

AN ABSTRACT OF THE THESIS OF

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Abstract approved: _____
Keith L. Levien

Abstract approved: _____
/ J. Antonio Torres \

The principal aim of this study was the use and evaluation of dynamic modeling techniques to identify mathematical models for cereal drying rates and quality changes that best describe thin-layer malt drying data. Seven thin-layer malt drying experiments were performed at the Great Western Malting pilot facilities, Vancouver, WA. Malt moisture content, temperature, β -amylase activity, endo-barley- β -glucanase activity, and color were all monitored as the malt was dried with air at various temperature and relative humidity values. A constrained direct search optimization method was used to fit available drying, enzyme deactivation, and color formation models to the data obtained by minimizing the error between predicted and experimental values. Because the deactivation of β -amylase observed during the kiln experiments was less than the error involved in

β -amylase measurement, β -amylase modeling efforts were dropped from the study. The end result is a computer simulation of the malt kilning process that can predict malt drying rates, color formation, and endo-barley- β -glucanase deactivation based on the drying air temperature, relative humidity, and time spent in the kiln. Further research is suggested towards modeling malt drying rates at high moisture contents, (above 40%) analysis of drying model applicability when drying conditions fall outside those encountered in this study, and development of assay procedures and models so that the fate of other important malt quality indicators during kiln drying can be predicted.

Dynamic Simulation of Drying and Quality Changes
During Malt Kilning

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Vincent M. Coonce

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APPROVED:

Assistant Professor of Chemical Engineering in charge of major

Assistant Professor of Food Science and Technology in charge of major

Interim Head of Department of Chemical Engineering

Head of Department of Food Science and Technology

Dean of Graduate School

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Typed by the author Vincent M. Coonce

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DYNAMIC SIMULATION OF DRYING AND QUALITY CHANGES DURING MALT KILNING

INTRODUCTION

The U.S. brewing industry is currently producing 180 million barrels annually accounting for well over \$10 billion in revenues (Beverage World, 1989). Accordingly, there is much interest in new methods and techniques for increasing and maintaining beer quality at a low cost. This can be achieved in part by controlling the quality of raw materials and conditions used during processing. An important process in beer production is the malt kilning step, in which wet germinated barley (green malt) is dried in a hot forced-air flow. Malt kilning is generally considered a beneficial process, producing a low moisture content malt which is microbiologically and enzymatically stable, facilitating rootlet removal, enhancing milling characteristics, and generating the characteristic malt flavor and color. Unfortunately, changes which are detrimental to malt quality also occur during kilning, and reduction of malt quality is not uncommon, especially when high drying temperatures are used (Briggs et al., 1981). Traditionally, there has been a lack of adequate means for controlling malt quality changes as they occur during kilning because little attention has been paid to reaction kinetics of malt quality changes during kilning. Malt quality improvements are accomplished using trial-and-error type approaches which are both costly and time consuming.

The principal aim of this study is to use available process modeling techniques to mathematically simulate the conditions and quality changes that

occur during malt kilning so that, with the aid of a computer, changes in quality due to modification of processing conditions can be predicted. Use of a computer simulation could greatly decrease the cost and time involved in development, improvement, and control of malt kilning.

REVIEW OF LITERATURE

Modeling Malt Temperature Changes During Kiln Drying

When modeling product temperature during the drying of foods and grains, it is most common to assume isothermal conditions throughout the drying piece (Bruin and Luyben, 1980; Chirife, 1983). The isothermal grain temperature model is developed by performing an energy balance about a thin layer of drying grain, accounting for energy transferred to the grain surface by convection, energy used to evaporate water at the grain temperature, energy used to heat the water vapor from the grain temperature to the air temperature, and energy used to increase the temperature of the grain. It is also assumed that changes in kernel density, heat capacity, and volume are small and can be neglected:

$$\frac{dT_g}{dt} = \frac{ha(T_a - T_g) + \rho \frac{dM_{avg}}{dt} (h_{fg} + C_v(T_a - T_g))}{\rho C_g + \rho C_w M_{avg}} \quad (1)$$

Equation (1) can be solved given the initial grain temperature, $T_g(0)$ at time = 0, and the rate of moisture loss, dM_{avg}/dt .

The isothermal kernel model has been used successfully to describe product temperature changes during the drying of a wide range of agricultural materials, including cherry pits (Bakker-Arkema et al., 1967), English walnuts (Rumsey and Thompson, 1984), wheat (O'Callaghan et al., 1971) and barley (Boyce, 1965; O'Callaghan et al., 1971).

In some more recent studies, temperature has been modeled assuming that internal kernel temperature gradients are significant (Sokhansanj and Bruce, 1987; Tolaba et al., 1988). The temperature gradient model is developed by performing an energy balance about a differential element within the grain. The most commonly used gradient model in grain drying assumes a spherically shaped kernel with temperature gradients only in the radial direction and constant thermal conductivity, density, and heat capacity:

$$\frac{\partial T_g(r,t)}{\partial t} = \frac{k}{\rho C_g} \left[\frac{\partial^2 T_g(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial T_g(r,t)}{\partial r} \right] \quad (2)$$

The initial grain temperature, $T_g(r,0)$, must be known to solve equation (2). The boundary conditions can be written by recognizing the symmetry condition at the center of the sphere and by performing an energy balance about the outermost spherical differential element, resulting in equations (3) and (4) respectively.

$$r^2 \frac{\partial T_g(0,t)}{\partial r} = 0 \quad (3)$$

$$-ka \frac{\partial T_g(r,t)}{\partial r} = ha(T_a - T_g(r,t)) + \rho \frac{dM_{avg}}{dt} [h_{fg} + C_v(T_a - T_g(r,t))] \quad \text{at } r = R \quad (4)$$

From a conceptual standpoint, there are problems with the use of both temperature models. First, the assumption of isothermal kernel conditions used in model (1) is certainly suspect. However, Bruce (1985) cites the early work of Pabis and Henderson (1962), which indicates that the rate of heat equalization within a drying kernel is two orders of magnitude greater than the rate of moisture

equalization. Brooker et al. (1973) state that only for very precise calculations is it necessary to include the effect of intra-kernel temperature gradients in grain drying simulations. Sokhansanj and Bruce (1987) showed that temperature gradient models fit surface temperature data better than isothermal kernel models only during the first 200 seconds of drying, which seems insignificant when compared to the 15 to 24 hours required to kiln dry malted barley. Second, the assumption of spherically shaped grain in model (2), which was used to model temperature changes during the drying of both maize (Tolaba et al., 1988) and barley (Sokhansanj and Bruce, 1987) is unrealistic, since neither maize kernels nor barley kernels have a spherical shape. In these applications, the internal temperature gradients predicted by model (2) have no physical interpretation.

Modeling Malt Drying Rates During Kilning

Moisture movement during the drying of a porous solid is a complex process (Chirife, 1983). Upon examination of moisture histories during the air drying of food materials, several regimes can be observed, possibly including a period of constant drying rate followed by one or more falling rate periods (Fortes and Okos, 1980; Chirife, 1983). Each regime is controlled by different moisture movement mechanisms. The current view is that during drying, the rate of moisture movement is controlled by internal mass transfer, which can be made up of one or a combination of mechanisms. Diffusion of liquid due to concentration gradients, liquid movement due to capillary forces, and vapor transport due to

differences in partial vapor pressure can all play a role in water transport depending upon which drying regime is encountered.

Many theoretical drying models developed to account for single or coupled moisture movement mechanisms are available in the literature. In an excellent review, Fortes and Okos (1980) examined some of the most widely accepted theoretical drying models and concluded that, in general, existing theories for heat and moisture movement in capillary-porous bodies are not physically sound. Although a gross simplification, it is typical, when modeling grain drying rates, to assume that moisture movement is limited to one mechanism over the entire drying range. Several authors have assumed Ficks' second law of diffusion to apply.

$$\frac{\partial M(r,t)}{\partial t} = \nabla(\nabla M(r,t)) \quad (5)$$

To solve equation (5), the initial grain moisture content, $M(r,0)$, must be known, and boundary conditions depend upon assumptions for grain shape and moisture content at the grain surface. In the grain drying literature, many different approaches were found to solve equation (5). Sokhansanj and Bruce (1987) assumed a spherical shape and a moisture and temperature dependent moisture diffusivity, D , to successfully describe barley drying rates. Husain et al. (1973) assumed an infinite cylinder shape and a moisture and temperature dependent diffusion coefficient to describe rice drying rates. Pabis and Henderson (1961) assumed an infinite plane shape and a constant diffusion coefficient to describe

the drying rates of maize kernels. Whitaker and Young (1972) compared the results of solving equation (5) assuming a constant diffusion coefficient for infinite plane, infinite cylinder, sphere, and finite cylinder shaped kernels and concluded that the choice of cylindrical shape gave the best fit to peanut kernel drying data. Ingram (1976) found that the choice of an infinite slab geometry provided better results than the choice of a spherical geometry when simulating barley drying. It should be noted that in all of these studies, average moisture contents were calculated from the predicted moisture gradients. The average moisture contents were then compared with grain moisture content data; the moisture gradients predicted by equation (5) were never experimentally verified.

From a conceptual viewpoint, use of the diffusion model for grain drying is questionable. First, the shape of the grain is very important, and choosing an unrealistic geometric kernel shape based on closeness of fit to average moisture content data is incorrect. Second, grain is not a homogeneous material throughout, and physical differences would cause differences in diffusive characteristics within a kernel. Therefore, equation (5) certainly can not predict the actual moisture gradients present in grain during drying. Finally, using the diffusion model for predicting average grain moisture contents is a fairly difficult task, and much simpler models with similar predictive capabilities are available in the literature.

One very popular grain drying model, commonly chosen for simplicity, has been developed by assuming that at constant air temperature and relative

humidity, the rate of moisture loss of a grain kernel during drying is proportional to the difference between the average kernel moisture and the equilibrium moisture content of the kernel (Brooker et al., 1973):

$$\frac{dM_{avg}}{dt} = -K(M_{avg} - M_{eq}) \quad (6)$$

Equation (6) can be solved if the initial moisture content, $M_{avg}(0)$, and the drying conditions are known. O'Callaghan et al. (1971) used equation (6) to simulate barley and wheat drying in deep bed static driers and obtained acceptable results. Boyce (1965) used equation (6) to successfully simulate barley moisture changes in deep bed driers. The value of the drying coefficient, K , was assumed to have an Arrhenius-type dependence upon drying temperature:

$$K = K_0 e^{\frac{-E_a}{RT}} \quad (7)$$

Bala and Woods (1984) incorrectly used air temperature instead of grain temperature in equation (7) to estimate K for malt drying simulations. This common practice is appropriate only when grain temperature can be approximated by air temperature, such as when low-moisture grain is dried (Boyce, 1965; O'Callaghan et al., 1971). Evidence has been presented (Bruce, 1985) which suggests that the predictions of equation (6) would be much more accurate if an allowance was made for the dependence of K on grain moisture content. This seems reasonable because as the grain becomes drier, different mechanisms

control the drying rate and thus K may not remain constant. With a constant K and M_{eq} , the solution to equation (6) is:

$$M_{avg} = (M_0 - M_{eq}) e^{-Kt} + M_{eq} \quad (8)$$

Other equations have been used in grain drying simulations with varying results. Bala and Woods (1984) compared drying predictions using a modified form of equation (8)

$$M_{avg} = (M_0 - M_{eq}) e^{-Kt^u} + M_{eq} \quad (9)$$

and found no significant difference between the predictions of equations (8) and (9), even though equation (9) contains an extra data-fitting parameter, u . Tolaba et al. (1988) used yet another equation to simulate drying rates during corn drying,

$$\frac{dM_{avg}}{dt} = G_1 e^{-k_1 t} + G_2 e^{-k_2 t} \quad (10)$$

and obtained very good results. However, Tolaba's use of four fitting parameters, which have no physical basis, is inappropriate for process modelling. ~~Bure~~

(1985) compared the predictions from several equations including (5), (6) and (8) with data collected from unmalted barley drying experiments and found that the diffusion equation, equation (5), in spherical coordinates with a moisture and temperature dependent diffusion coefficient worked the best. The effect of moisture content and temperature on the diffusion coefficient, D , was described using the following complicated expression:

$$D = c_1 e^{c_2 T_{g,avg}} \left[e^{c_3 e^{c_4 (T_{g,avg} - c_5)^2 M_{avg}}} \right] \quad (11)$$

Bruce (1985) assumed that the value of the diffusion coefficient, D , equation (10), was dependent upon the grain temperature and moisture content. However, when comparing model predictions he assumed that the drying coefficient, K in equation (6), was a function of air temperature and when using equation (7), was assumed not to be affected by grain moisture content. Therefore, the comparison made by Bruce (1985) is really not a comparison of the prediction ability of actual models, but a comparison of the prediction ability of the number of fitting parameters used in the models. The results of Bruce (1985) would probably have been quite different if he had assumed that K had a complex dependence on moisture content and temperature and modeled it using five fitting parameters.

Malt Quality Indicators

American maltsters typically use over 20 different indicators to characterize the quality of one malt sample (Anonymous, 1987). Diastatic power, α -amylase, wort color, wort extract density, malt grinding properties, and many other indicators are collectively used to form an overall assessment of malt quality. In choosing indicators to examine kilning processes, consideration must be given to the importance of the indicator in brewing, and to the magnitude of change that the indicator experiences during kilning. The greatest quality changes observed during kiln drying are the alteration of color and flavor and the reduction of the

enzyme potential of the malt (Briggs et al., 1981). The activity of many different types of malt enzymes, including proteases, glucanases, and diastases, is important during the brewing process. Malt color also has a significant effect on beer quality.

Proteases - Malt proteases perform several important functions during the mashing step of beer production (Briggs et al., 1981). First, high molecular weight soluble proteins, which can later lead to haze problems in the finished beer, are degraded by proteases to smaller proteins which are less likely to contribute to haze formation. Increased concentration of smaller proteins and peptides in the wort also adds flavor, contributes to palatfullness and mouthfeel characteristics, and improves foam stability in the finished beer. Finally, proteolytic activity liberates free amino acids for later utilization by yeast during fermentation; the spectrum of amino acids metabolized by yeast ultimately influences the volatile composition of the finished beer and hence is very important in determining beer flavor and aroma.

The proteases consist of a complex mixture of endopeptidases and exopeptidases. During mashing, the endopeptidases are responsible for protein solubilization and the breakdown of large soluble proteins into smaller proteins. Therefore, this group of enzymes could be important in eliminating beer haze formation and adding to beer organoleptic properties. In brewing, the carboxypeptidases are the most important exopeptidases since they are responsible

for the liberation of the bulk of the amino acids produced during mashing (Baxter, 1978; Sopanen et al., 1980). However, Sopanen et al. (1980) showed that the carboxypeptidases were not the rate limiting enzymes in the liberation of amino acids during mashing; carboxypeptidases and other exopeptidases are present in malt in such an excess that the extent of amino acid liberation is controlled by the available peptide substrates, which are produced by the limiting action of endopeptidases on large proteins. Denault et al. (1981) showed the importance of the endopeptidases in amino acid liberation by showing a good correlation between the amount of free amino nitrogen present in wort and the endopeptidase activity in the mash. The excess of the exopeptidases could be due to either the presence of only small quantities of endopeptidase in germinated barley, or endopeptidase could be more extensively degraded during kilning than other proteases. Baxter et al. (1980) have shown that the endopeptidases are more heat sensitive during high temperature germination than other proteases.

