Activation Energy of Water Release Rate from Corn Kernel During Convective Drying

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Summary

This paper presents a mathematical model describing convective drying of corn kernels of different hybrids. The convective drying process was examined at four air temperatures (70, 90, 110 and 130°C). using hybrids 'Bc 462', 'Bc 4982', 'Bc Jumbo 48', 'Florencia' and 'Stefania' The drying process was able to be described by a model based on exponential equations. Activation energy necessary for the onset of the drying process, namely water activation in kernel, was determined using the Arrhenius equation. Results show that activation energy is in the ranges from 10.39 kJ/mol (hybrid Bc Jumbo 48) to 15.56 kJ/mol (hybrid Stefania). Data and analysis together indicate that the increase in energy necessary to induce the water release process from corn kernel is proportional to the increase in the activation energy of drying.

Key words

water activation energy, convective drying, corn hybrids

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Introduction

Corn production in Croatia is aimed at grain production. Due to peculiarities of the local climate, it is not always possible to harvest the crop under the most favourable conditions. Corn is harvested at 26-38% kernel moisture. Consequently, kernel harvested requires additional processing so that it can be successfully stored and preserved for a longer period of time. The most common processing method is drying, aimed at removal of excess humidity from kernel (Katić, 1997; Putier, 1993).

The process of drying, i.e. treating the kernel with heated air, results in the increase in quality in some crops. In some crops it is an obligatory procedure, due to the fact that humid kernel can cause problems in feeding of domestic animals (soy bean). In heated corn kernel the content of gelatinized starch increases (Katić, 1997; Kričkа et al., 2001). Treating soybean with high temperatures decreases the content of the undesirable trypsin inhibitor and urease (Krička et al., 2003).

Corn harvesting is ideally conducted at the 25-28% kernel moisture content, because this moisture level results in the highest yield and the lowest loss and damage. In order to achieve this level of moisture, certain requirements need to be fulfilled, such as proper hybrid selection for a specific area (FAO group), adequate production technology, properly timed harvesting and some other factors.

The principal purpose of the drying process is an elimination of excess water from kernel in order to preserve its quality (germination and nutrition value) during long term storage. In addition to quality preservation, the process of drying must be economical and the effectiveness of the dryer should be as high as possible. Drying can be conducted using unheated environment air (ventilation) and heated warm or hot air.

The process of drying is a continuation and completion of the natural process of ripening which did not happen due to unfavourable climatic conditions. In order to affect longer and quality storage, this process must be aimed at preserving kernel quality. Thus the process of drying aims at leaving in the kernel only the amount of moisture that is needed for kernel's latent life. Since in the process we encroach upon relevant biological status of certain kernel components, it is necessary to develop a closer understanding of the role of water and other factors important for achieving longer, successful storage of kernels. Also, all perishable products must be treated with preservatives, which destroy microorganisms or stop their growth and reproduction. This procedure makes it possible to store the products with no change for certain period of time, i.e. the product can be used throughout the year (McLean, 1980).

The speed and the quality of the drying process depend on the way it is conducted. In the case of natural drying, the temperature is similar to kernel temperature, which prolongs the process of drying. If heated air is used as the medium, the process of drying is faster. By increasing the air temperature, its relative humidity decreases, which further increases the difference between kernel humidity and air humidity, which facilitates the process of drying. The efficiency of drying is influenced by the thermal intensity of air, relative humidity of air, air flow velocity and the construction of the dryer (Sito, 1993).

During the process of drying, the kernel releases moisture until it reaches the state of hygroscopic equilibrium of humidity. The level of kernel humidity at which the hygroscopic equilibrium will be established depends on air temperature and relative air humidity. Hygroscopic equilibrium of humidity at various levels of air temperature and relative air humidity is illustrated by sorption isotherm (Katić, 1997).

