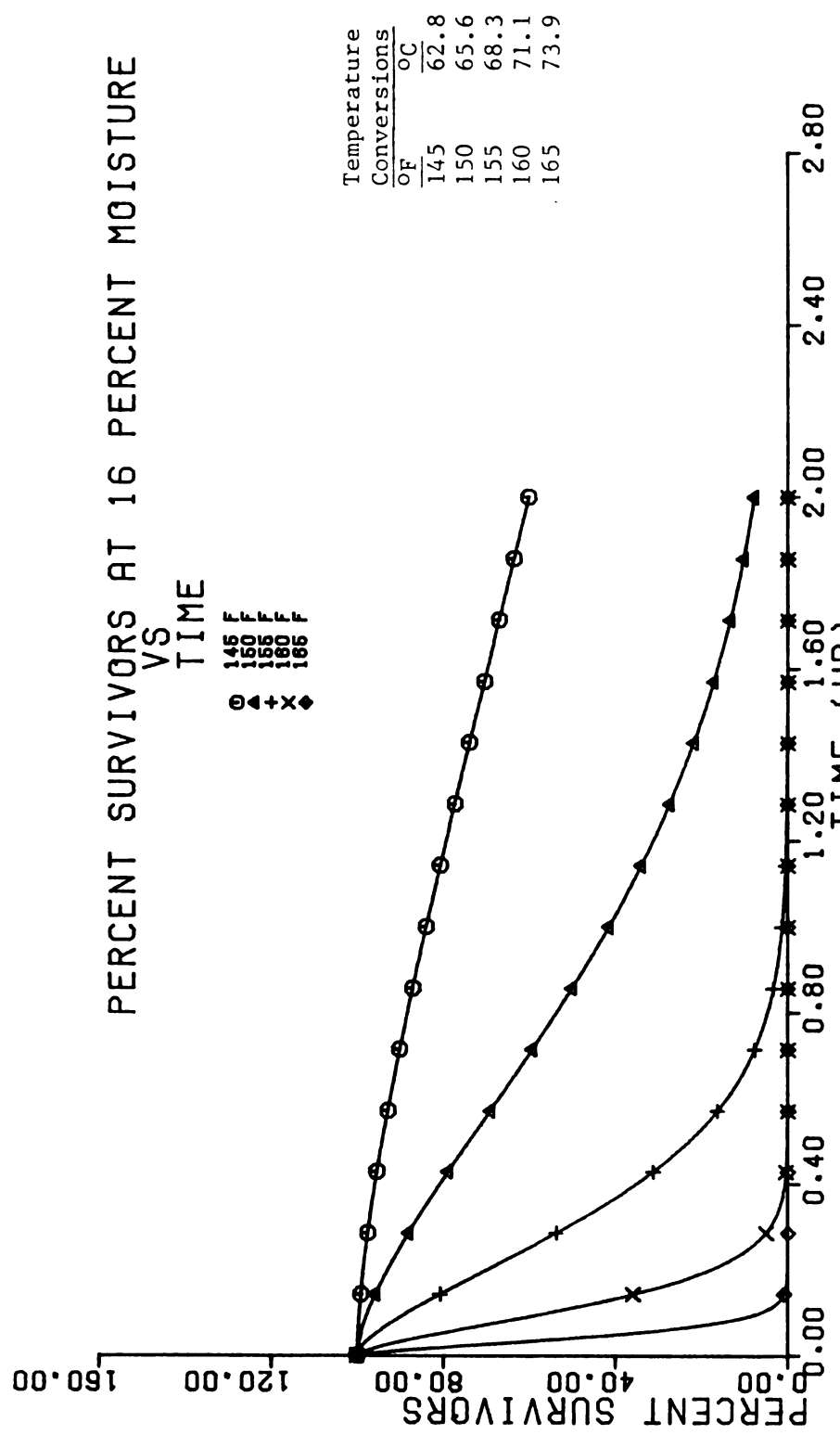


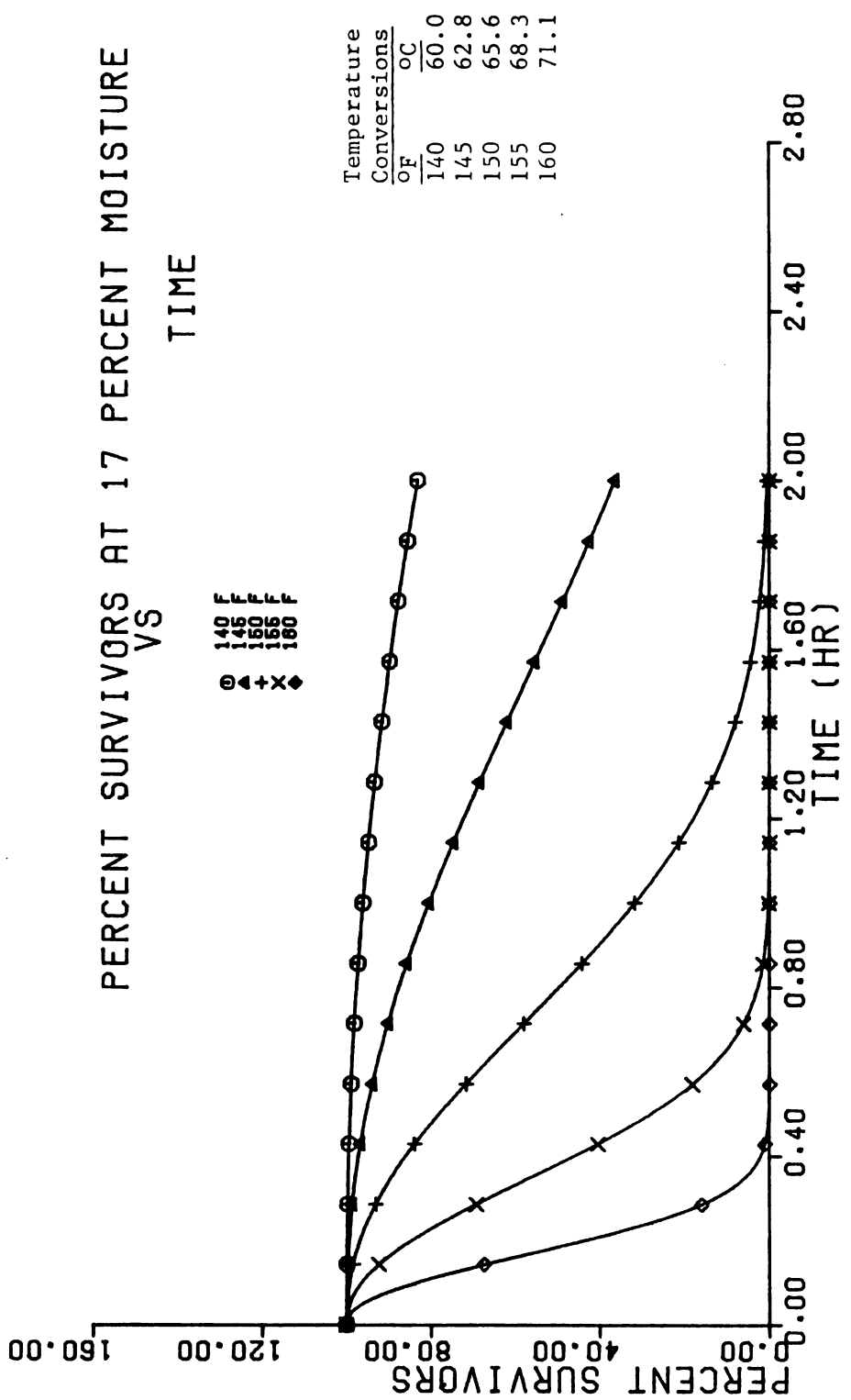
Figure C.6 Comparison of Germination Model and Data at 28% w.b. Moisture Content.