From a malt quality perspective, it appears that the ability to model endopeptidase deactivation during kilning would be advantageous. However, there appear to be between 12 and 16 different endopeptidases in barley, each one hydrolyzing a specific protein linkage (Burger and Schroeder, 1976). In addition, the activity of an endopeptidase mixture determined using one model substrate may be completely unrelated to the activity of that mixture determined using a different model substrate (Baxter, 1978). The endopeptidases have been difficult to characterize because apparently most do not hydrolyze the simple model

substrates used for activity determination (Burger and Schroeder, 1976). Because of the large number of unique endopeptidase enzymes present in barley and because of the difficulty in monitoring the deactivation of each individual enzyme, monitoring and modeling endopeptidase deactivation during kilning seems extremely difficult.

β -Glucanases - During mashing, the β -glucanases are responsible for the degradation of β -glucan gums. β -glucan gums, long chained polysaccharides composed of β -D-glucopyranose residues connected by β -(1,4) and β -(1,3) glycosidic linkages, can greatly increase wort viscosity and create problems in the brewing process (Briggs et al., 1981; Bamforth, 1985). Increasing β -glucanase activity during mashing has been shown to significantly increase filtration rates, lower wort viscosity, improve brewhouse yields, and retard β -glucan related colloidal instability problems, especially when high amounts of unmalted barley, corn or rice are used as adjunct (Enari, 1974; Denault et al., 1981).

The β -glucanases consist of a complex mixture of enzymes. High molecular weight, wort soluble β -glucan is produced by the action of β -glucan solubilase, a carboxypeptidase which releases protein-bound β -glucan from the barley cell walls (Bamforth et al., 1979). Soluble β -glucans are further degraded by systems of endo- β -glucanases and exo- β -glucanases. The endo- β -glucanases are the most important in brewing because they are most responsible for reduction of viscosity of the wort. Although Scott (1972) found that the endo- β -glucanases were not the

rate limiters of malt β -glucan breakdown during mashing and consequential viscosity reduction of the wort, his conclusions were based on mashing at 65°C, a temperature at which barley endo- β -glucanase deactivates quite rapidly (Briggs et al., 1981). Baxter et al. (1980) have shown that endo- β -glucanase in green malt is highly sensitive to heat, which suggests that endo- β -glucanase could be extensively degraded during kilning. Endo- β -glucanase activity can be an important indicator of malt quality and it would be advantageous to monitor and model the deactivation of endo- β -glucanase during kilning.

Several endo- β -glucanases have been identified in malted barley and each is unique with respect to physical characteristics and substrate specificity. Endo- β -1,3-glucanase, also referred to as endo-laminarinase and carboxymethyl-pachymanase depending on the model substrate used for activity determination, hydrolyses β -glucans which contain only β -1,3 glycosidic linkages (Manners and Marshall, 1969). Endo- β -1,3-glucanase cannot degrade β -glucans with mixed β -1,4:1,3 glycosidic linkages and therefore cannot hydrolyse high molecular weight barley β -glucan. Endo- β -1,4-glucanase, also referred to as cellulase (Fincher, 1980), has the capability of hydrolyzing the β -1,4 glycosidic linkage of β -glucans containing only β -1,4 linkages (cellulose) and β -glucans containing mixed β -1,4:1,3 linkages. Endo- β -1,4:1,3-glucanase, also named endo-barley- β -glucanase (Fincher, 1980), hydrolyses β -1,4 glycosidic linkages only in mixed β -1,4:1,3 linked glucans and is specific for sites which are adjacent to residues connected by a β -1,3 glycosidic link. Because of the ability to degrade mixed β -1,4:1,3 linked glucans,

endo- β -1,4-glucanase and endo- β -1,4:1,3-glucanase are considered to be the most important enzymes in the viscosity reduction of wort (Manners and Marshall, 1969). However, endo- β -1,4-glucanase, which arises in malt from microbes associated with the husk (Hoy et al., 1981) has been reported in only low levels in germinated barley and is affected little by kilning (Manners and Marshall, 1969). Endo- β -1,4:1,3-glucanase, on the other hand, has been found in high levels in germinated barley and deactivates significantly during kilning (Manners and Marshall, 1969).

Diastases - The diastatic enzymes are the most important enzymes in brewing because they are responsible for starch hydrolysis and subsequent production of fermentable and non-fermentable sugars during mashing. Diastatic degradation of the amylopectin and amylose that make up starch produces a mixture of glucose, maltose, maltotriose, maltotetraose, dextrans, and small quantities of many other sugars. The sugar composition of the wort determines the wort fermentability and ultimately influences the character of the beer it makes. The relative levels of sugars produced during mashing are dependent upon the temperature and duration of mashing and the quantity and quality of the diastase supplied by the malt.

Several malt diastatic enzymes have been characterized in the literature, including α -amylase, β -amylase, phosphorylase, α -glucosidase, and β -limit dextrinase (Briggs et al., 1981). Malt α -amylase, which exists as a complex system

of iso- α -amylases (MacGregor, 1978), randomly hydrolyses α -1,4 glycosidic linkages within amylopectin and amylose. α -amylase activity slows near chain ends and ceases near the α -1,6 branch points, producing from amylopectin a complex mixture of sugars of which only 20% is fermentable (glucose, maltose, and isomaltose) and 80% unfermentable (maltotetraose, higher order polysaccharides, and dextrans, the collective name for sugars which contain α -1,6 glycosidic linkages). β -amylase, which can be separated into two isoenzymic fractions by ion exchange chromatography (MacGregor et al., 1971a), rapidly releases maltose from the non-reducing end of amylose by catalyzing the hydrolysis of α -1,4 glycosidic linkages. β -amylase cannot hydrolyse α -1,6 glycosidic linkages nor can it hydrolyse α -1,4 linkages adjacent to α -1,6 linkages. The lone action of β -amylase on amylopectin is inadequate for brewing purposes, producing strictly maltose but leaving behind a large fraction of β -limit dextrin (amylopectin in which all outer amylose chains have been degraded to stubs at α -1,6 branch points). Phosphorylase releases glucose-1-phosphate by catalyzing the reversible hydrolysis of α -1,4 linkages at the non-reducing end of amylose. α -glucosidase has the ability to catalyze the hydrolysis of α -1,4 and α -1,6 glycosidic linkages at the non reducing end of amylopectin to produce glucose. α -glucosidase can also catalyze transglucosidation reactions, in which sugar residues from one amylopectin chain are transferred to another chain. β -limit dextrinase, also known as R-enzyme and debranching enzyme, catalyzes the hydrolysis of α -1,6 glycosidic linkages in dextrans. Although the presence of the other diastatic enzymes

contributes slightly to diastatic ability, the combined activities of α -amylase and β -amylase present the majority of diastatic action during mashing (Briggs et al., 1981). β -amylase produces maltose by degrading starch to β -limit dextrin. α -amylase hydrolyses internal β -limit dextrin α -1,4 bonds, which exposes non-reducing ends that are again susceptible to attack by β -amylase. α -amylase and β -amylase acting in concert will produce a wort that is about 75% fermentable and 25% non-fermentable, a composition which is ideal for brewing. The non-fermentable fraction is important because it survives into the finished beer where it contributes to beer sensory properties, although the degree of contribution is still questionable (Ragot et al., 1989; Brefort et al., 1989).

α -amylase has long been considered the most important diastatic enzyme (Schwimmer, 1981) and much research has been devoted to characterize it (MacGregor et al., 1971a,b; MacGregor, 1977, 1978). However, recent research (Delcour and Verschaeve, 1987) suggests that β -amylase activity is a far more critical indicator of diastatic power than α -amylase activity. Surprisingly, Delcour and Verschaeve (1987) present a simple linear relationship between diastatic power and β -amylase activity, independent of the α -amylase activity of the diastase. β -amylase is known to be much less heat stable than α -amylase (MacGregor et al., 1971a; Briggs et al., 1981) and much of the loss of diastatic power during kilning is due to the loss of β -amylase (Schwimmer, 1981). Narzi β and Rusitzka (1977) found that β -amylase is very sensitive to heat during the curing stage of kilning, i.e. when low-moisture-content malt is subjected to high

temperatures. β -amylase would be a good malt quality indicator to monitor during kilning.

Color - Malt color is a very important indicator of malt quality because the color of the final beer product is determined largely by the color of the malt used to produce it. The intensity of beer flavor and aroma contributed by malt, although difficult to monitor, is related to the intensity of malt color (Briggs, et al., 1981). Malt color is known to increase dramatically with kilning, especially during the curing stage, when the kiln temperature can be higher than 100°C (Hopkins and Krause, 1937). Because malt color is a very important indicator of malt quality and is dependent upon kilning conditions, malt color formation should be included in kilning modeling efforts.

Simulation of Enzyme Deactivation During Kilning

Very little information is available in the literature concerning the deactivation kinetics of β -amylase and endo- β -glucanase. In food systems, enzyme deactivation has been modeled using first order reaction kinetics (Luyben et al., 1980):

$$\frac{dE}{dt} = -k_E E \quad (12)$$

The dependence of the rate constant, k_E , on temperature is commonly described by the simple Arrhenius equation:

$$k_E = k_{EO} e^{\frac{-E_{aE}}{RT}} \quad (13)$$

The effect of moisture content on enzyme stability has been shown to be complicated (Rockland and Nishi, 1980) but has been modeled by Luyben et al. (1980) for the deactivation of catalase, lipase, and alkaline phosphatase as:

$$E_{aE} = E_{aEO} + (E'_{aEO} - E_{aEO}) e^{-pM} \quad (14)$$

$$\ln(k_{EO}) = \ln(k'_{EO}) + \ln(k''_{EO}) e^{-pM} \quad (15)$$

Modeling Malt Color Formation During Kilning

Color formation in malt arises via several different kinetic mechanisms (Fennema, 1976; Briggs et al., 1981; Thausing, 1887). Caramelization occurs when the soluble sugars present in green malt are subjected to heat, resulting in the transformation of sugars into highly unstable compounds which react to produce brown polymers. Pilar Buera et al. (1987a) showed that caramelization in model sugar solutions can contribute significantly to browning at temperatures as low as 55°C. Maillard browning is initiated with the condensation reaction involving amino acids and reducing sugars followed by Amadori rearrangement reactions; the resulting Amadori compounds react with amines to produce brown melanoidin pigments. Pilar Buera et al. (1987b) showed that Maillard browning in model solutions of glucose and glycine peptides can be a significant contributor to color formation at temperatures as low as 55°C. Thausing (1887) suggested that there

is a browning mechanism in malt involving oxygen uptake, most probably catalyzed by one or more oxidases. The complexity of the browning mechanisms has been illustrated by Pilar Buera et al. (1987a,b) who showed that browning rates are dependent upon which types of sugars and amines are present.

In modeling malt color formation during kilning, it would be extremely difficult to separate the effects of each individual browning mechanism, especially if differences in malt sugar, peptide, and oxidase content must be considered. A simpler approach would be to use a model commonly used to describe browning in foods (Labuza and Saltmarch, 1981) which assumes zero order reaction kinetics:

$$\frac{dB}{dt} = k_B \quad (16)$$

The effect of temperature on the zero order rate constant, k_B , is usually described by the Arrhenius relationship (Labuza, 1980a; Saguy and Karel, 1980; Labuza and Saltmarch, 1981):

$$k_B = k_{B0} e^{\frac{-E_{aB}}{RT}} \quad (17)$$

Labuza (1980b) used thermodynamic considerations to conclude that the magnitudes of the activation energy, E_{aB} , and the pre-exponential factor, k_{B0} , depend upon moisture content. From studies on browning in skim milk powders, Labuza (1980b) found that the log of the rate constant, k_{B0} , varied linearly with moisture content but found no difference in E_{aB} at different moisture contents.

To model color formation during potato disk drying, Mishkin (1983) chose to describe moisture effects by:

$$\ln k_{B0} = b_1 \ln M + b_2 \quad (18)$$

$$E_{aB} = b_3 M + b_4 \quad (19)$$

Another color formation model developed to describe data reflecting a mechanism other than zero order kinetics is (Pilar Buera et al., 1987a,b):

$$\frac{1}{\left(\frac{dB}{dt}\right)} = \frac{1}{K_{B0}} + \frac{1}{K_{B1} B} \quad (20)$$

where the kinetic constants K_{B0} and K_{B1} were each described by Arrhenius relations similar to equation (17).

Dynamic Modeling of Drying Processes

The use of dynamic modeling techniques has become increasingly popular due to the savings in experimentation time over the use of the traditional static modeling methods (Saguy and Karel, 1980). Dynamic modeling has been especially successful when applied to the simulation of drying rates and food quality losses during air drying (Mishkin, 1983); during drying processes, product temperature and moisture content are usually not constant so static experimentation is not feasible. Bruce (1985) used a combination of static and dynamic testing to determine the grain moisture and temperature functionality of the diffusion coefficient in barley drying simulations. Tolaba et al. (1988) used

dynamic modeling methods to determine four constants which best fit a double-exponential drying rate equation to corn drying data. Mishkin (1983) used dynamic techniques to model ascorbic acid degradation, color formation, and drying rates during air drying of potato disks, and presents an excellent description of the methodology involved.

The differences between static and dynamic modeling methods are best described using an example. Consider the first-order thermal deactivation of an enzyme with an Arrhenius-type rate constant:

$$\frac{d[E]}{dt} = -k_E[E] \quad (21)$$

$$k_E = k_{E0} e^{\frac{-E_{aE}}{RT}} \quad (22)$$

With static modeling, experiments are run at various constant temperature, T. At each constant temperature, enzyme levels ([E]) are monitored with time and plots of $\ln([E]/[E]_0)$ versus time can be fit by straight lines with slope $(-k_E)$. A plot of the set of $\ln(k_E)$ versus $(1/T)$ values can be fit by a straight line with slope $(-E_a/R)$ and intercept $\ln(k_{E0})$. Thus a set of isothermal experiments can be used to determine the constants k_{E0} and E_{aE} .

Alternatively, dynamic modeling methods can also be used to model enzyme deactivation. However, instead of static experimentation, dynamic or non-constant temperature histories are used. In this case, temperature is monitored as well as enzyme levels with time. The constants k_{E0} and E_{aE} are chosen so that

the model most closely fits the enzyme deactivation data found during the non-constant temperature period. k_{E0} and E_{aE} determination is most easily accomplished using an optimization method which finds the values of k_{E0} and E_{aE} by minimizing an objective function J such as:

$$J = \sum ([E]_{predicted} - [E]_{observed})^2 \quad (23)$$

Given a multivariable function $V = v(x_1, x_2, \dots, x_m)$, the minimum can be approached using two constraint types. If ℓ_i and u_i are lower and upper limits for the variable x_i , explicit constraints can be expressed as $\ell_i \leq x_i \leq u_i$ ($i = 1, 2, \dots, m$). Implicit constraint could be expressed as $G_j \leq 0$ with $G_j = g_j(x_1, x_2, \dots, x_m)$ for $j = 1, 2, \dots, n$. An initial feasible point must be provided in the Complex method where all constraints must be satisfied (Box, 1965). The calculation procedure begins by the search for $2m-1$ additional feasible solutions using the initial feasible point and random numbers. The next step is a systematic and iterative search for an improvement on the worst feasible solution. The convergence criterion to stop this iteration process is a negligible improvement in the objective function (23).