The process of drying can start only when the difference between partial pressures and the surrounding air is such that facilitates the transfer of water from the kernel in the air. The process of drying also requires the movement of water and water vapor inside a kernel. The movement of water inside the capillaries is caused by osmotic pressure and meniscus on water surface tension in capillaries. During the process of drying, moisture moves from the inside of kernel towards its surface, and then from its surface it moves into the air used for drying (Mujumdar, 2000).

Li and Morey (1984) studied thin-layer drying of yellow dent corn and found that it is affected by drying air temperatures, air flow rate, initial moisture content and relative humidity. They also found that air temperatures and initial moisture content effect drying rates, but air flow and relative humidity have negligible effects.

Bloome and Gene (1971) analyzed thick-layer drying with cold air and found that its effects are influenced by the time and therefore limits are necessary when this type of system is used. The authors believe that the factors that influence the process of drying are a combination of drying air, hygroscopic equilibrium and the date of harvest. It is interesting that the authors claim that no equation of drying can serve as a model, but all logical sequences must have a positive result.

However, in order to fully describe the kinetics of the process of drying, it is necessary to understand a large number of parameters (Mujumdar, 1995). In addition to the type of the drier, its geometry and the type of heating, the parameters primarily comprise the features of the material that requires drying. It is important to understand the geometry of the material, such as particle sizes, the distribution of particle sizes, the distribution of pore sizes and particle shape. It is especially important to know what transfer features of the material are. Regarding the transfer of matter, it is important to take into consideration the activation energy of water release from the kernel and the drying constant. It is also important to be aware of the changes of these features during the process of drying. Since all of these features change along with the changes of working environment, it is clear that modeling the process of drying is a difficult task, which is further complicated by the fact that concurrent processes of heat and substance transfer occur during the process of drying. This paper concentrates only on the transfer of the substance, i.e. the relationship of moisture content with time. Many research papers have aimed to find a simple mathematical model that will successfully describe the kinetics of drying. Mostly these are exponential models with a small number of parameters. A basic drawback of all of these models is the fact that a physical validation of their parameters was never determined. What is known about the parameters so far is the influence of certain conditions and certain material features on the parameters (Sander and Glasnović, 2004). It has been determined that the process of drying can be described by mathematical modeling by means of exponential, logarithm or polynomial equations regardless of which crop is involved. The comparison of polynomial equations, i.e. the interrelation of the inclinations, can be expressed by means of derivations $dw/d\tau$ (Martins and Stroshine, 1987).

Krička (1993) established exponential equations for drying of ten different corn hybrids and found that different hybrids have different drying time in identical conditions of temperature, relative humidity of the environment and the air temperature at the point of entering the dryer, and moisture content of the kernels were kept constant. The author analyzed the equation exponents and found that the exponents indicate the tendency of drying rate: with higher exponent value drying is faster.

Bala (1997) defined the activation energy or the energy of reaction activation (E_a) as the energy that needs to be supplied to molecules so they can interact. In order for the molecules of water to chemically react, they need to collide with each other, but only those molecules that have a higher energy level than activation energy can interact. In chemical kinetics the activation energy is the size of the potential barrier that separates the products from the reactants. Molecules supply the activation energy by turning their kinetic energy into potential energy. Therefore, if kinetic energy in a kernel is not high enough, it can at the point of collision turn into potential energy, but it will not create an activated complex. The molecules will merely travel wider apart from each other that decreases the potential energy. If the system of water molecules in kernels is supplied with energy, i.e. through heating (by temperature increase), a higher number of molecules will cross the potential barrier per second, i.e. the speed of the reaction increases as temperature increases. If the potential energy barrier is high, i.e. the energy of reaction activation is high, fewer molecules will be able to cross the top of the energy barrier and the reaction will be slower.

The aim of this paper is to determine the differences in water release rate from the kernel in the process of drying between those corn hybrids that are commonly used in corn production in Croatia. This will be achieved by using a mathematical model that describes the kinetics of drying. The paper will also define the activation energy for initiating the process of water release during the convective drying of corn kernels.