Temperature Conversions

°F	°C
145	62.8
150	65.6
155	68.3
160	71.1
165	73.9

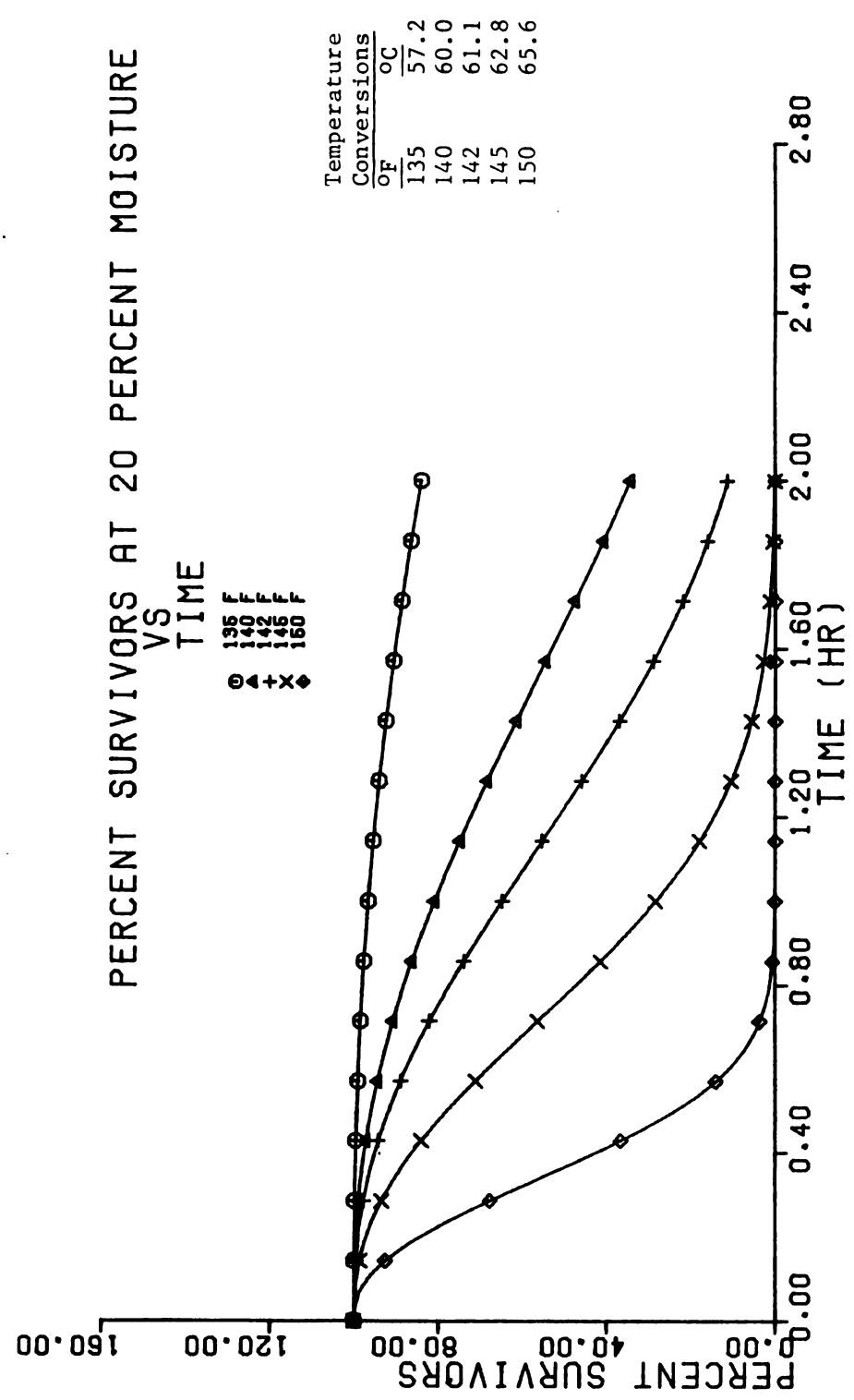
Figure D.2 Germination Model at 16% w.b. Moisture Content for 2 Hours.