In our case this criterion was specified as follows:

$$\frac{V_{worst} - V_{best}}{V_{best}} \leq 0.001 \quad (24)$$

where V_{worst} and V_{best} are selected from the $2m$ objective function values available at a given iteration point.

RESEARCH GOALS AND OBJECTIVES

The principle objective of this research is the use and evaluation of dynamic modeling techniques to identify appropriate mathematical models which can be satisfactorily used to simulate malt drying and selected quality changes that occur during kilning. Dynamic modeling methods will be used to fit equations (1), (6), and (7) to malt temperature and moisture histories observed during thin-layer kilning experiments. The color formation model presented in equations (16) and (17) will be fit to malt color formation observed during kilning. The enzyme deactivation model given in equations (12), (13), (14), and (15) will be fit to observed β -amylase deactivation and endo-barley- β -glucanase deactivation data, also using dynamic modeling techniques. The end result will be a computer simulation of malt kilning that can estimate changes in malt moisture, temperature, color, β -amylase activity, and endo-barley- β -glucanase activity as they occur during kiln drying, and based on the temperature and relative humidity of the drying air.

DYNAMIC MODELING OF MALT DRYING DURING KILNING

ABSTRACT

Dynamic modeling techniques were evaluated and used to identify mathematical models best describing drying data obtained from thin-layer malt drying experiments. Seven thin-layer kiln trials were performed using air at various temperatures and relative humidities. Malt temperature and moisture content were monitored during drying. A constrained direct search optimization method was used to fit a common grain drying model to the data. In general, the resulting drying model estimated well the moisture and temperature histories observed during experimentation. The model under-predicted actual drying rates only at high malt moisture contents (above 40%). Further research is suggested to examine malt drying rates at these moisture contents, and to determine the applicability of the models and model parameters when drying conditions fall outside of those here examined.

INTRODUCTION

A computer simulation of the malt kilning process could be of great practical importance to the malting industry allowing the mathematical analysis of kiln operation parameters necessary to achieve desirable product characteristics. A mathematical malt drying model can be used to reduce the cost and time involved in kiln design, improvement, and control by reducing the number of experimental tests. Finally, the ability to predict moisture and temperature changes during drying is essential to describe temperature and moisture dependent changes in malt quality during kilning.

The thin-layer drying of cereal grains and barley malt has been successfully modeled using a simple equation (Boyce, 1965; O'Callaghan et al., 1971; Brooker et al., 1973; Bala and Woods, 1984):

$$\frac{dM_{avg}}{dt} = -K(M_{avg} - M_{avg, eq}) \quad (1.1)$$

The drying coefficient, K , was described using the Arrhenius model:

$$K = K_0 e^{\frac{-E_a}{RT_s}} \quad (1.2)$$

The governing equation describing malt temperature changes during drying has been developed by assuming uniform temperature throughout the kernel and performing an energy balance about the drying grain (Boyce, 1965; Bakker-Arkema et al., 1967; O'Callaghan et al., 1971; Rumsey and Thompson, 1984):

$$\frac{dT_g}{dt} = \frac{ha(T_a - T_g) + \rho \frac{dM_{avg}}{dt} (h_{fg} + C_v(T_a - T_g))}{\rho C_g + \rho C_w M_{avg}} \quad (1.3)$$

Traditionally, static experimentation has been required to determine the individual model parameters describing a physical process. However, during grain drying, grain temperature and moisture contents constantly change, and so static modeling attempts are not possible. This has led to model simplifications using unrealistic assumptions. For example, several authors (Boyce, 1965; O'Callaghan et al., 1971; Bala and Woods, 1984) have assumed that air temperature and not grain temperature determines the value of the drying coefficient used with equation (1.2). Grain temperature would be more realistic since moisture movement in grains during drying is controlled by internal mass transfer (Chirife, 1983) which is a function of conditions within the grain and not the air.

Numerical optimization techniques for fitting model parameters, particularly models using dynamic data, have become increasingly popular because of the increased availability of digital computers (Mizrahi and Karel, 1977; Saguy et al., 1978; Mishkin, 1983; Almonacid et al. 1992a,b). The aim of this work is the use of a dynamic modeling methodology to determine the parameters for the grain drying model described by equations (1.1 to 1.3) using malt kilning data obtained in a commercial pilot plant laboratory.

MATERIALS AND METHODS

Thin-layer Drying Experiments

Thin-layer malt drying experiments, with malt layers less than two kernels deep, were performed between January and December of 1990 using the pilot kiln (apparatus # 3-98, C. Seeger Maschinenfabrik, Stuttgart, Germany) at the malting pilot plant facilities of Great Western Malting in Vancouver, WA. One bag of 1989 Montana Klages barley was used to make all of the green malt needed in this study. Standardized conditions for the steeping cycle (9 h steep, 8 h air rest, 8 h steep, 8 h air rest, 8 h steep, and 8 h air rest, all at 12°C) and the germination schedule (4 d, above 45% moisture wet basis, 14.5°C, and 100% relative humidity) were used with Seeger steeping (Apparatus # 1-98, C. Seeger Maschinenfabrik, Stuttgart, Germany) and germination (Apparatus # 2-98, C. Seeger Maschinenfabrik, Stuttgart, Germany) equipment. Ninety grams of the resulting wet green malt (46% to 48% wet basis moisture content) were placed in a thin layer, less than two kernels deep, in each of the seven canisters available inside the kiln. Hypodermic thermocouple probes (Model hyp-0, Omega Scientific, Inc., Stamford, CT) were inserted into a malt kernel in two randomly-selected canisters to monitor grain temperature during drying. Error caused by heat conduction along the length of the probes was minimized by threading four malt kernels on the probe before inserting the final kernel whose temperature was to be measured. Two thermocouples (chromel constantan) were placed under the grain bed to determine the drying air temperature. All temperature values were

recorded using a data logger (Model 21X Micrologger, Campbell Scientific Inc., Logan, UT). The relative humidity of the drying air was determined from local atmospheric condition data (Anonymous, 1990) and use of a psychrometric chart.

The flow rate of the drying air was kept constant at 0.124 kg/s per m² of kiln bed. The drying air temperatures were chosen to cover the range commonly used in malt kilning. To observe drying behavior under different malt moisture content conditions, some of the kilning trials were begun after pre-drying the malt in the kiln at 45°C. No attempt was made to control the relative humidity of the drying air. The relative humidity values observed during experimentation were completely dependent upon local atmospheric conditions.

At regular time intervals, either 30 or 60 min, a randomly selected canister of malt was removed from the kiln and immediately replaced with another canister containing 90 g of wet malt; canister replacement was performed to insure a constant air flow rate throughout the kilning operation. The removal and replacement process was repeated until all of the original seven canisters were removed. The canisters containing the hypodermic thermocouple probes were the two canisters removed last. Immediately following removal from the kiln, the malt samples were placed in a cloth bag, immersed in a liquid nitrogen bath for rapid cooling, and stored in a freezer (-17°C) to await laboratory analysis.

Malt moisture content was determined using a modified convection oven method. After an initial period of pre-drying in the convection oven for 4-6 h at 103°C, malt samples were ground and assayed for final moisture content following

the standard convection oven methodology (Anonymous, 1987). The pre-drying step was performed so that the samples could be ground before moisture content determination as specified in the standard methodology (Anonymous, 1987).

Malt Drying Modeling and Simulation

The model describing the drying rate of malt is given in equation (1.1). Substituting equation (1.1) for dM/dt in equation (1.3) results in the following equation describing grain temperature during drying:

$$\frac{dT_g}{dt} = \frac{ha(T_a - T_g) - K\rho(M - M_{eq})[h_{fg} + C_v(T_a - T_g)]}{\rho C_g + \rho C_w M_{avg}} \quad (1.4)$$

The effect of grain temperature on K , the value of the drying coefficient, is given in equation (1.2). The value of the equilibrium moisture content, a function of drying air relative humidity and temperature, was modeled using an equation presented by Nellist (1976):

$$M_{eq} = q_1 - q_2 \log_{10}(1 - RH) - q_3 \log_{10} T_{air} \quad (1.5)$$

The heat of evaporation of water (J/kg) as a function of temperature is given by Luyben et al. (1980):

$$h_{fg} = 3.1146 \cdot 10^6 - 2,250(T_g + 273.15) \quad (1.6)$$

Many of the physical property parameters used in the malt drying model have been presented in the literature. The heat capacity of dry malted barley was determined by Bala and Woods (1984) who examined heat capacity data from two

different varieties of malt to obtain $C_g = 1,651$ (J/kg K). The heat capacity of water vapor, C_v , is approximately 1,880 J/kg K, and the heat capacity of liquid water is 4,187 J/kg K (Sokhansanj and Bruce, 1987). The density of the dry malt, ρ , was determined to be 570 kg/m³.

The simulation of malt moisture and temperature changes during kilning using the presented equations relies on iteration over successive time increments of Δt . Starting at time = 0, the values of K , M_{eq} , and h_{fg} are calculated from equations (1.2), (1.5), and (1.6). The values of the time derivatives of grain moisture and temperature, given in equations (1.1) and (1.4), are then calculated. Based on Euler's method (Constantinides, 1987), the derivative values are assumed constant over a small time increment Δt and are used to update the moisture and temperature values after the time increment. All calculations are repeated for successive time increments to generate moisture and temperature histories for the entire drying time. No significant changes in moisture or temperature predictions were encountered using time increments smaller than 10 s, so this was the value used throughout the study.

The model parameters not available in the literature, K_0 and E_a in equation (1.2), h_a in equation (1.4), and q_1 , q_2 , and q_3 in equation (1.5), were determined using a constrained direct search optimization method (Box, 1965; Reklaitis et al., 1983) to find the values which minimized the following objective function:

$$J = w_1 \sum (T_{g,observed} - T_{g,predicted})^2 + w_2 \sum (M_{avg,observed} - M_{avg,predicted})^2 \quad (1.7)$$

$T_{g,observed}$ are individual measurements obtained from each thermocouple. The weighing factors w_1 and w_2 were determined from an equation presented by Constantinides (1987). Assuming a standard deviation in moisture observations of 0.3% dry basis and a standard deviation in temperature measurements of 0.5°C with an overall ratio of 9.8 temperature measurements to 1 moisture measurement, the resulting values for the weighing factors are, $w_1 = 1/0.5^2$ and $w_2 = 9.8/0.3^2$. The use of the weighing factors ensure that variances in moisture and temperature data each have the same influence on the value of the objective function, equation (1.7).

In the fitting of the drying model to the malt kilning data, it was necessary to remove from the data set the first hour of experimental data for kiln runs #1 and #2, i.e. those with the highest initial moisture content. Inclusion of these data resulted in an inadequate fit of the model throughout the remainder of these two drying curves and increased fitting error on all remaining drying curves.

RESULTS AND DISCUSSION

A complete summary of the thin-layer drying conditions and observed data is given in Figures 1.1 through 1.7. The conditions of the drying air ranged from 50°C to 83°C and 1.8% to 7.3% relative humidity. Initial malt moisture content varied from 18.7% to 47.2% wet basis and final moisture contents fell in the range of 4% to 10.7% wet basis.

The unknown model parameters that best fit equations (1.1), (1.2), (1.4) and (1.5) to the experimental kiln data are presented in Table 1.1. The parameter values compare favorably to values found from similar drying experiments presented in the literature. Bala and Woods (1984) used Equation (1.2) to describe the temperature functionality of the drying coefficient in malted barley drying and reported a K_0 value of $1.196 \cdot 10^7 \text{ min}^{-1}$ and an E_a/R value of 6,820 K. The fact that values of K_0 and E_a determined in this study do differ somewhat from those presented previously is not surprising since Bala and Woods based the values of the drying coefficient on air temperature and not grain temperature. Also, drying rates are certainly dependent on the variety of barley and the degree of modification experienced during the steeping and germination processes used to produce the wet green malt before kilning. Using an empirical equation which relates the volumetric heat transfer coefficient of malted barley to air flow rate (Bala and Woods, 1984), an $h \cdot a$ value of $11,653 \text{ W/m}^3 \text{ K}$ was calculated at an air flux rate of $0.124 \text{ kg/m}^2 \text{ s}$ used in the kiln trials, which is in good agreement with the $h a$ value of $12,020 \text{ W/m}^3 \text{ K}$ obtained by fitting the drying model using the optimization method. Equation (1.6) has not been used previously to calculate the equilibrium moisture content of malted barley so a direct comparison of the values of q_1 , q_2 , and q_3 is not possible.

It is stressed that the parameter values should only be used in simulations when drying conditions fall within the ranges encountered in this study. For example, when simulating deep bed grain driers using layer-by-layer calculations

(Brooker et al., 1973), air relative humidity can be considerably higher than the upper limit observed in this study (7.3%), especially near the top of the bed. It is doubtful that the model predicting equilibrium moisture content, equation (1.6), would correctly predict the equilibrium moisture content in such a case, resulting in unrealistic drying rates.

Figures 1.1 through 1.7 illustrate the results of the drying simulations for all seven kiln trials. In general, the drying model fit well the data generated from the kilning trials. However, the model could not adequately predict the drying rates at the high moisture content range. Because of the complexity of moisture and heat transport mechanisms during drying, many authors have experienced difficulty in using grain drying models to estimate drying rates throughout the entire range of drying (Troeger and Hukill, 1971; Bruce, 1985). Also, in the drying of malted barley, the complexities increase because of the presence of grain rootlets (Briggs et al., 1981), and because of shrinkage which occurs primarily during the early stages of grain drying (Fortes and Okos, 1980). It is suggested that at high moisture contents, the rootlets contribute significantly to both moisture and heat transfer. As the water is removed from the grain, the rootlets quickly dry and shrink, resulting in a decrease in evaporative surface area and decreased energy transfer by convection. After a given moisture content is reached, no more shrinkage occurs and the malt maintains an approximately constant surface area throughout the remainder of drying. Therefore, drying models which assume constant surface area, such as the one used here, work well

only at lower moisture contents. A more comprehensive model for the prediction of drying rates at high moisture contents is a subject for further research.

CONCLUSION

A constrained direct search optimization method was a powerful aid in modeling the malt kilning process which allowed the determination of unknown model parameters that best fit experimental data. The thin-layer drying model developed can be used in the simulation of deep-bed malt drying operations, although it is suggested that the same methodology be used to determine model applicability when drying conditions fall outside the ranges encountered in this study. The modeling of malt drying rates with moisture content above 40% (wet basis) is a subject for further research.

TABLE 1.1 Parameter values for the best fit of model equations to the experimental malt kilning data.