Materials and methods

The corn hybrids used in the research were grown on the experimental grounds of the Institute for Special Plant Production in Maksimir in 2004 in a standard three-field crop rotation system. The soil where the hybrids were grown was alluvial soil, with low humus content (2.1-2.2%), and the reaction with KCl was neutral. The soil was characterized by homogenous stratigraphic build; according to its texture it was a silty loam with a high content of silt particles in the surface layer (68,6%), which makes the soil prone to the development of a crust (Pucarić et al., 1996).

Three hybrids in the research, 'Bc Jumbo 48', 'Bc 4982' and 'Bc 462', are Croatian hybrids produced by the Bc Institute in Zagreb. 'Florencia' and 'Stefania' have been produced by the company Pioneer from the USA. The hybrids were selected because of their wide presence in plant production, which makes this research practically applicable. It has also been taken into consideration that the hybrids in research differ according to kernel structure (dents and semi-flints) and according to the rate of water release from the kernel after reaching the point of physiological maturity.

Since the corn kernel samples had different input humidity, it was necessary to equalize these values so that the samples can be compared. All samples were research-hydrated to approximately 32% moisture content, i.e. the average moisture content at the time of harvest. This made further procedures comparable, since average moisture contents of research-hydrated kernels were not significantly different. Impurities and admixtures were removed from the samples and only healthy kernels were taken for the purposes of the study. Research-hydration was conducted by applying a fixed amount of distilled water directly to the kernels. The preparation of samples and the amount of water to achieve the desired input moisture were set according to Metrology Instructions by Croatian Standards Institute (Pliestić and Varga, 1995).

Drying was conducted in a thick layer in a stationary laboratory dryer able to simulate the conditions in a large industrial dryer. The air velocity in the dryer was kept to 1.0m s^{-1}; the samples were dried at four different air temperature levels: 70, 90, 110 and 130°C. They were chosen based on the practical considerations; namely, in the first phase of drying in industrial dryers in Croatia kernels are dried at 110 and 130°C, and in the second phase kernels are dried at 70 and 90 °C until reaching final moisture.

Before the process of drying was initiated, kernels were measured for moisture content, after which kernel mass at which the process of drying stops was mathematically calculated. Before each cycle of drying was initiated, air temperature and humidity of the space where the drying was to take place (a bin with the perforated bottom) had been measured by means of a psychrometer placed in the room where the dryer was located. The kernels were weighed on a digital scale at intervals of five minutes.

The convective drying of biological materials in the falling rate period is diffusion controlled process and may be represented by Fick's second law of diffusion. Humidity of a certain material in the process of drying can be predicted at any given moment of time by means of any of the equations of drying, especially so if the drying rate constant "k" has been calculated or measured. Rate constant is normally employed for calculating the temperature of air used for drying.

Henderson and Pabis (1961) suggested an equation for the calculation of drying rate constant which is based on Arrhenius equation used when calculating the energy necessary for the initiation of the process of water release from kernels. The Arrhenius equation correlates the temperature of drying, moisture release rate constant and activation energy needed for initiating the process of moisture release from the kernel. So, the activation energy can be determined through the temperature of drying (T), moisture release rate constant (k), i.e. by means of the slope of the straight line comparing In k and 1/T. Consequently, activation energy is calculated by multiplying the slope of the abovementioned straight line and the gas constant 8.314 J mol^{-1} K.

Kernel moisture in samples was determined by means of etalon method of drying in a dryer at 130°C in a period of 90 minutes until reaching the constant mass when it is assumed that the sample does not contain any other (other than moisture) volatile components or products that can cause the change in mass of the sample in research. (Šuko and Petek, 1970).

Results and discussion

Regardless of the crop that kernel belongs to, it needs to be preserved from one harvest to the other. At the harvesting time, most grain products (including corn) have higher moisture content than hygroscopic moisture. Therefore they need to be conserved before they can be stored. Thanks to the great efforts invested in plant breeding, we have a good selection of corn hybrids available for all corn production areas. This has resulted not only in yield increase, but also in greater variety of harvested grain. Kernels are characterized by different levels of moisture, which presents a problem in drying Therefore a number of different drying technologies were developed (Pelllizzi, 1987).