Temperature Conversions

°F	°C
140	60.0
145	62.8
150	65.6
155	68.3
160	71.1

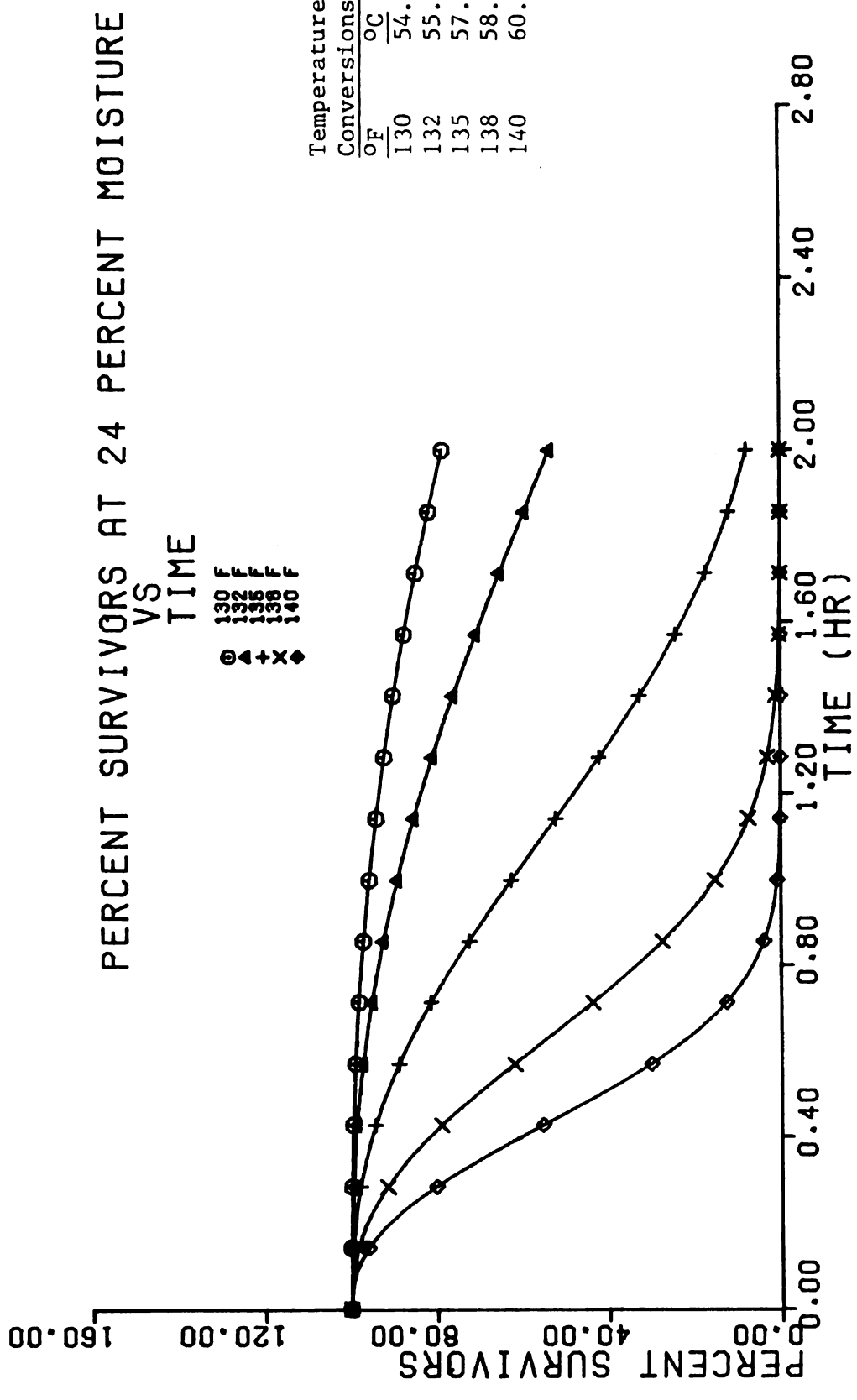
Figure D.3 Germination Model at 17% w.b. Moisture Content for 2 Hours.



Temperature Conversions

°F	°C
135	57.2
140	60.0
142	61.1
145	62.8
150	65.6

Figure D.4 Germination Model at 20% w.b. Moisture Content for 2 Hours.



Temperature Conversions

°F	°C
130	54.4
132	55.6
135	57.2
138	58.9
140	60.0

Figure D.5 Germination Model at 24% w.b. Moisture Content for 2 Hours.