Parameter	Value
K_0	$8.127 \cdot 10^6 \text{ min}^{-1}$
E_a/R	6,582 K
ha	12,020 W/m ³ K
q_1	0.3465 fraction, dry basis
q_2	0.0183
q_3	0.0661

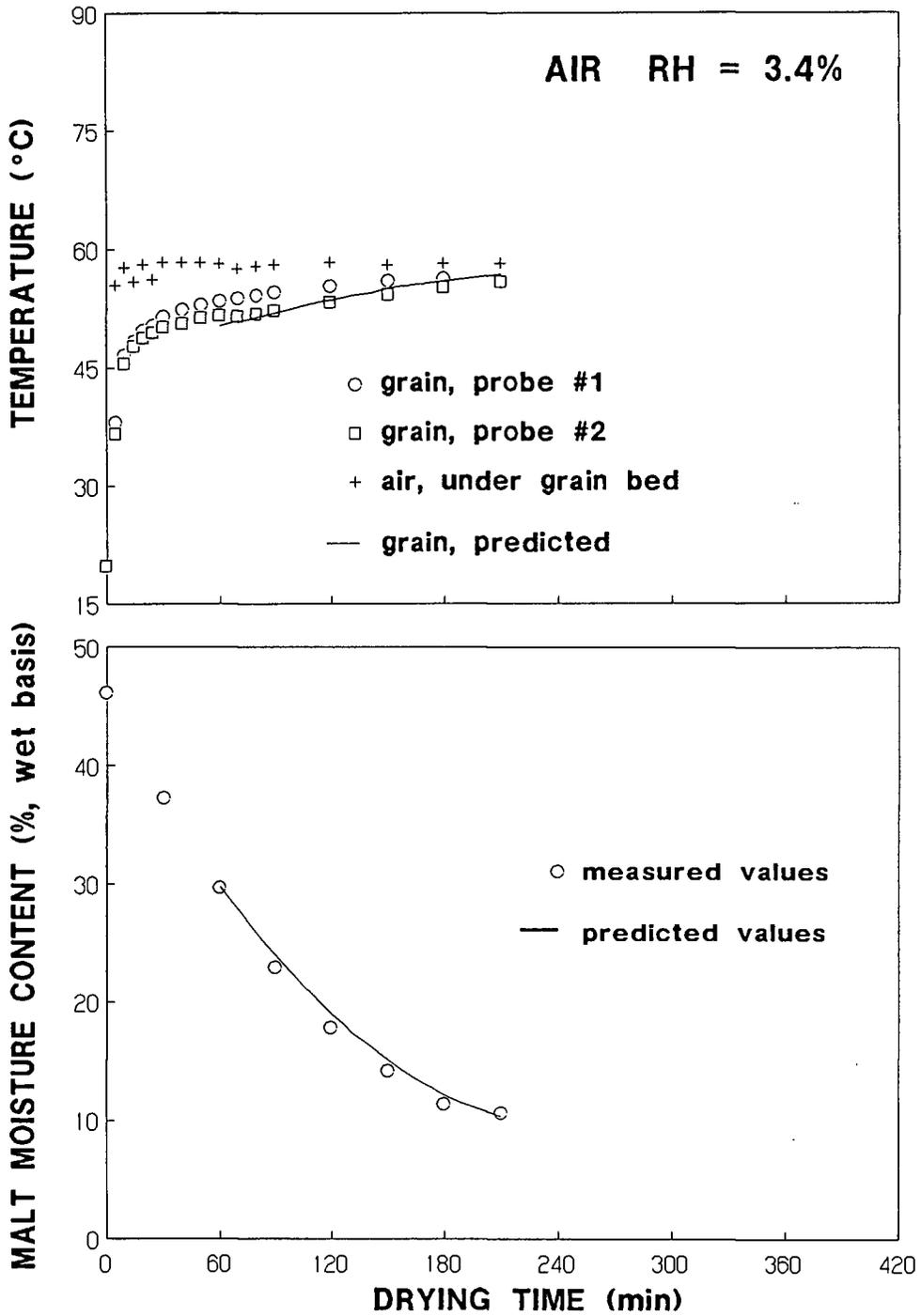


Figure 1.1 Drying conditions and malt moisture and temperature histories for kiln trial #1

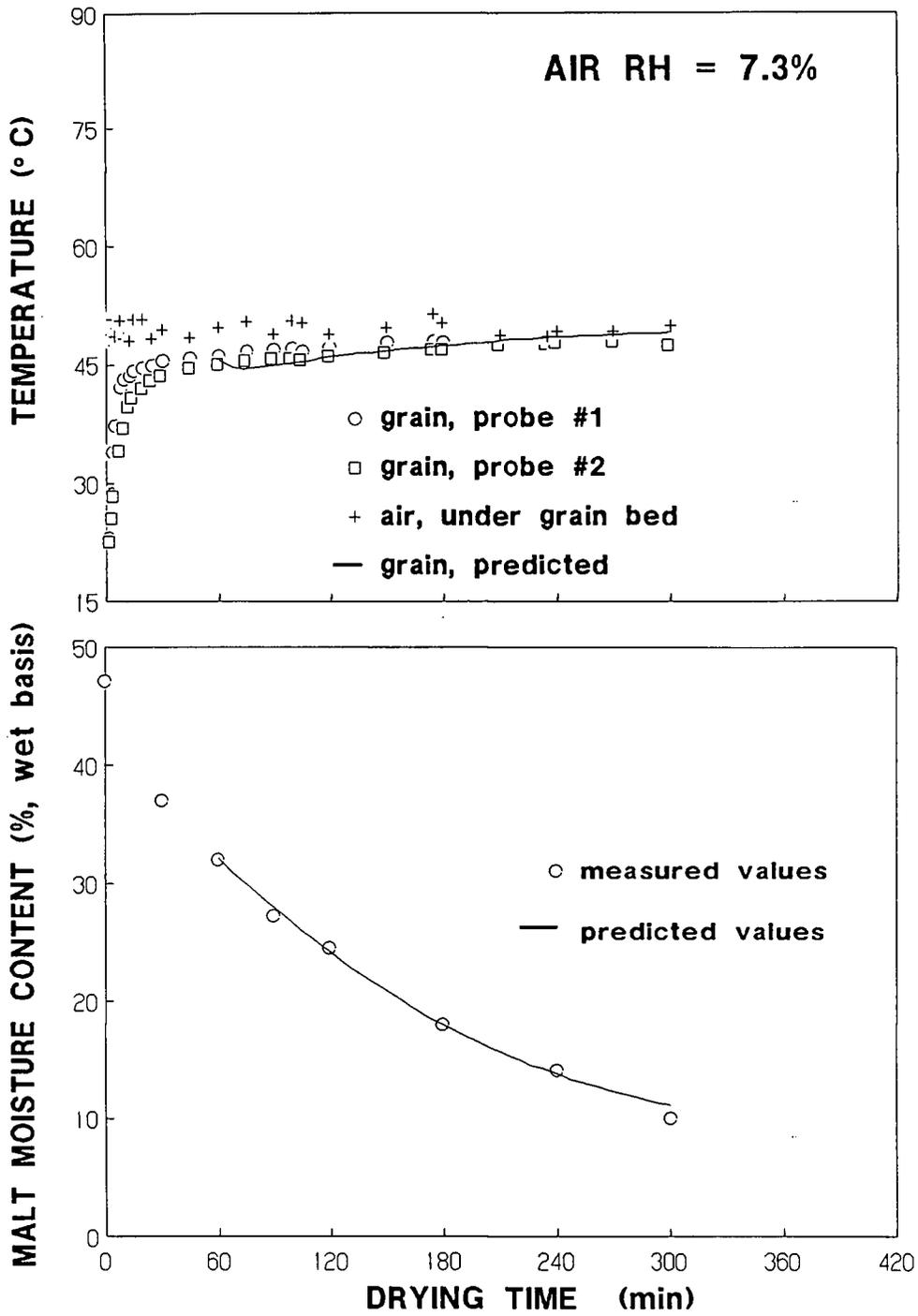


Figure 1.2 Drying conditions and malt moisture and temperature histories for kiln trial #2

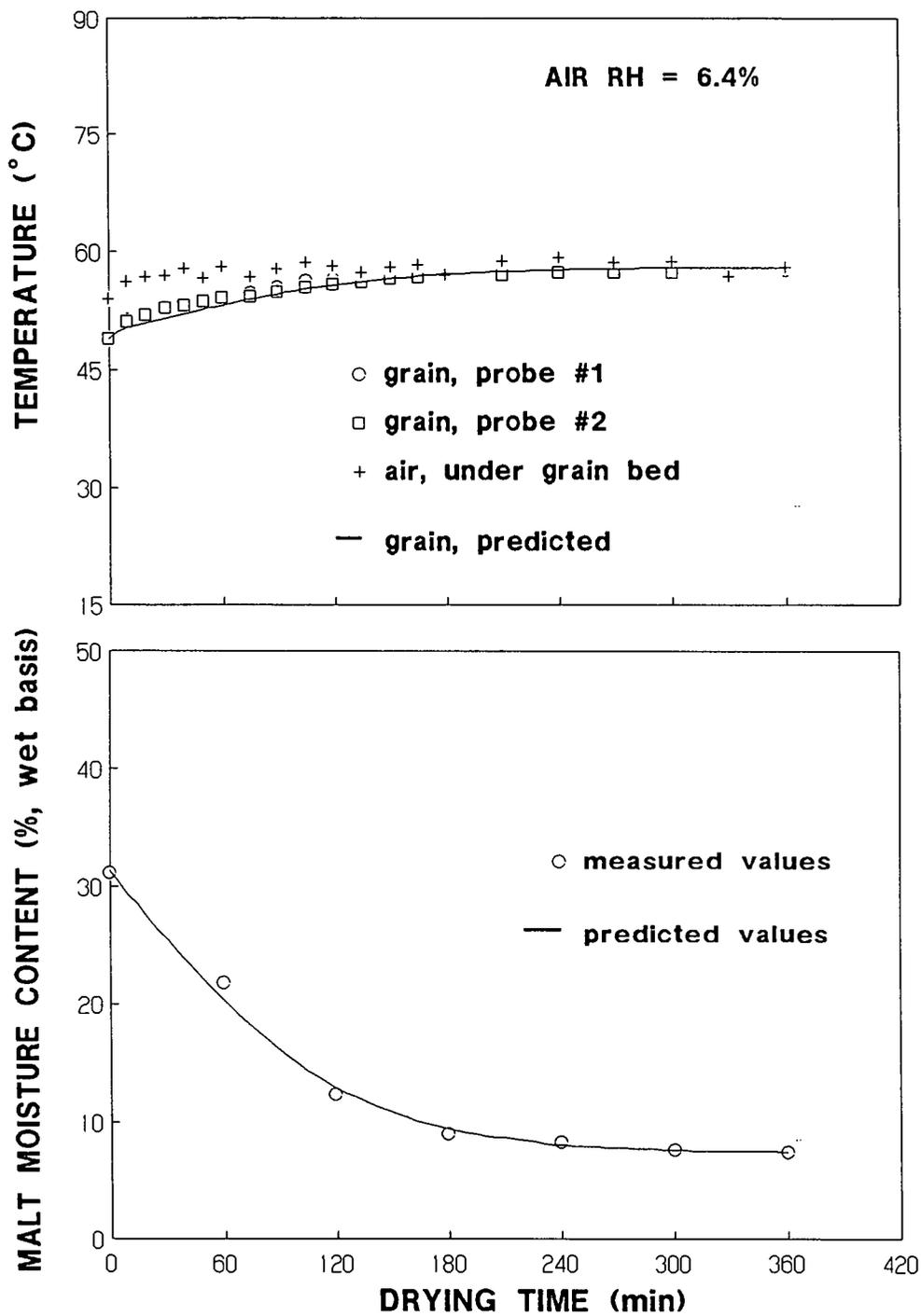


Figure 1.3 Drying conditions and malt moisture and temperature histories for kiln trial #3

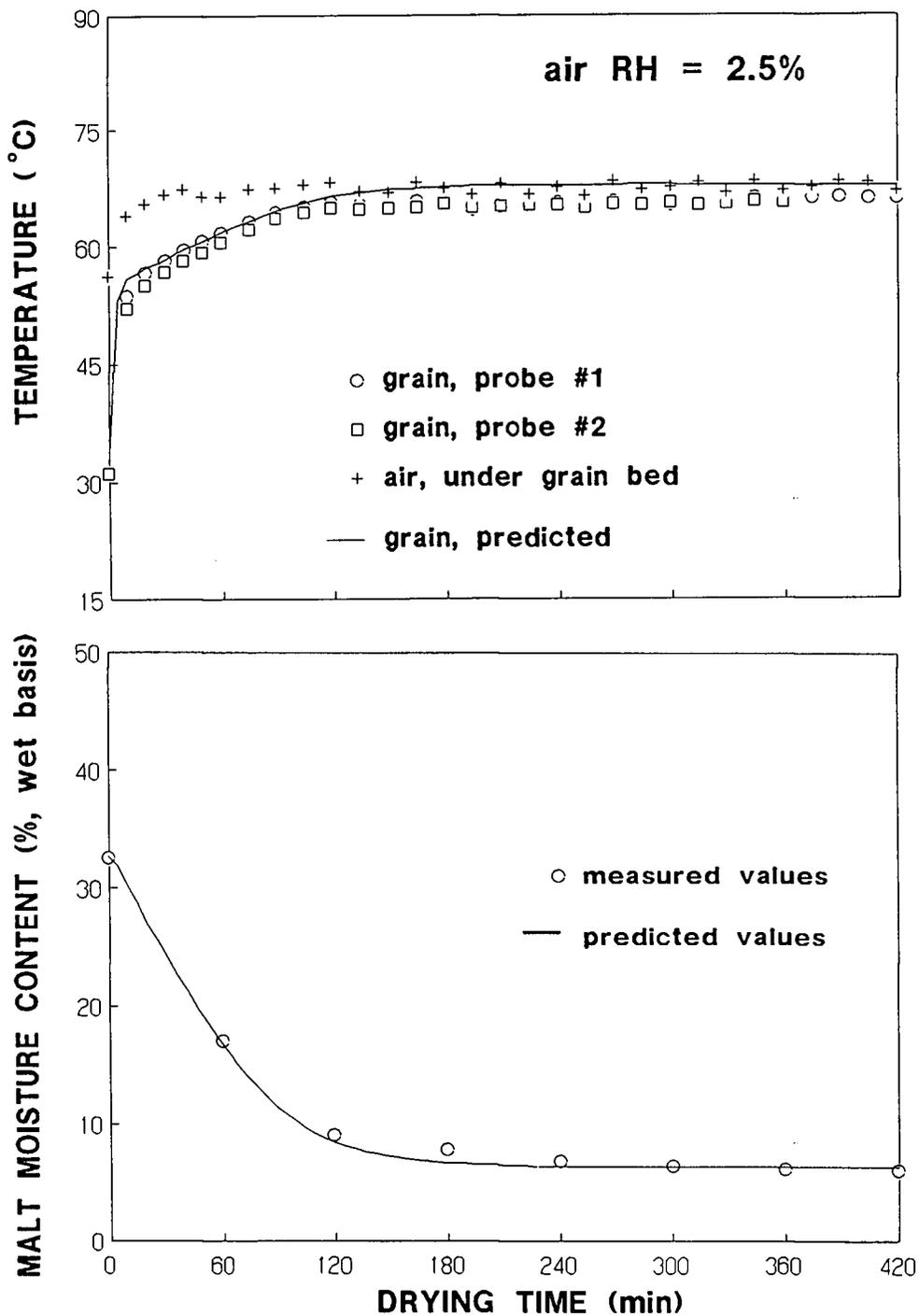


Figure 1.4 Drying conditions and malt moisture and temperature histories for kiln trial #4