Since it is necessary to determine the differences in moisture release rate in corn kernels, drying was conducted at four different levels of air temperature (70, 90, 110 and 130°C) with airflow velocity at 1m s^{-1}. Based on the data on mass loss taken at intervals of five minutes, exponential equations were calculated for certain temperature values for every corn hybrid in the research until they have reached equilibrium moisture (14%). Mathematical modeling produced the value of moisture release rate up to the level of equilibrium moisture in order to make an exact determination of the differences in moisture release in different hybrids. In all investigated exponential equations, the coefficient of correlation was found to be ranging from 0.93 to 0.99, which indicates that the measuring of moisture release rate from kernels was conducted properly and that the results can be mutually correlated.

Table 1 shows exponential equations and moisture release rate constants from kernels up to the equilibrium moisture (14%) of the hybrids in the research.

The kinetics of convective drying were investigated for five hybrids at four different drying temperatures. The curves of drying for individual hybrids are regular. When kinetic drying curves are determined for different drying conditions, it results in geometrically similar curves that are material specific. For the purpose of comparing the drying curves of the hybrids in the research, mathematical modeling of moisture release equations was used (Martins and Stroshine, 1987; Krička, 1993). When the equation describing drying were generally analyzed, it can be seen in each case that exponential coefficient of the variables is negative, which means that the curve is falling, i.e. shows the tendency of drying rate. If the absolute value of the coefficient is higher, drying is faster.

By calculating the moisture release rate coefficient, we can exactly determine which hybrid releases moisture at the highest rate, and which one releases moisture at the lowest rate. At 70°C the lowest moisture release rate was found for hybrid Florencia, and the highest rate was found for 'Jumbo 48'. At other drying temperatures, the highest

Table 1. Exponential equations and the values of moisture release rate constant at four levels of drying temperature

Hybrid	70 °C		90 °C		110 °C		130 °C	
	Equation of water release	k (1/s)	Equation of water release	k (1/s)	Equation of water release	k (1/s)	Equation of water release	k (1/s)
Bc 462	$y = 30.14e^{-0.0038x}$	0.047	$y = 30.40e^{-0.0068x}$	0.061	$y = 31.19e^{-0.0108x}$	0.080	$y = 32.23e^{-0.0168x}$	0.104
Bc 4982	$y = 31.74e^{-0.0042x}$	0.048	$y = 31.60e^{-0.0058x}$	0.052	$y = 32.91e^{-0.0077x}$	0.071	$y = 33.03e^{-0.0125x}$	0.084
Bc Jumbo 48	$y = 32.17e^{-0.005x}$	0.050	$y = 31.45e^{-0.005x}$	0.049	$y = 31.70e^{-0.0075x}$	0.060	$y = 33.60e^{-0.0133x}$	0.088
Florencia	$y = 29.26e^{-0.0042x}$	0.042	$y = 29.92e^{-0.0059x}$	0.053	$y = 29.27e^{-0.01x}$	0.070	$y = 32.14e^{-0.0122x}$	0.089
Stefania	$y = 29.05e^{-0.0037x}$	0.039	$y = 29.76e^{-0.0063x}$	0.054	$y = 30.10e^{-0.0069x}$	0.058	$y = 32.57e^{-0.0137x}$	0.093

moisture release rate was found for Bc 462, and the lowest moisture release rate were found for hybrid Bc Jumbo at 90°C, hybrid Stefania at 110°C and hybrid Bc 4983 at 130°C. The abovementioned indicates that corn hybrids behave differently during drying, depending on the temperature at which process is performed. However, hybrid Bc 462 was found to be the fastest moisture releasing hybrid in three cases (at drying temperatures 90, 110 and 130°C).