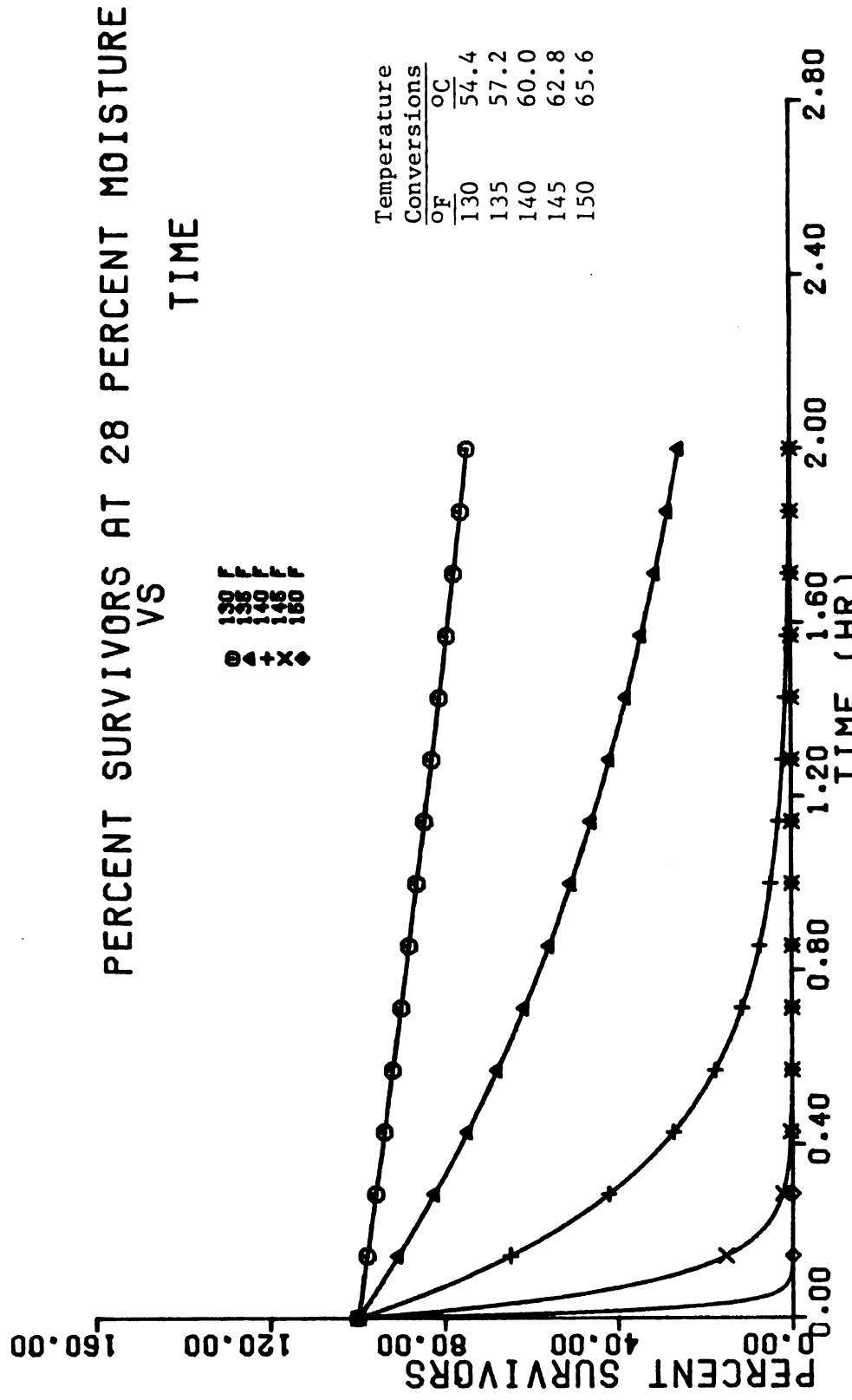
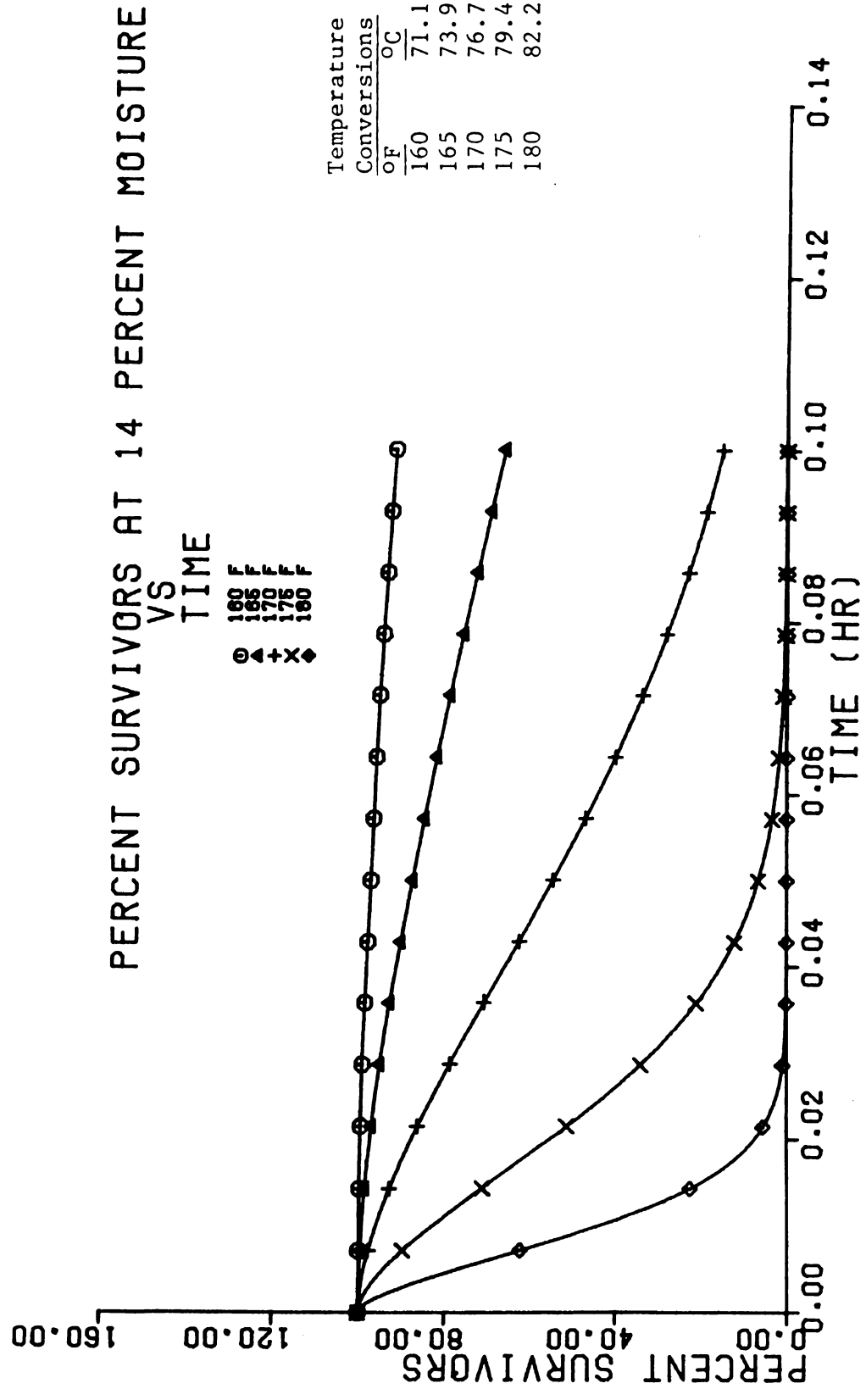


Figure D.6 Germination Model at 28% w.b. Moisture Content for 2 Hours.