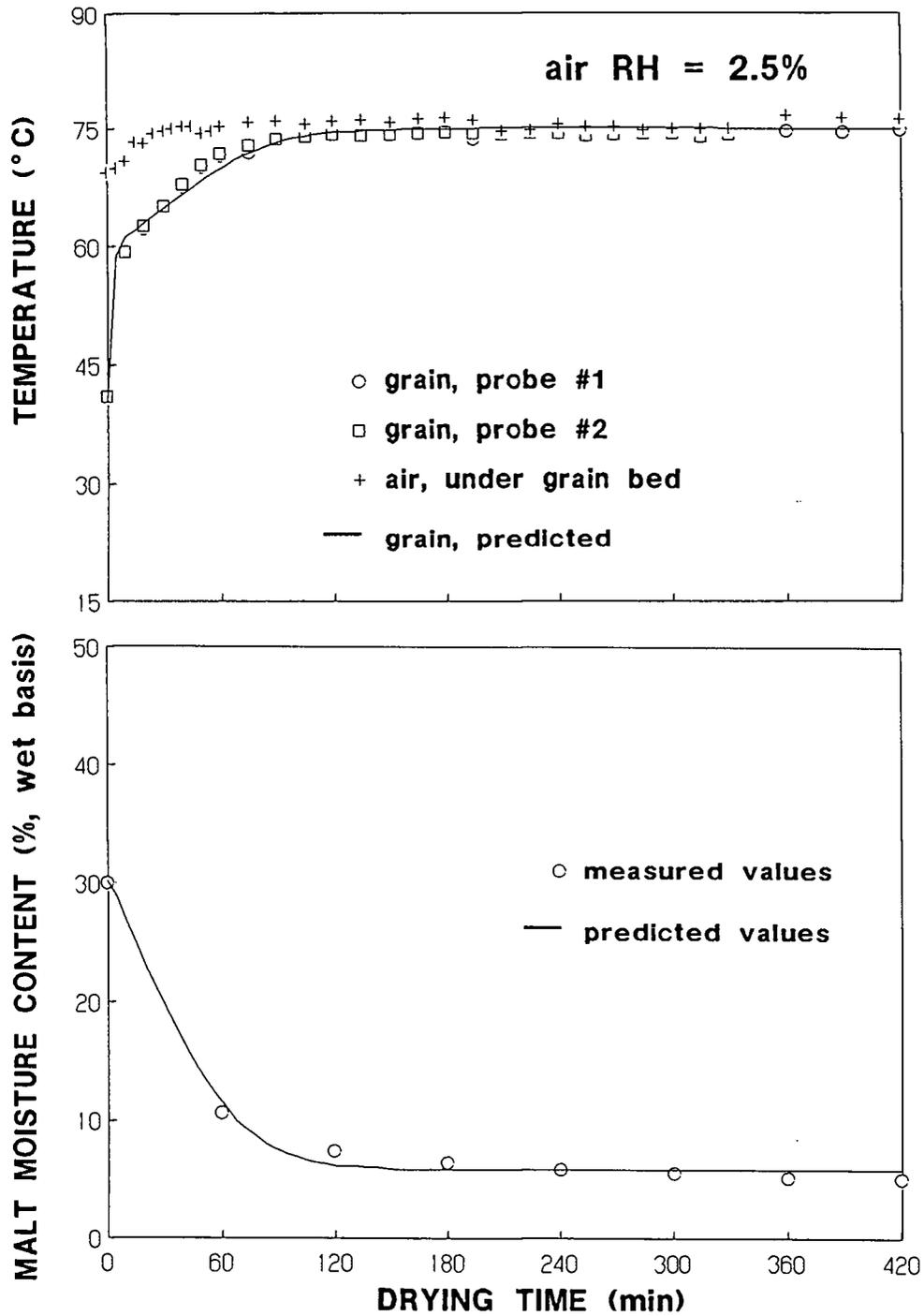


Figure 1.5 Drying conditions and malt moisture and temperature histories for kiln trial #5

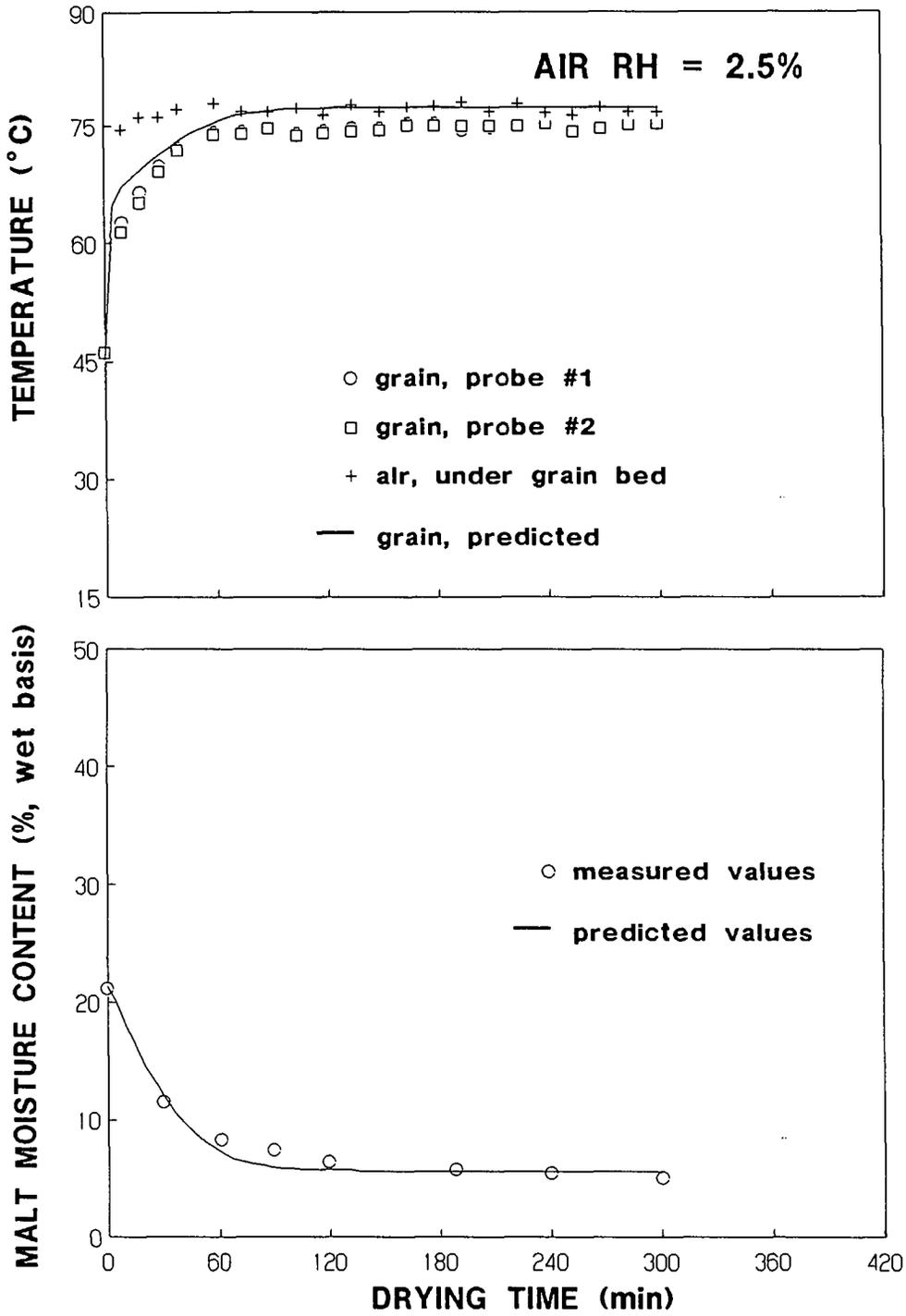


Figure 1.6 Drying conditions and malt moisture and temperature histories for kiln trial #6

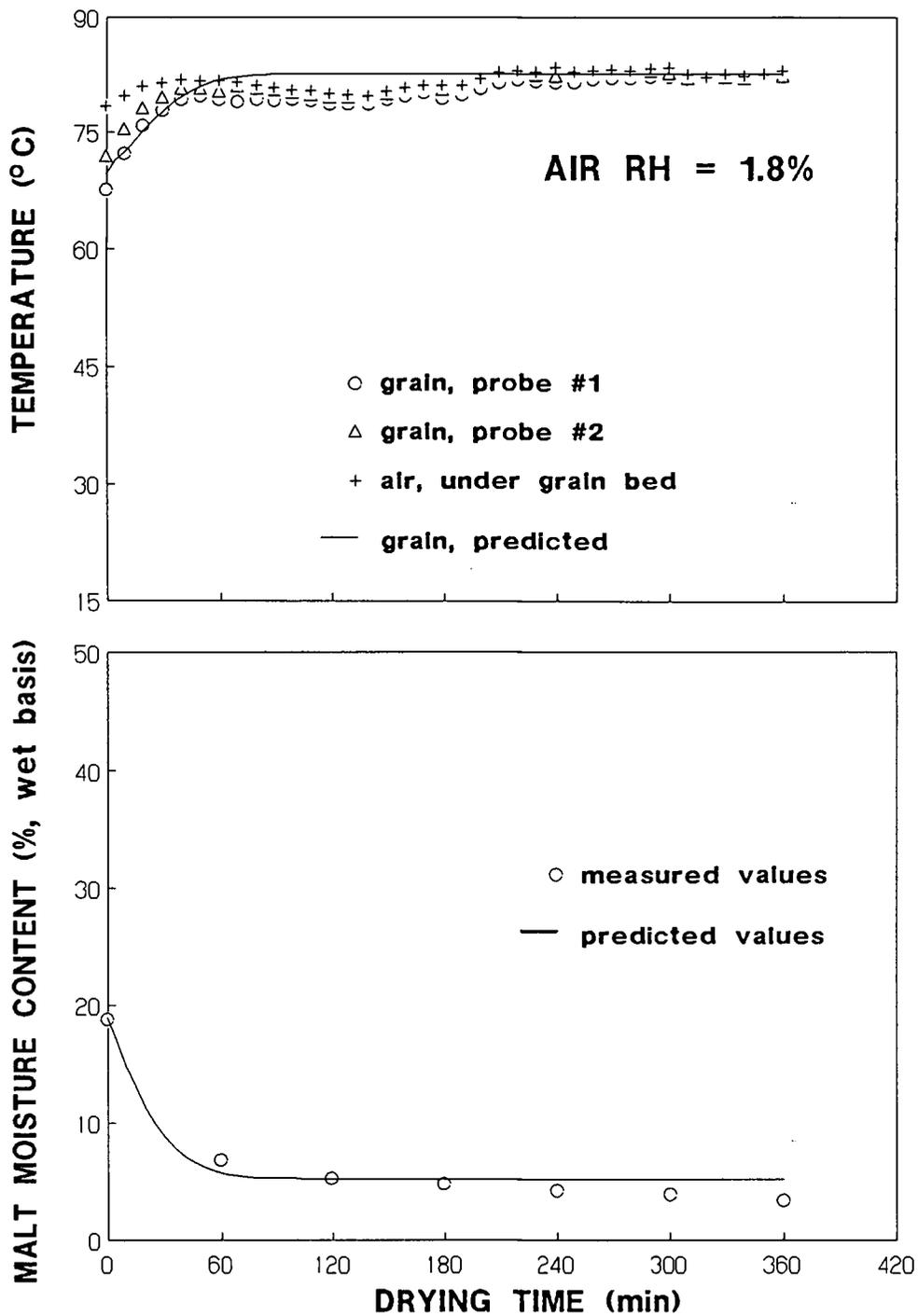


Figure 1.7 Drying conditions and malt moisture and temperature histories for kiln trial #7

**DYNAMIC MODELING OF MALT QUALITY CHANGES DURING
KILNING**

ABSTRACT

Dynamic modeling techniques were used to identify the parameters of mathematical models describing changes during kilning in color, β -amylase and endo-barley- β -glucanase activity. Seven thin-layer malt drying experiments were performed within a range of air temperature and slightly varying relative humidity. Malt temperature, moisture content, color, β -amylase activity, and endo-barley- β -glucanase activity were monitored during kilning. A zero-order color formation model and a five-parameter enzyme deactivation model were fit to the data using a constrained direct search optimization method. β -amylase deactivation was found to be insignificant and thus was not modeled. The color formation model adequately predicted the observed data while the enzyme deactivation model correctly predicted the observed deactivation trend of endo-barley- β -glucanase, but inaccurately predicted quantitative values.

INTRODUCTION

A general consideration when choosing a kilning schedule for the air drying of malted barley are the final malt characteristics. Biochemical changes that occur during malt kilning influence the acceptability of the finished malt and attempts must be made to control them. Before control of malt quality can be initiated, however, the effects of processing conditions on quality factors need to be determined. During the kilning process, the intensity of malt color can increase considerably depending on the drying conditions in the kiln (Hopkins and Krause, 1937; Briggs et al., 1981). The color, flavor, and aroma of finished beer are all significantly influenced by the malt from which the beer is made (Briggs et al., 1981). In many cases, brewers use color as a primary indicator of overall malt quality (Anonymous, 1987).

Enzyme deactivation is a detrimental result of malt kilning (Briggs et al., 1981). The activity of many different types of malt enzymes is important during beer production. Malt diastatic power, a factor used by the malting industry as an overall assessment of malt quality (Anonymous, 1987), indicates the degree of starch hydrolysis and sugar production that can occur during the mashing step of beer production. β -amylase, a relatively heat sensitive diastatic enzyme in malt (MacGregor et al., 1971; Briggs et al., 1981) is a significant contributor to diastatic power (Delcour and Verschaeve, 1987). Much of the loss of diastatic power during malt kilning is attributed to the deactivation of β -amylase (Narzi β and Rusitzka, 1977; Schwimmer, 1981). Endo-barley- β -glucanase is an extremely heat

sensitive malt enzyme (Baxter et al., 1980) and very important in the hydrolysis of β -glucan gums during mashing (Manners and Marshall, 1969). β -glucan hydrolysis increases filtration rates during sparging, lowers wort viscosity, increases yields, and improves beer stability (Enari, 1974; Denault et al., 1981). Although malt endo-barley- β -glucanase activity is not currently used in industry to assess malt quality, it is an important indicator of malt quality.

The ability to mathematically simulate color formation, β -amylase deactivation, and endo-barley- β -glucanase deactivation in malt during kilning would allow the determination of kilning conditions required to control malt quality. Mathematical models for color formation and enzyme deactivation during drying are available in the literature. Color formation in foods is commonly modeled assuming zero order reaction kinetics (Labuza and Saltmarch, 1981):

$$\frac{dB}{dt} = k_B \quad (2.1)$$

The zero order rate constant, k_B , is usually given an Arrhenius temperature dependence (Labuza, 1980a; Saguy and Karel, 1980; Labuza and Saltmarch, 1981):

$$k_B = k_{B0} e^{\frac{-E_{aB}}{RT}} \quad (2.2)$$

The equation describing enzyme deactivation as a function of product temperature and moisture content is due to Luyben et al. (1980), who have modeled enzyme deactivation in food systems using first order reaction kinetics:

$$\frac{dE}{dt} = -k_E E \quad (2.3)$$

The rate constant, k_E , was assumed to follow an Arrhenius temperature dependence:

$$k_E = k_{E0} e^{\frac{-E_{aE}}{RT}} \quad (2.4)$$

with k_{E0} and E_{aE} assigned the following moisture functionality:

$$E_{aE} = E_{aE0} + (E'_{aE0} - E_{aE0}) e^{-pM} \quad (2.5)$$

$$\ln k_{E0} = \ln k'_{E0} + \ln k''_{E0} e^{-pM} \quad (2.6)$$

Equations (2.4) through (2.6) can be combined and rewritten in terms of fitting constants x_i ($i=1$ to 5) to obtain an equivalent model for k_E :

$$k_E = e^{x_1 - \frac{x_4}{T}} - \left(x_2 + \frac{x_5}{T} \right) e^{-x_3 M} \quad (2.7)$$

Because malt temperature and moisture content continually change during drying, the traditional static methods of kinetic modeling are not applicable. Dynamic modeling methods are available and have been used to model the kinetics of nutrient loss (Saguy et al., 1978; Mishkin, 1983) and enzyme deactivation (Mishkin, 1983) during the drying of foods.