Total time of drying reduced substantially with the increase in temperature of hot air. The rate constant, k, which is a measure of the drying rate, significantly increased with the drying air temperature. Results indicated that the Arrhenius law may be used to relate the dependence of the rate constant on drying air temperature. In this way, the curves of moisture release constants and the drying temperatures for each thermal procedure were made, based on the linear relationship of the constant of moisture release from kernels for every temperature in the research and applying the Arrhenius equation. The curves are displayed in Figure 1 (Henderson and Pabis, 1961; Bala, 1997). The value of activation energy for the corn hybrids in the research was determined from the slope of the straight line. The calculation of activation energy indicates the energy that needs to be supplied to kernels by means of thermal procedure of convective drying for the purpose of facilitating the interaction of molecules, which means initiating the process of drying. Namely, if the activation energy is higher, the reaction is slower, i.e. moisture release from kernels is slower.

The graph displaying the correlation of moisture release coefficient with the time of drying provides us with a straight line. The slope of the straight line is the basis for the calculation of activation energy of moisture release from kernel, which is shown in Figure 1.

The plot was found to be a straight line in the range of temperatures investigated, indicating Arrhenius dependence. The activation energy for moisture release from corn kernel was calculated from the slope of the straight line.

The highest energy level needed for initiating the process of moisture release from kernel was found in hybrid Stefania (15.56 kJ mol^{-1}). However, hybrid Bc 462 has the activation energy of 14.89 kJ mol^{-1}, and hybrid Florencia has the activation energy of 14.52 kJ mol^{-1}, which is not significantly different from the highest value found in hybrid Stefania. Hybrid Bc Jumbo has the lowest value of activation energy, 10.39 kJ mol^{-1}. Hybrid Bc 4982 has the value of activation energy of 11.51 kJ mol^{-1}. It can be stated that the differences in the values of activation energy in the investigated hybrids do exist, but in some cases they are not significant.

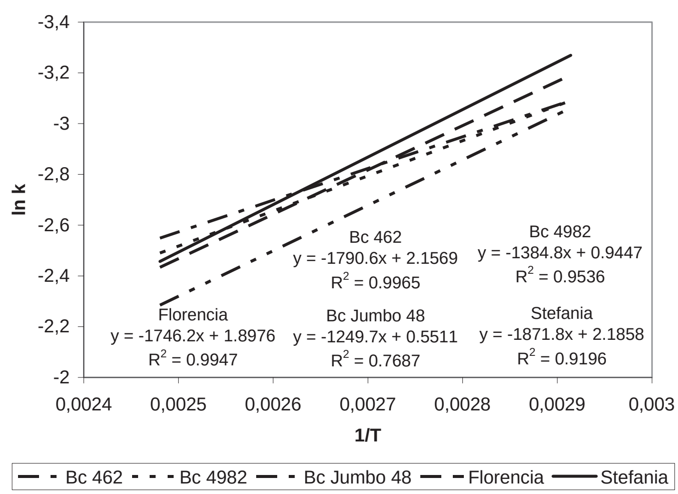

Figure 1. The relationship between the temperature of drying and the coefficient of moisture release from kernel

Conclusion

The research of water release from kernel was conducted on the samples of corn kernel of the following hybrids: 'Bc 462', 'Bc 4982', 'Bc Jumbo 48', 'Florencia' and 'Stefania'.

Drying took place in the falling rate period and an exponential equation was found to describe the drying behavior of investigated corn kernels well. Exponential equations of drying proved to be comparable for individual temperatures of drying; they indicated the differences in moisture release from kernel for all investigated hybrids. Of all the five hybrids, the exponential model gave an excellent fit to experimental data obtained with a value for R2 greater than 0.93. Increase in the air temperature caused a decrease in the drying time. The research indicated that there is a significant difference between the moisture release rates for all of the investigated hybrids in convective drying of kernels. Also it indicated that the hybrids behave differently in identical drying conditions. The drying rate constant was related to temperature using Arrhenius relationship and the activation energy values ranged from 10.39 kJ mol-1 to 15.56 kJ mol-1.

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