APPENDIX E

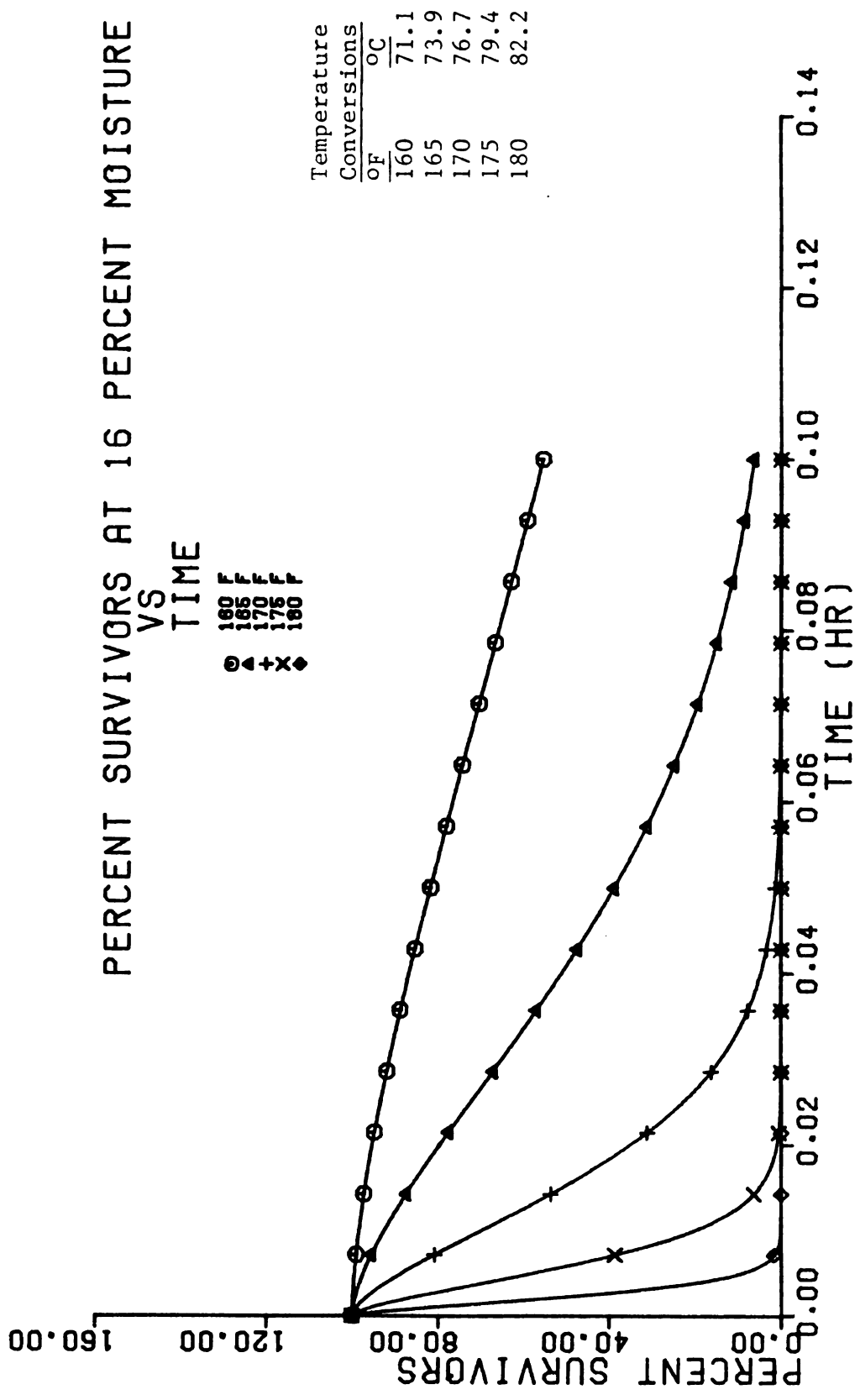
Germination Model--High Temperature



Temperature Conversions

°F	°C
160	71.1
165	73.9
170	76.7
175	79.4
180	82.2

Figure E.1 Germination Model at 14% w.b. Moisture Content at High Temperatures for 6 Minutes.



Temperature Conversions

°F	°C
160	71.1
165	73.9
170	76.7
175	79.4
180	82.2

Figure E.2 Germination Model at 16% w.b. Moisture Content at High Temperatures for 6 Minutes.

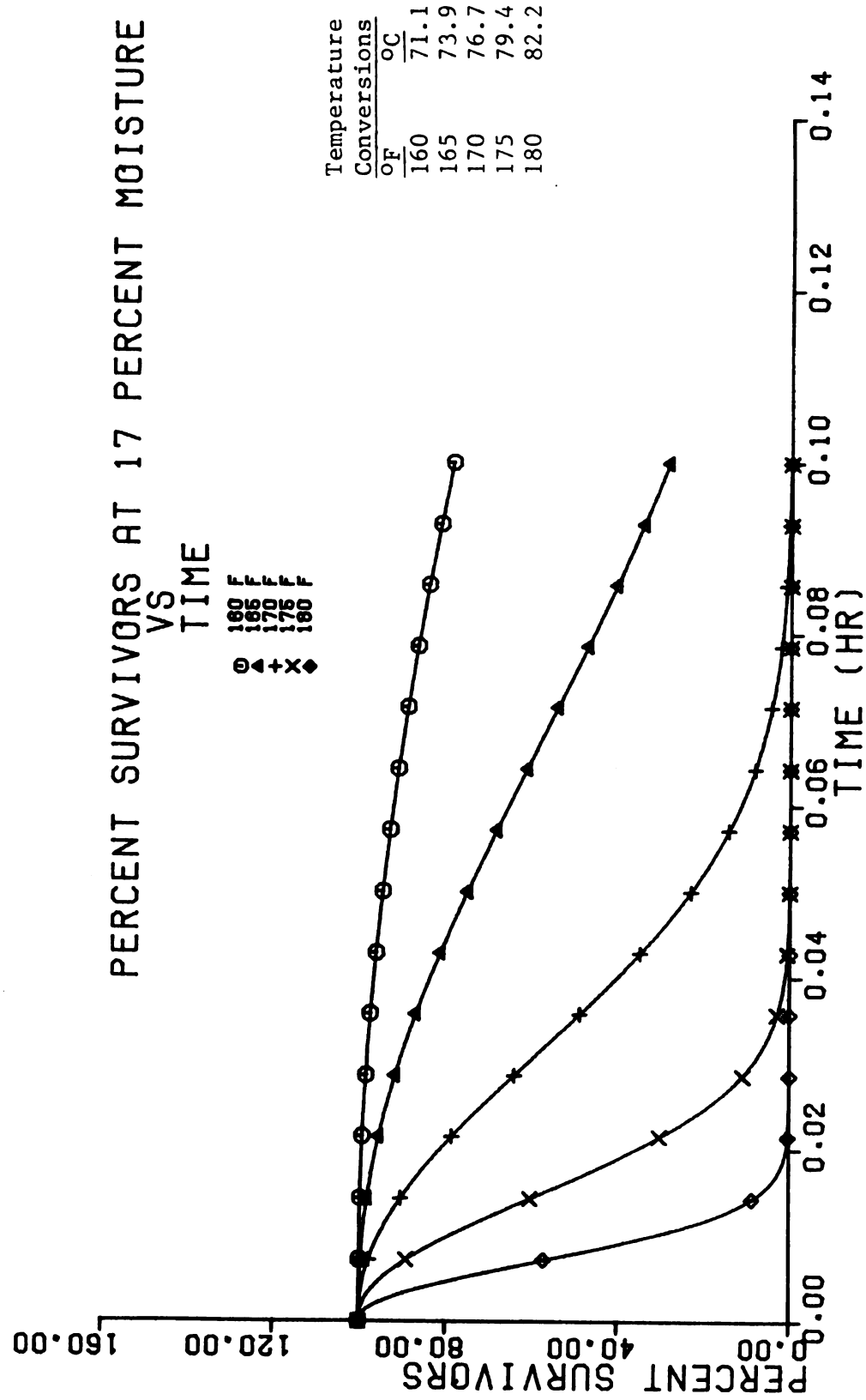
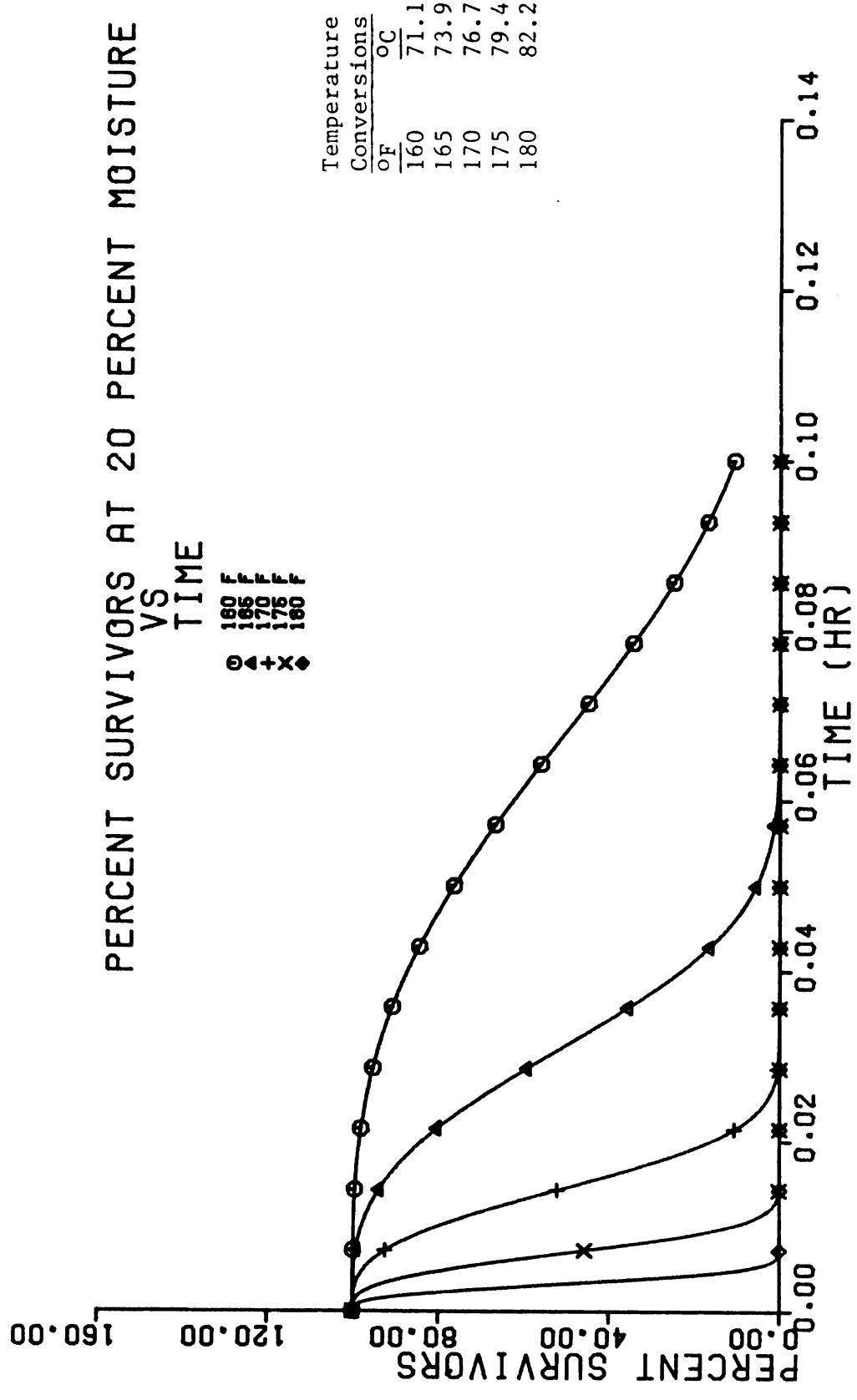