The purpose of this study is to examine the changes during kilning of three malt quality factors, color, β -amylase activity, and endo-barley- β -glucanase activity,

and to use dynamic modeling techniques to determine the fitting parameters for the conventional models presented above.

MATERIALS AND METHODS

Thin-layer Drying Experiments

Seven thin-layer malt drying experiments, employing malt layers less than two kernels deep, were performed between January and December of 1990 using the Seeger pilot kiln (Apparatus # 3-98, C. Seeger Maschinenfabrik, Stuttgart, Germany) at the malting pilot plant facilities of Great Western Malting in Vancouver, WA. Malt temperature was measured with two hypodermic thermocouple probes, each implanted in a different malt kernel. Error caused by heat conduction along the length of the probes was minimized by threading four malt kernels on the probe before inserting the final kernel whose temperature was to be measured. Malt samples were removed from the kiln at regular time intervals and stored for later laboratory analysis.

The temperature and relative humidity conditions of the drying air used for all kiln trials are presented in Table 2.1. A complete summary of the sample handling procedures and the malt temperature and moisture content histories experienced during drying was presented in a previous chapter (Figs. 1.6-1.7). Samples obtained during kiln trials #1 through #6 were assayed for endo-barley- β -glucanase activity. Samples obtained during kiln trials #1, #4, #5, and #7 were

assayed for wort color. Samples obtained during kiln trials #1, #3, #4, #5, and #6 were assayed for β -amylase activity.

Color Assay Methodology

The color assay procedure is based upon the standard reference method (Anonymous, 1987). Because malts with a large range moisture contents were assayed, the procedure was altered by assaying samples on an equal dry weight basis instead of an equal total weight basis. All specified sample and reagent volume and weight measurements were reduced by 50% because of sample size limitations.

Samples corresponding to 25 g dry basis were weighed (± 0.02 g) into a tared grinding container and made to 150 g total (± 1 g) with deionized water. The sample was then ground in water for 120 s using an Osterizer Pulse-Matic blender (Oster Corp., #890-16L, Milwaukee, WI) on the "liquify" setting. The resulting suspension was placed into a tared mashing container. The grinding container was rinsed with 50 mL deionized water and the rinse was added to the suspension in the mashing container. The sample was then mashed according to the American Society of Brewing Chemists (ASBC) standard mash time and temperature. During mashing, further addition of deionized water as stated in ASBC methods was not performed because water had already been added during grinding. After mashing, deionized water was added to a final total weight of 225 g. Filtering and spectrophotometric measurements were performed following the

ASBC methodology. Color was reported as °SRM (degrees, standard reference method).

β -amylase Assay

The assay method for evaluating malt β -amylase activity in the presence of α -amylase is based upon the work presented by Mathewson and Seabourn (1983) and sold in kit form by BIOCON (Lexington, KY). The method is based upon the rapid degradation of p -nitrophenyl- α -maltopentaoside (PNP5), a reaction catalyzed specifically by β -amylase. In the presence of β -amylase, PNP5 is degraded to p -nitrophenol, which exhibits a yellow color under basic conditions. The degree of color formation, measured spectrophotometrically, is proportional to the degree of PNP5 degradation and thus indicates β -amylase activity. One unit of β -amylase activity is defined as the amount of enzyme required to provide 1 μ -mole p -nitrophenol/min under assay conditions. Assays were conducted on an equal dry weight basis of 5 g instead of an equal total weight basis because of the extreme range in malt moisture content conditions encountered in this study. Also, to decrease the error associated with measurement of the small quantities specified by BIOCON, the weight and volume amounts of all substrates and samples were doubled.

Endo-barley- β -glucanase Assay

An assay for the evaluation of endo- β -glucanase activity in malt has been presented by Scott (1972) and consists of an enzyme extraction from malt followed by an activity determination. Although Scott (1972) monitored the reduction in viscosity of the β -glucan solution while it was acted upon by the enzyme extract, the FIA method presented by Mekis et al. (1983) was used in this study. This method is based on the fluorescent characteristics of the complex created by combining the calcofluor reagent and large β -glucans (greater than 10,000 Dalton). A malt extract is injected into a flow of calcofluor solution, which is passed through a fluorometer and measured for fluorescence (350 nm excitation, 420 nm emission). This method is currently used by Great Western Malting to evaluate β -glucan content in barley and malt. The procedures for the preparation of β -glucanase extracts of malt and for performing the enzyme/substrate incubation are similar to those presented by Scott (1972). Assays were performed on an equal dry weight basis because of the large difference in moisture content between individual samples. Enzyme and substrate concentrations and incubation times were changed to simplify the procedure and reduce the assay time. Also, the samples were not heated following incubation after addition of mercuric chloride because it was found that mercuric chloride addition effectively deactivated the enzymes and further heating was not necessary. Again, the concentration of β -glucan in solution was determined using the FIA method and not viscometrically.

Samples, 4 g dry basis, were weighed into a tared grinding container (± 0.02 g). Buffer (0.1 M sodium chloride, 20 mM phosphate, 10 mM citrate, and 1 mM cysteine hydrochloride at pH 5.0) was added to obtain a total weight of 200 g (± 0.1 g). The sample was ground in buffer for 120 s with an Osterizer Pulse-Matic blender (Oster Corporation, #890-16L, Milwaukee, WI) on the "liquify" setting. The resulting suspension was allowed to sit at room temperature for extraction. The suspension was then filtered through standard lab filter paper (Ahlstrom Filtration #509) and 4.8 mL filtered extract was mixed with 5 mL of 600 ppm solution of barley β -glucan (BIOCON, Lexington KY, batch #724086) in buffer and incubated at 25 °C for 15 min. A 0.2 mL aliquot of 0.1 M mercuric chloride was then added to deactivate the enzyme with the mixture immediately cooled in an ice bath. Final β -glucan concentration was determined using the FIA method presented by Mekis et al. (1983). An additional 4.8 mL of filtered extract was mixed with 0.2 mL of 0.1 M mercuric chloride before adding 5 mL of 600 ppm β -glucan substrate, to give a non-incubated sample. β -glucan concentration of the non-incubated sample was also determined by the FIA method. One unit of endo-barley- β -glucanase activity is defined as the amount required to degrade 1 ppm β -glucan/15 min.

Fitting Quality Deterioration Models

The differential equations of the model were solved by Euler's method which assumes that derivatives are constant over a small time step and equal to

the value at the beginning of that time step (Constantinides, 1987). No improvement was observed in the predictions using time increments less than 10 s, so 10 s was used throughout this study. Grain temperature, which was not constant during the drying operation, was used to calculate the rate constant for the color formation model using equation (2.2). Grain moisture and temperature were used in equation (2.7) to calculate the enzyme-deactivation rate constant. Malt temperature histories were fitted by averaging the values from the two thermocouple probes and performing linear interpolations between the data points. Malt moisture values were obtained by linear interpolation between experimental data points. A summary of actual malt temperature and moisture histories observed during the kilning trials was presented in Figures 1.1 to 1.7.

The unknown parameters, k_{B0} and E_{aB} in equation (2.2), were determined using a constrained direct search optimization method (Box, 1965) to find the values of the parameters which minimize the following objective function:

$$J = \sum (B_{observed} - B_{predicted})^2 \quad (2.8)$$

The unknown parameters x_1 , x_2 , x_3 , x_4 , and x_5 in equation (2.7) were determined using the same procedure to minimize a second objective but similar objective function:

$$J = \sum ([E]_{observed} - [E]_{predicted})^2 \quad (2.9)$$

In mathematical terms, the color formation model and the enzyme deactivation model are both initial value problems; that is, each model requires

an initial value of the quality indicator at time = 0 to predict the values of the indicator for $t > 0$. A false initial value results in a false prediction of the change in the quality indicator over time. The initial indicator variable values have errors associated with their experimental determination. The effect of these experimental errors on model predictions were reduced by including the initial indicator variable values as fitting parameters when minimizing the objective functions (2.8) and (2.9).

RESULTS AND DISCUSSION

The observed deactivation of malt β -amylase is shown in Figure 2.1. A statistical analysis on 5 replications of a green malt sample indicated a standard deviation of 149 β -amylase units/g. All β -amylase history data fall within 2 standard deviations of the average of the data. Therefore, β -amylase deactivation was considered insignificant and was dropped from the modeling analysis. β -amylase may have been significantly deactivated during kiln trial #7, which was the highest temperature used in all kiln trails. However, kiln trial #7 was performed only to obtain more data for the color formation model and analysis for β -amylase activity was not performed for this trial. The lack of β -amylase deactivation is surprising, since β -amylase deactivation during kilning at high temperature has been reported in the literature (Narzi β and Rusitzka, 1977). However, within the range of kilning temperature used in this study, which was chosen to cover the range of temperatures used in normal kilning operations,

β -amylase deactivation can be considered insignificant and results of modeling β -amylase deactivation are not presented.

It is interesting to note the affect of moisture content on the deactivation of endo-barley- β -glucanase shown in Figures 2.4 through 2.6. At high moisture content, the enzyme deactivates rapidly with deactivation slowing or ceasing as the grain becomes drier. The model parameters for the best-fit of the color formation model to the experimental data are given in Table 2.2. Color modeling was quite successful as indicated in Figures 2.1 and 2.2. Malt browning during kilning appears to be very heat sensitive and is reflected in a high value for the activation energy (Table 2.2). Browning rates more than double when grain temperature is raised from 75°C to 82°C.

The observed color formation, shown in Figures 2.2 and 2.3, indicate an almost linear relationship between color and time of kilning, so a zero-order rate model should describe the data well. The model parameters for the best-fit of the endo-barley- β -glucanase deactivation model to the experimental data are given in Table 2.3. Figures 2.3 through 2.5 show that although the endo-barley- β -glucanase deactivation model does not fit the data extremely well, the model can still be used to analyze processing effects. The lack of model fit to the actual data suggests complex moisture and temperature functionality of the deactivation of endo-barley- β -glucanase. Models of enzyme deactivation during food drying are quite scarce and further work should be considered to develop more acceptable models.

CONCLUSION

A dynamic modeling methodology was used successfully to fit available quality deterioration models to malt color formation and endo-barley- β -glucanase deactivation data. Even though the enzyme deactivation model does not quantitatively describe the deactivation of endo- β -glucanase very well, it does describe the general trend and can still be used to estimate processing effects trends. The deactivation of β -amylase was found to be insignificant within the range of drying conditions used. Finally, the models obtained can be combined with malt drying rate models to estimate changes in malt quality as affected by air temperature, relative humidity, and drying time. Also, the methodology presented in this paper can be extended to model other quality changes during malt kilning. However, further research is required to develop assay procedures for the determination of other important compounds in malt, including toxins, pesticides, and herbicides. The development of adequate mathematical models with which to describe chemical reaction kinetics during drying for these factors is a subject for future research.

TABLE 2.1 Drying air temperature and relative humidity conditions during kiln trials #1 through #7

Kiln trial #	Air temperature (°C)	Relative humidity (%)
1	58	3.4
2	50	7.3
3	58	6.4
4	68	2.5
5	75	2.5
6	78	2.5
7	82	1.8

TABLE 2.2 Parameter values for Equations (2.1) and (2.2) determined by dynamic modeling of experimental malt color formation

Parameter	Value
K_{B0}	$2.24 \cdot 10^{21} \text{ min}^{-1}$
E_{aB}/R	19,200 K

TABLE 2.3 Parameter values for Equations (2.3) and (2.7) determined by dynamic modeling of experimental endo-barley- β -glucanase deactivation

Parameter	Value
x_1	53.2
x_2	0.29
x_3	3.78 kg dry solid/kg
x_4	19,330 K
x_5	3,317 K

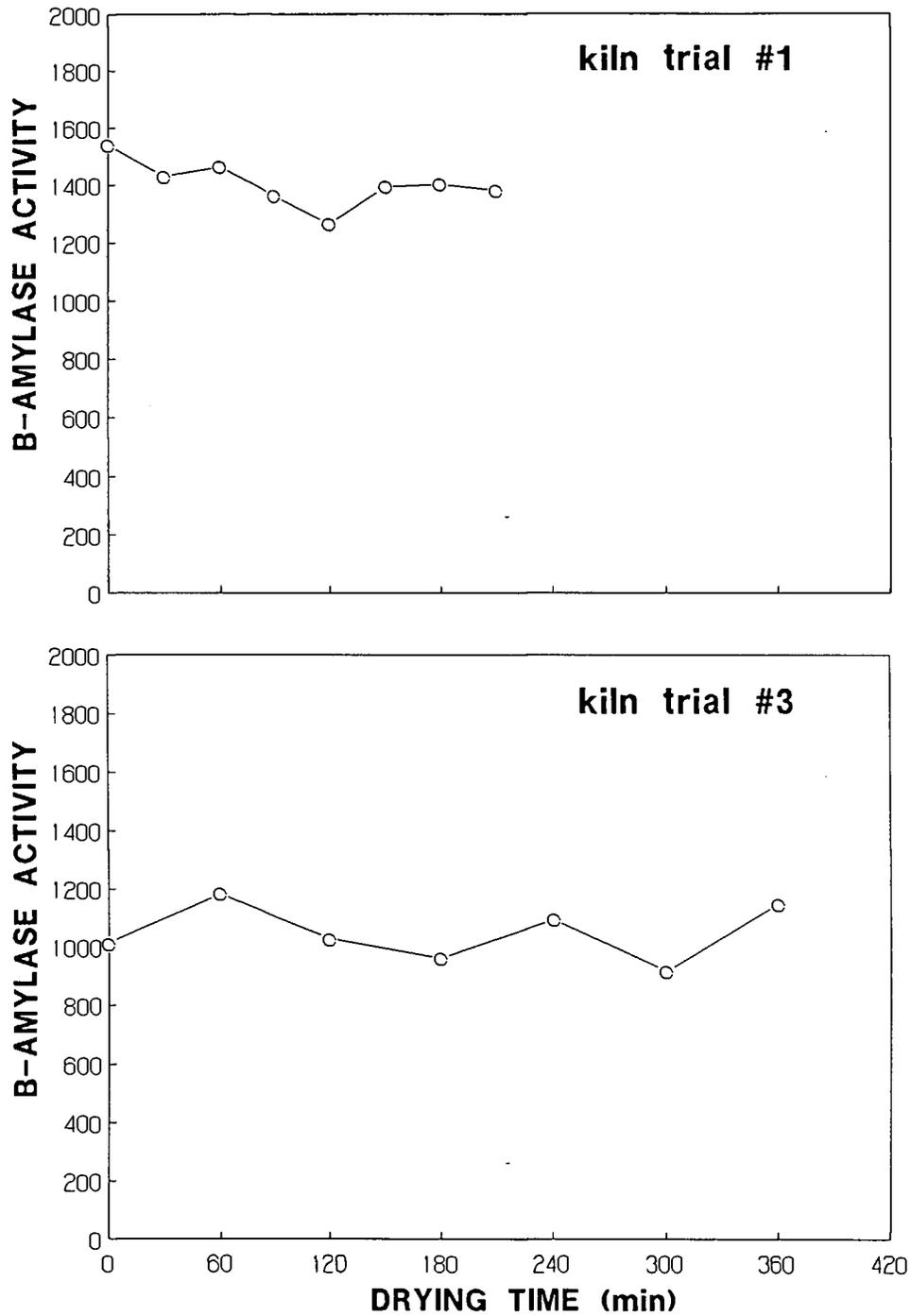
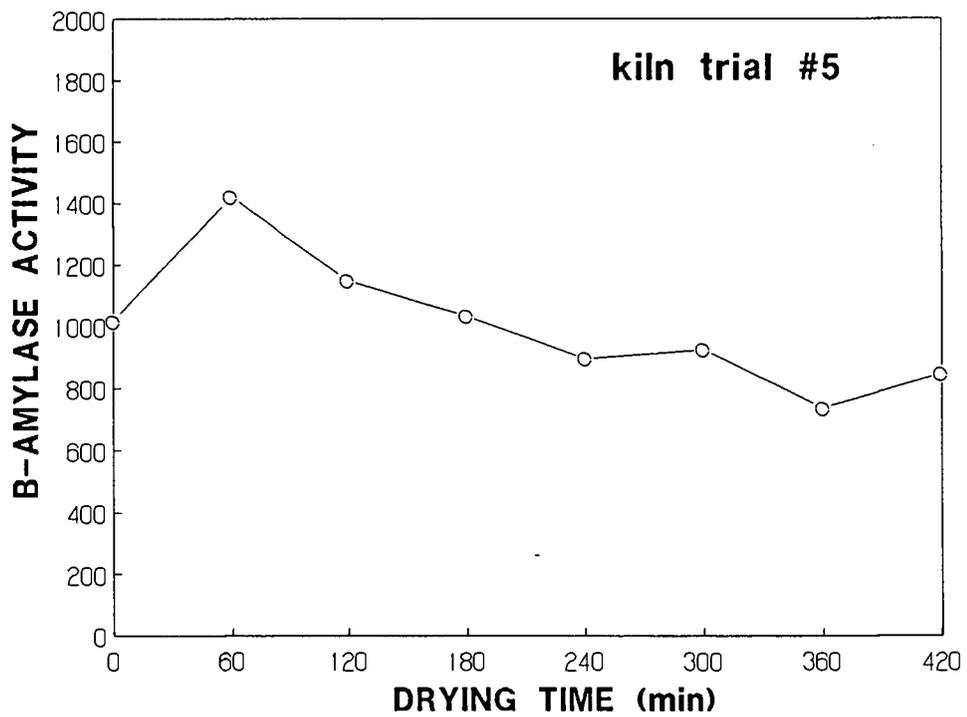
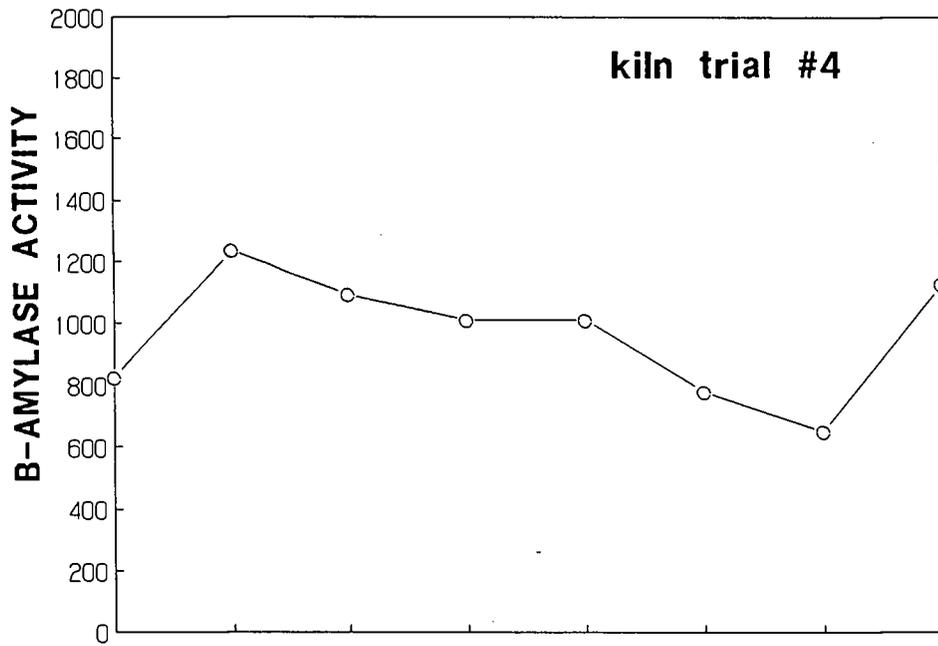
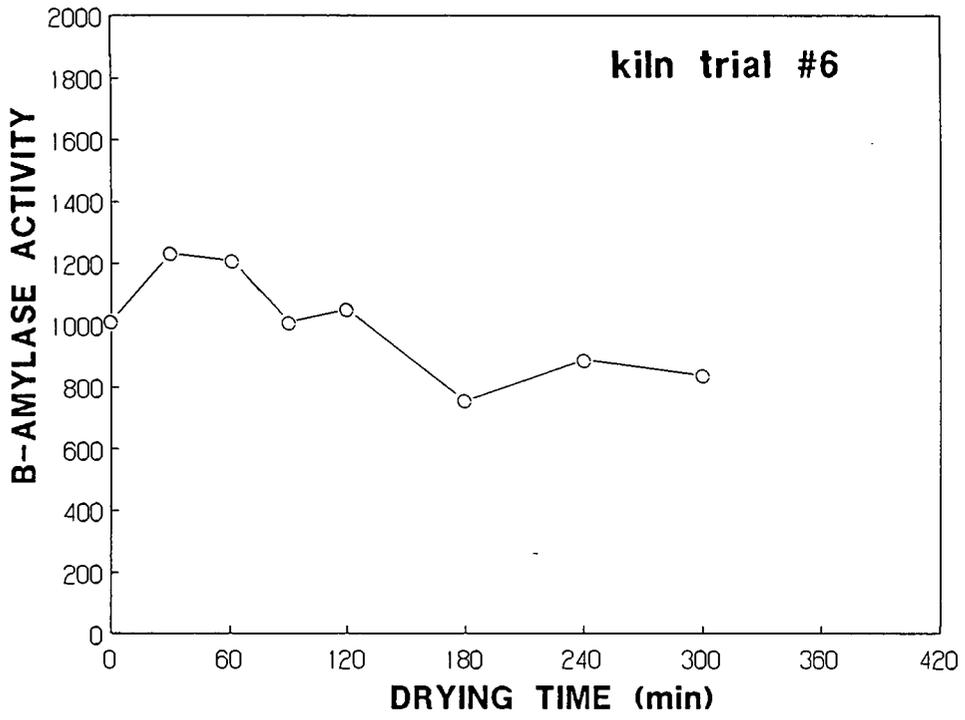


Figure 2.1 β -amylase deactivation during kiln trials #1, #3, #4, #5, and #6.





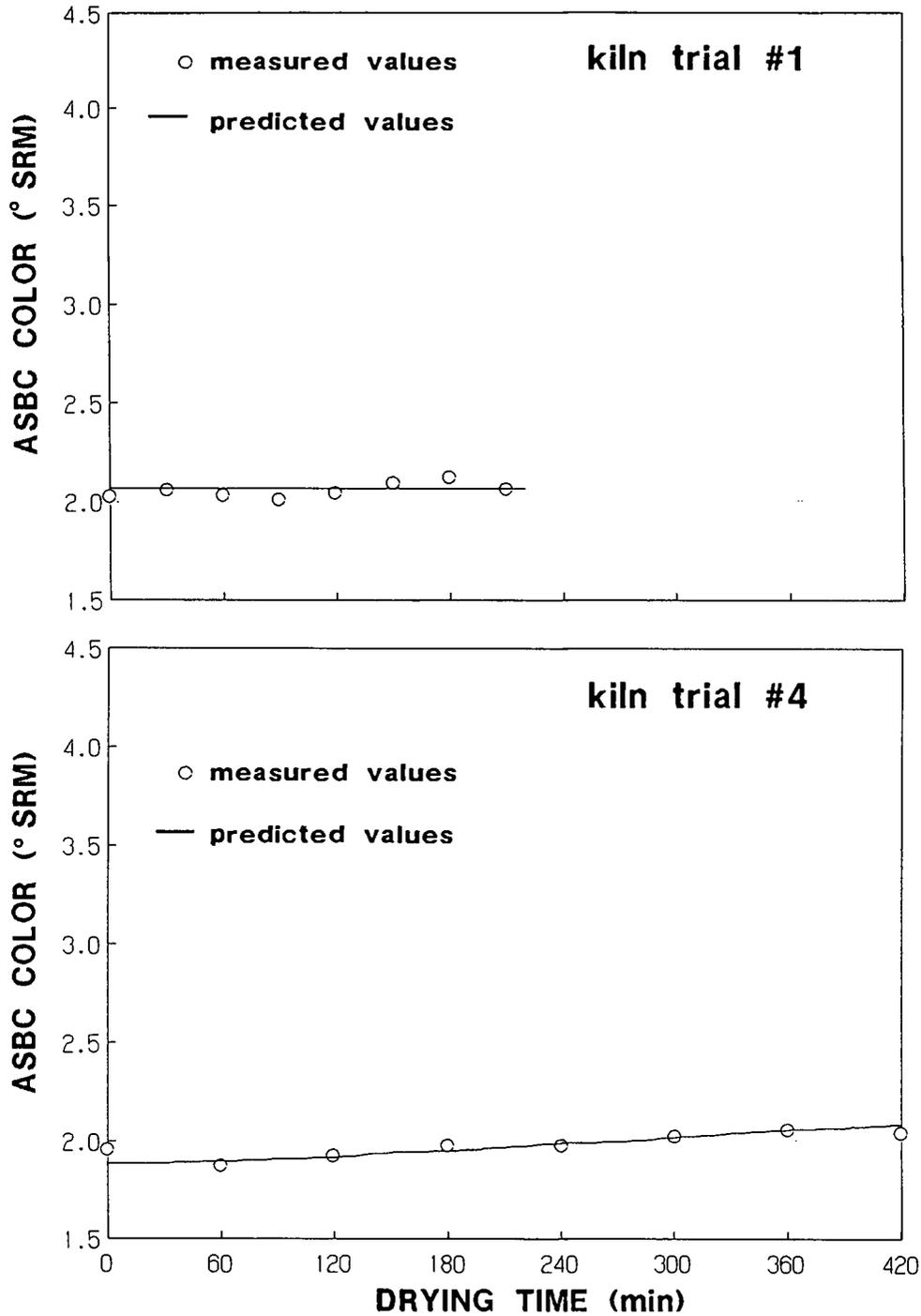


Figure 2.2 Observed and predicted color formation during kiln trials #1 and #4.

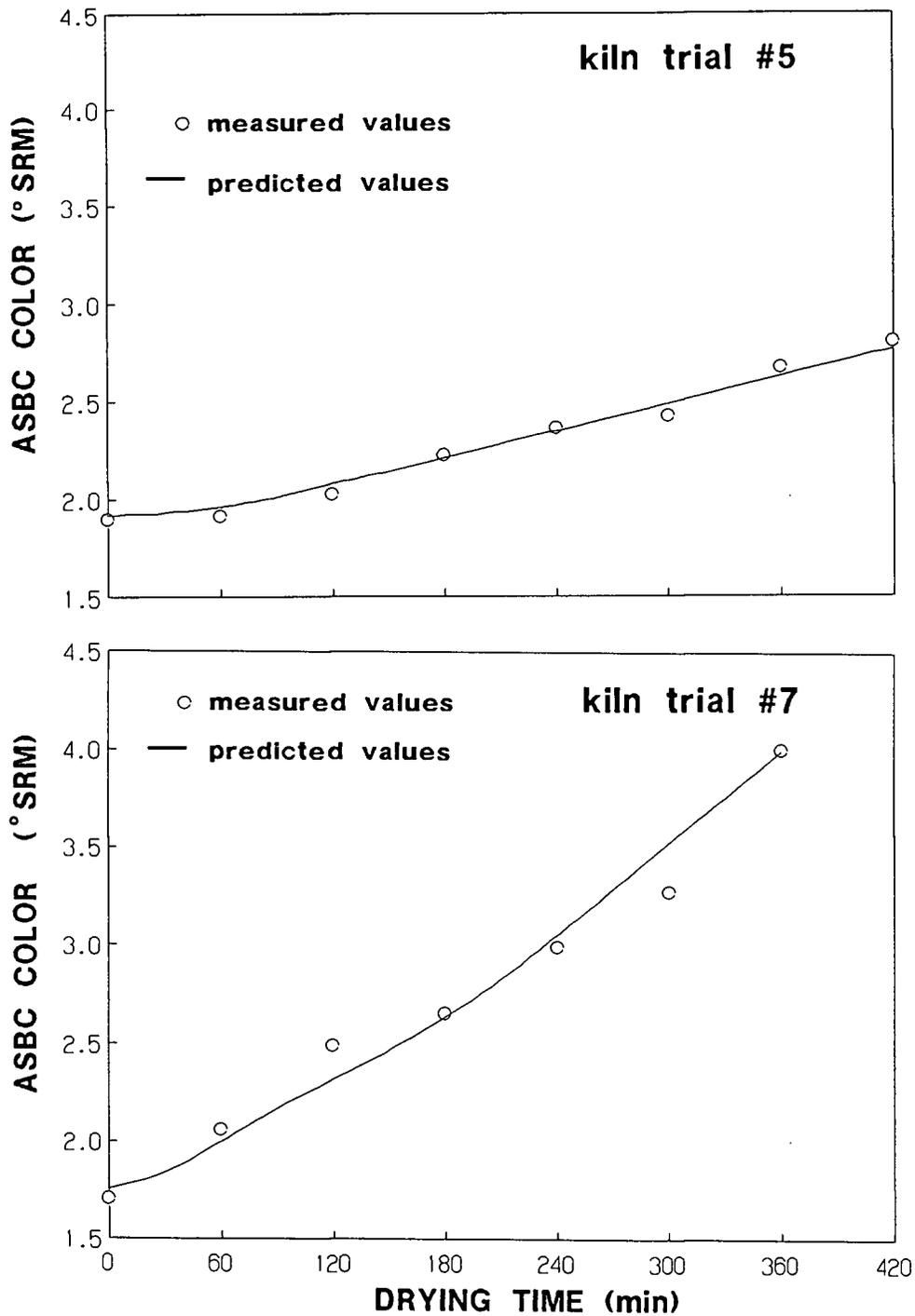


Figure 2.3 Observed and predicted malt color formation during kiln trials #5 and #7.