Figure E.3 Germination Model at 17% w.b. Moisture Content at High Temperatures for 6 Minutes.



Temperature Conversions

°F	°C
160	71.1
165	73.9
170	76.7
175	79.4
180	82.2

Figure E.4 Germination Model at 20% Moisture Content at High Temperatures for 6 Minutes.

APPENDIX F

Thermal Effects on Available Lysine

Table F.1 (cont.) Thermal Effects on Available Lysine

Test No.	Moisture Content	Temperature		Time	Concentration*	Standard Deviation**	Degrees of Freedom
	% wb	°F	°C	min.	moles AVL / mole N	moles AVL / mole N	
36	14	260	126.7	60	.1279E-01	.8256E-02	6
37	14	260	126.7	60	.2205E-01	.1188E-01	4
38	14	260	126.7	60	.4763E-02	.3254E-01	4
39	14	260	126.7	30	.1230E-01	.3142E-02	6
40	14	270	132.2	60	-.1092E-01	.1053E-01	6
41	14	270	132.2	50	.1869E-01	.4056E-02	6
42	14	270	132.2	40	.9252E-02	.3320E-02	3
43	14	270	132.2	30	.1589E-01	.4861E-02	6
44	14	270	132.2	20	.2596E-01	.1620E-02	6
45	14	270	132.2	10	.3029E-01	.9438E-02	6
46	14	280	137.8	60	.1308E-01	.4553E-02	6
47	14	280	137.8	60	.4195E-02	.3427E-02	6
48	14	280	137.8	50	.9145E-02	.2683E-02	6
49	14	280	137.8	40	.1174E-02	.5755E-02	6
50	14	280	137.8	30	.1349E-01	.2411E-02	6
51	14	280	137.8	30	.1190E-01	.1770E-02	6
52	14	280	137.8	20	.9390E-02	.6391E-02	4
53	14	280	137.8	10	.1676E-01	.3552E-02	6

* Average of multiple readings (see section 4.3).
** Standard deviation of single reading.

Table F.1 (cont.) Thermal Stress

Table F.1 (cont.) Thermal Effects on Available Lysine

Test No.	Moisture Content	Temperature		Time	Concentration*	Standard Deviation**	Degrees of Freedom
	% wb	°F	°C	min.	moles AVL / mole N	moles AVL / mole N	
109	20	290	143.3	60	-.1911E-03	.2726E-02	6
110	20	290	143.3	50	.6066E-02	.2279E-02	6
111	20	290	143.3	40	.1049E-01	.8231E-03	6
112	20	290	143.3	10	.1897E-01	.3628E-02	6
113	20	300	148.9	60	.2102E-02	.5496E-02	6
114	20	300	148.9	50	.1156E-01	.5892E-02	6
115	20	300	148.9	40	.1011E-01	.1019E-02	6
116	20	300	148.9	30	.1419E-01	.3561E-02	6
117	20	300	148.9	20	.4487E-02	.2702E-02	6
118	20	300	148.9	10	.1539E-01	.2658E-02	6

* Average of multiple readings (see section 4.3).
** Standard deviation of single reading.

Table F.1 (cont.) Thermal Effects on Available Lysine

Test No.	Moisture Content	Temperature		Time	Concentration*	Standard Deviation**	Degrees of Freedom
	% wb	°F	°C	min.	moles AVL / moles N	moles AVL / moles N	
73	16	280	137.8	60	-.3375E-02	.1128E-01	6
74	16	280	137.8	50	.4203E-02	.1618E-02	3
75	16	280	137.8	40	.1163E-01	.2545E-02	6
76	16	280	137.8	30	.1324E-01	.3948E-02	6
77	16	280	137.8	20	.1711E-01	.3810E-02	6
78	16	280	137.8	10	.1626E-01	.1679E-02	6
79	16	290	143.3	60	.3477E-02	.4472E-02	6
80	16	290	143.3	50	.7347E-02	.1842E-02	6
81	16	290	143.3	40	.1050E-01	.4952E-02	4
82	16	290	143.3	30	.1420E-01	.6788E-02	6
83	16	290	143.3	10	.1808E-01	.3380E-02	6
84	16	300	148.9	60	.4364E-02	.2903E-02	6
85	16	300	148.9	50	.2113E-02	.1631E-02	6
86	16	300	148.9	40	.3689E-02	.5693E-02	6
87	16	300	148.9	30	.2080E-02	.1310E-02	6
88	16	300	148.9	20	.4976E-02	.2462E-02	6
89	17	control		-	.2588E-01	.5935E-02	6
90	17	250	121.1	60	.1611E-01	.5431E-02	6
91	17	260	126.7	60	.1336E-01	.2120E-02	6

* Average of multiple readings (see section 4.3).
** Standard deviation of single reading.

APPENDIX G

Available Lysine Model and Data Plots

--Second Reaction Only

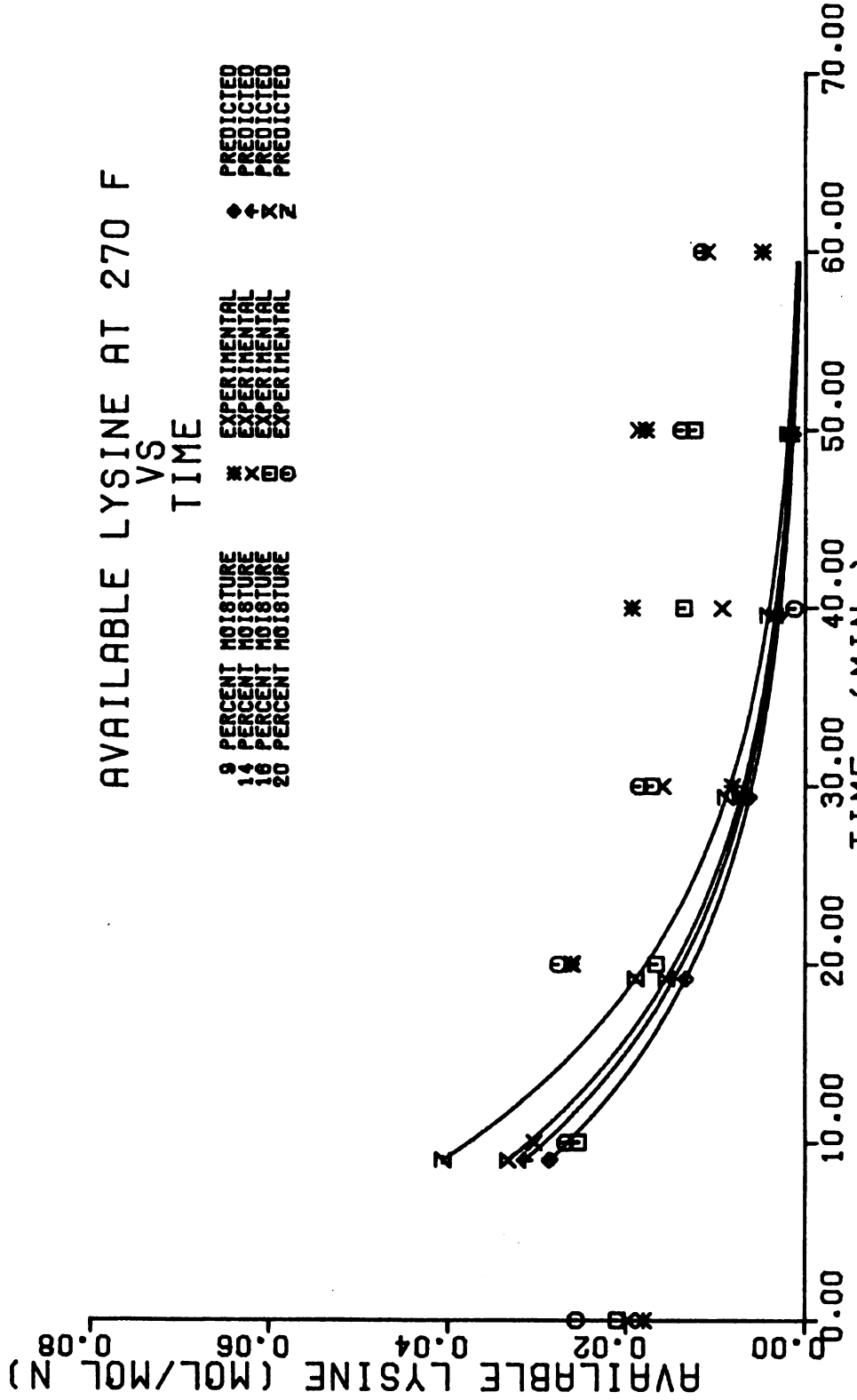


Figure G.1 First order model fit to AVL data at 270°F (132.2°C).

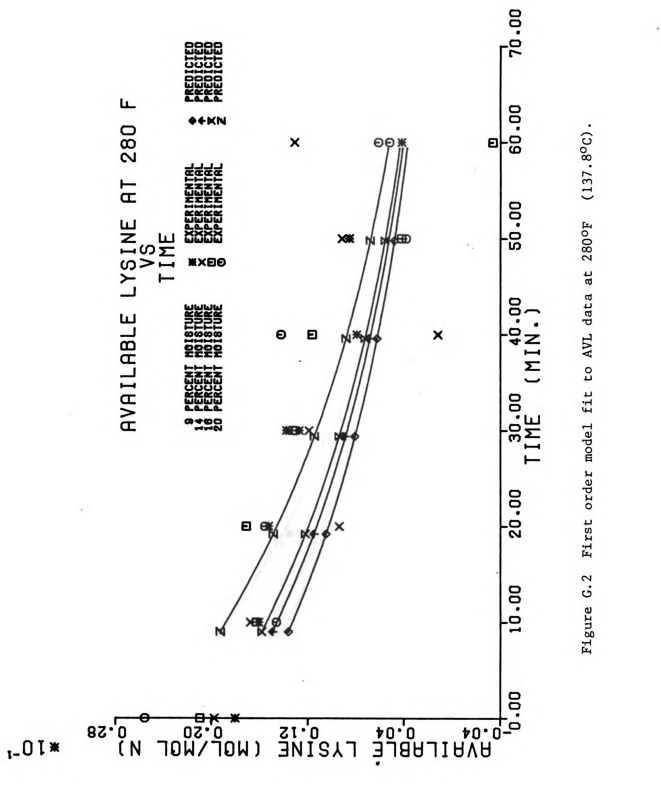


Figure G.2 First order model fit to AVL data at 280°F (137.8°C).