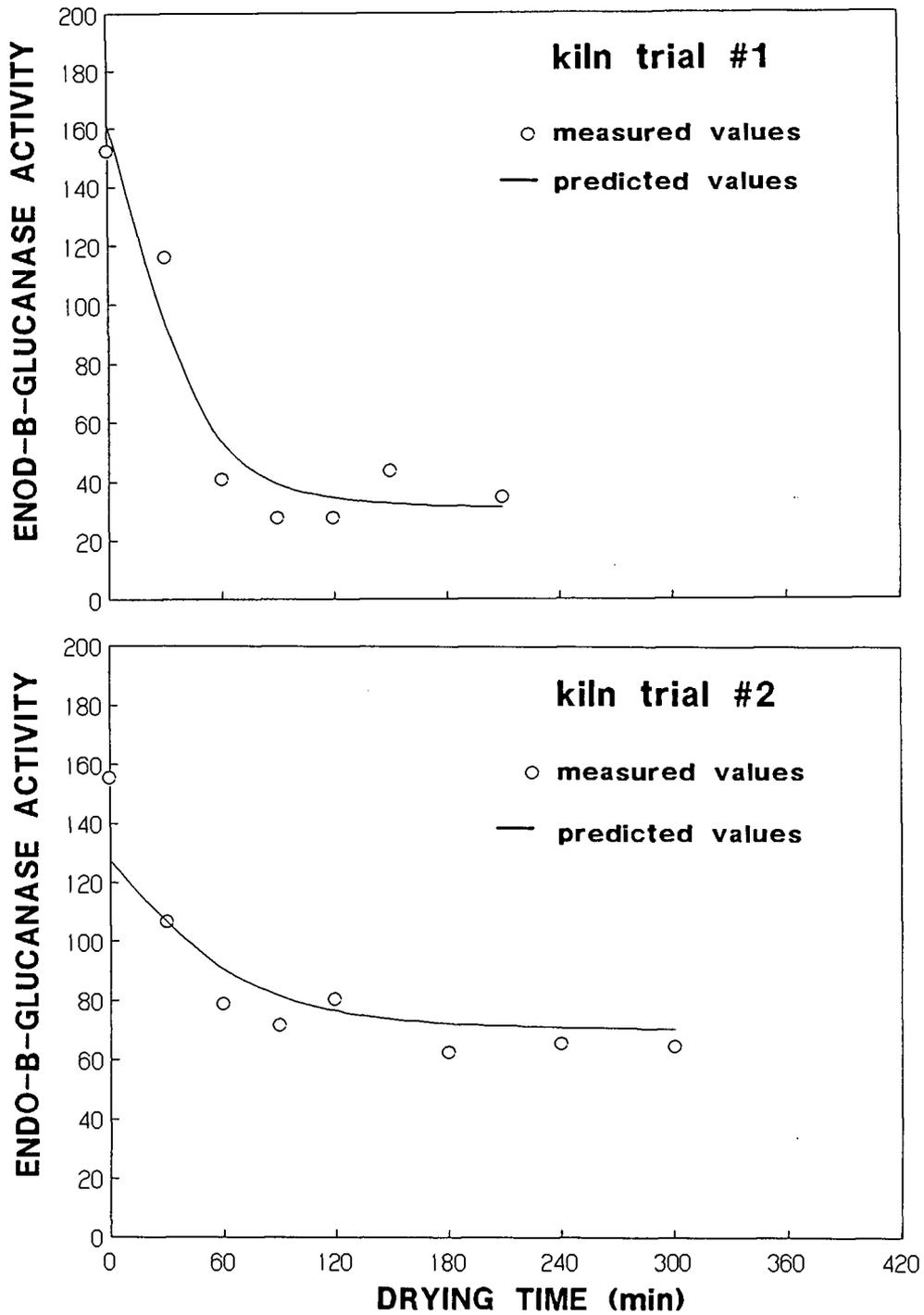


Figure 2.4 Observed and predicted malt endo-barley- β -glucanase deactivation during kiln trials #1 and #2.

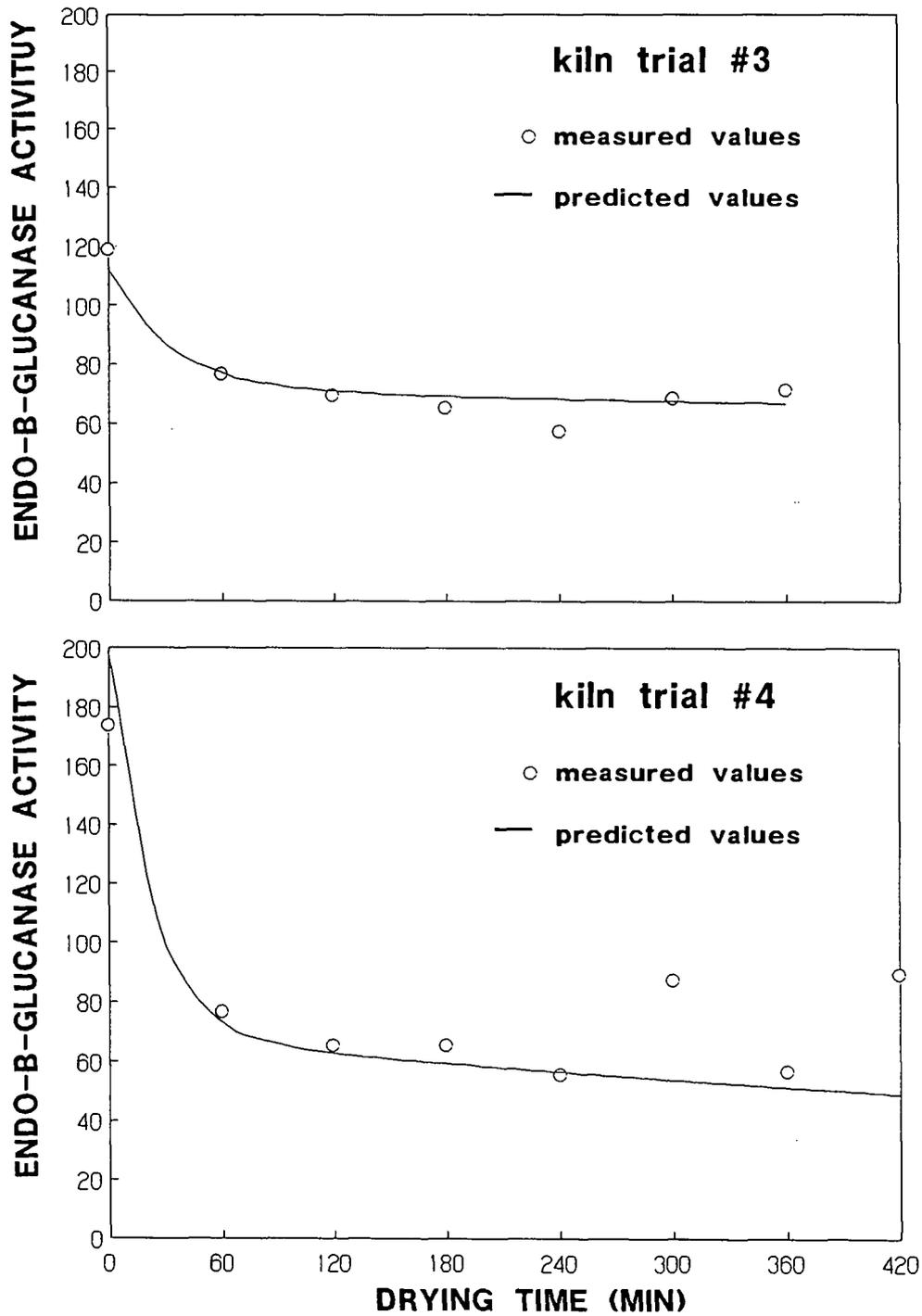


Figure 2.5 Observed and predicted malt endo-barley- β -glucanase deactivation during kiln #3 and #4.

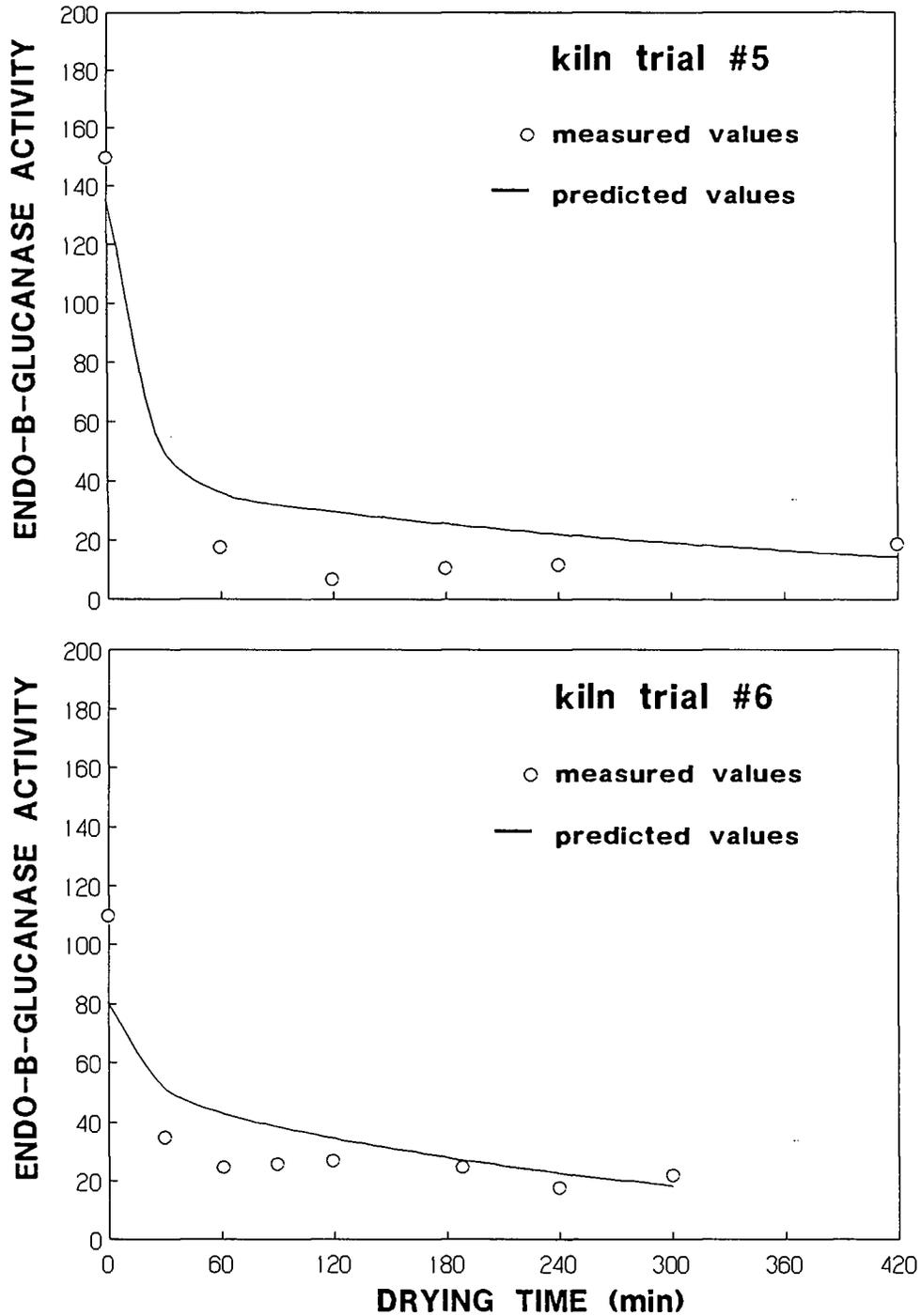


Figure 2.6 Observed and predicted malt endo-barley- β -glucanase deactivation during kiln trials #5 and #6.

CONCLUSIONS

A model was developed to predict the temperature and moisture of barley malt as it is kilned and is based on the temperature and relative humidity of the drying air. Malt color formation and endo-barley- β -glucanase deactivation can also be estimated based on these malt temperature and moisture content during drying. The end result of this study is a computer simulation of the malt kilning process which can be used to predict changes in malt temperature, moisture content, color, and endo-barley- β -glucanase activity in malt as it is kilned. The simulation can be used to eliminate much of the time, cost, and guesswork involved in achieving a variety of objectives. For example, processing times can be predicted to achieve a desired malt product based upon the temperature and relative humidity conditions of the drying air. The simulation can also be used to determine the optimum air temperature needed to dry malt to a desired moisture content in the shortest time while still maintaining acceptable color and endo-barley- β -glucanase activity.

Further study is suggested to determine the applicability of the drying models when drying air conditions fall outside of the ranges encountered during the thin-layer drying experiments, especially if it is desired to model malt drying in deep bed kilns. Also, the effects of rootlets and shrinkage, which possibly play a major role in malt drying rates at high moisture content, should also be examined in more detail.

Finally, the methodology here presented can be used to model the fate of other malt quality factors during kilning. More research directed toward the development of assay procedures and mathematical models for the determination and simulation of other malt quality factors during kilning is also suggested to further increase the ability to control the malt kilning process.

NOMENCLATURE

a	specific surface area (m^2/m^3)
B	color concentration ($^{\circ}\text{SRM}$)
b1, b2	fitting parameters (dimensionless)
b3, b4	fitting parameters (J/kg)
c1	fitting parameter (cm^2/sec)
c2, c4	fitting parameter (K^{-1})
c3	fitting parameter (dimensionless)
c5	fitting parameter (K)
C_g	dry grain heat capacity ($\text{J}/\text{kg K}$)
C_v	water vapor heat capacity ($\text{J}/\text{kg K}$)
C_w	liquid water heat capacity ($\text{J}/\text{kg K}$)
D	diffusion coefficient (cm^2/s)
[E]	enzyme concentration (units/4 g dry basis)
E_a	activation energy (J/kg)
E_{aB}	activation energy for browning reaction (J/kg)
E_{aE}	activation energy for enzyme deactivation (J/kg)
E_{aE0}, E_{aE0}'	fitting parameters (J/kg)
G1, G2	drying constants ($\text{kg}/\text{min}/\text{kg}$ dry solid)
h	convective heat transfer coefficient ($\text{W}/\text{m}^2 \text{K}$)
h_{fg}	heat of vaporization (J/kg)
J	objective function
k	thermal conductivity ($\text{W}/\text{m K}$)
K	drying coefficient (min^{-1})
k1, k2	fitting parameters (min^{-1})
k_B	rate constant for color formation ($^{\circ}\text{SRM}/\text{min}$)
k_{B0}, k_{B1}	fitting parameters ($^{\circ}\text{SRM}/\text{min}$)
k_E	rate constant for enzyme deactivation (min^{-1})
k_{E0}	fitting parameter (min^{-1})
k_{E0}', k_{E0}''	fitting parameters (min^{-1})
M	moisture content (kg/kg dry solid)
p	fitting parameter (kg dry solid/ kg)
q_1, q_2, q_3	$M_{c,q}$ fitting parameters (kg/kg dry solid)
r	radial dimension (m)
RH	relative humidity (fraction)
t	time (min)
T	temperature (K)
u	fitting parameter (dimensionless)
w_1	weighing factor ($^{\circ}\text{C}^{-2}$)
w_2	weighing factor ($[\text{kg}/\text{kg}$ dry solid] $^{-2}$)
x_1, x_2	fitting parameters (dimensionless)
x_3	fitting parameter (kg dry solid/ kg)

x_4, x_5	fitting parameters (K)
ρ	dry grain density (kg/m^3)
∇	substantial derivative

Subscripts

a	air
avg	average
eq	equilibrium
g	grain
0	initial value
s	surface
v	vapor

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