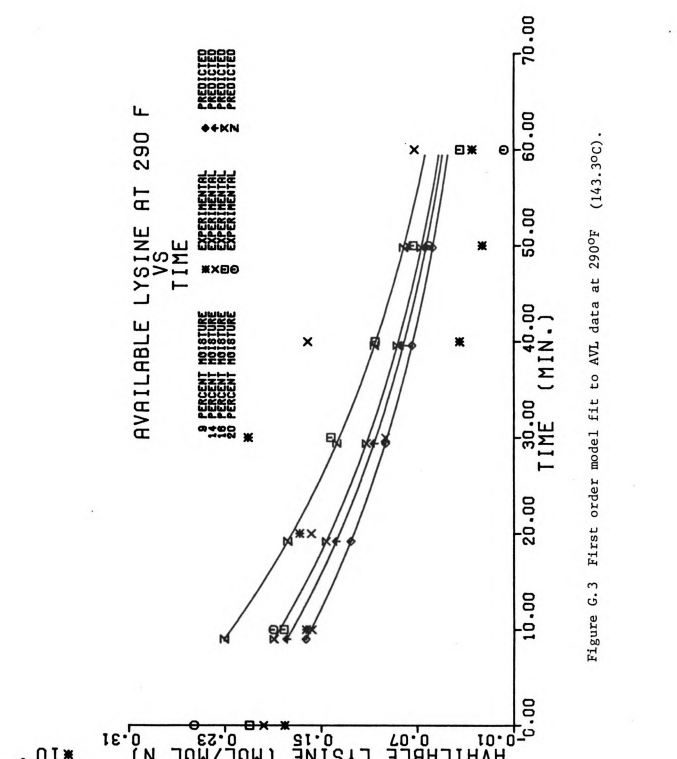


Figure G.3 First order model fit to AVL data at 290°F (143.3°C).

0^{-1}

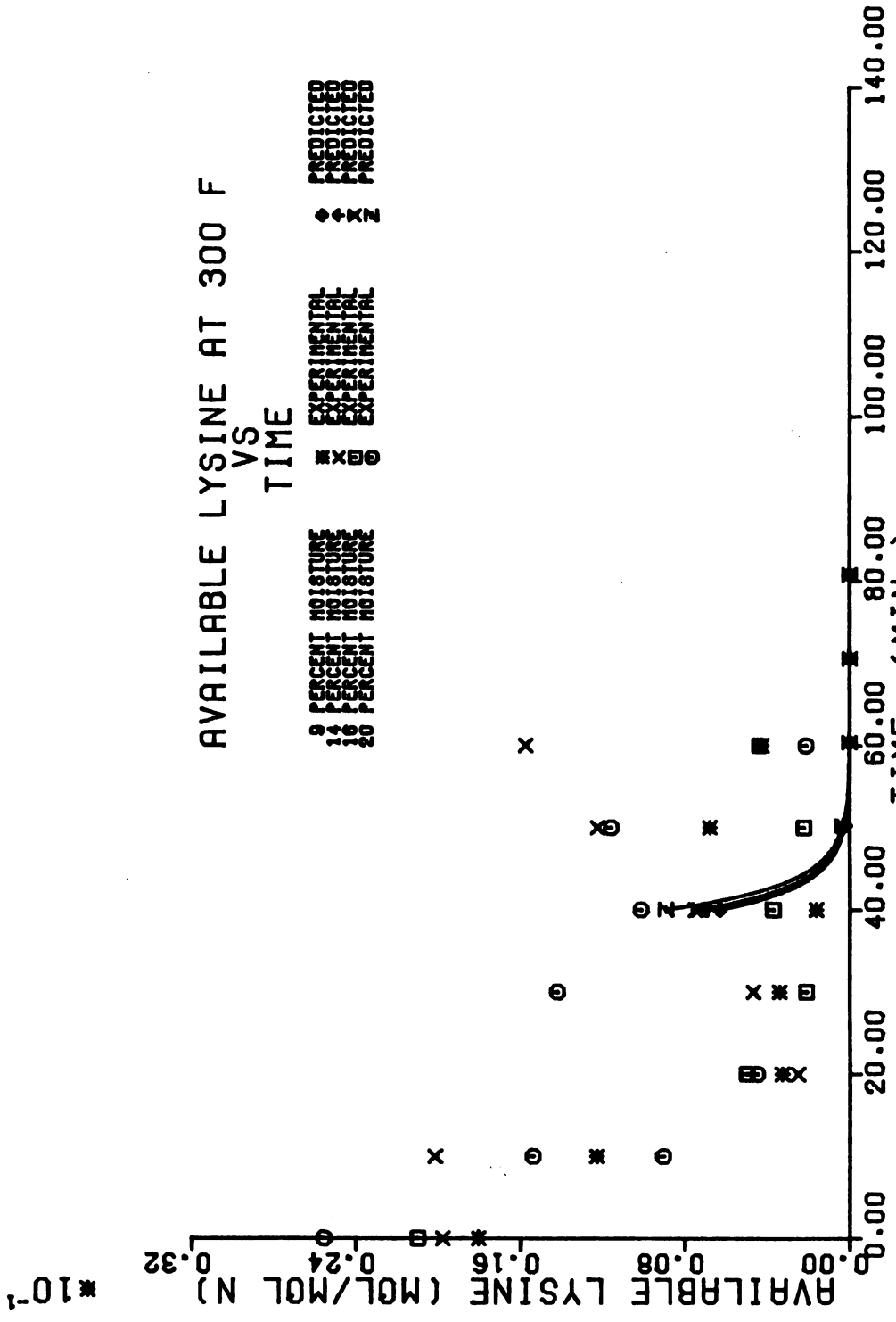


Figure G.4 First order model fit to AVL data at 300°F (148.9°C).