

# Effect of Moisture Content on Maillard Browning Kinetics of a Model System during Microwave Heating

Bruce I. Peterson, Chao-Hsiang Tong,\* Chi-Tang Ho, and Bruce A. Welt

Department of Food Science, Cook College, New Jersey Agricultural Experiment Station, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

A unique apparatus was developed to measure the browning reaction kinetics of a liquid model system on-line during microwave heating. The apparatus consisted of a sealable, microwave-transparent reaction vessel, microwave oven temperature controller, peristaltic pump, flow cell, and spectrophotometer (420 nm). The model system consisted of equimolar concentrations of L-proline and D-glucose in propylene glycol at added moisture contents of 0, 2.5, and 5%. The browning rate followed a zero-order reaction, with the rate constants drastically reduced with the addition of a small amount of water. The temperature dependence of the browning reaction was adequately described by the Arrhenius equation. The activation energies ( $a_v = 36.03 \pm 1.73$  kcal/mol) were independent of moisture content and were consistent with literature.

**Keywords:** Microwave; browning kinetics; propylene glycol; moisture content

## INTRODUCTION

Knowledge of kinetic parameters (rate constant and activation energy) is necessary to predict the extent of a specific chemical reaction. Optimization of microwave cooking is possible when the kinetic parameters are known but, unfortunately, the browning reaction kinetics during microwave heating are not well studied. It is well-known that one of the major problems associated with microwave cooking is the lack of desired color as well as flavors (Risch, 1989). The short cooking time and low temperatures common to microwave processing usually do not promote the Maillard reaction, which is responsible for the production of many flavor and colored compounds (Yeo and Shibamoto, 1991a).

Browning rate is a strong function of moisture content, yet when the effect of water on the Maillard reaction is studied, it is usually done not on the basis of water content but rather on the state of the water, as characterized by its thermodynamic availability or water activity ( $a_w$ ) (Labuza and Saltmarch, 1981). In a review by Labuza and Baisier (1992), the accepted scenario is that the rate of browning increases from the dry state, starting at a critical  $a_w$  of 0.2–0.3 for most foods, to a maximum at a water activity of 0.5–0.8 and then decreases at higher water activities.

Previously, open reactors have been used for microwave browning kinetic studies (Yeo and Shibamoto, 1991b). However, due to evaporation of water, the moisture content would continuously change during microwave heating because of the high temperature. Other problems identified in microwave kinetic studies are (1) the lack of on-line temperature measurement, (2) uneven heating, and (3) the lack of temperature control. Welt et al. (1993) introduced a microwave reaction kinetic system that solved these problems for studying browning reaction kinetics in a microwave environment. One of the objectives of this study was to further modify that system to allow on-line measurement of browning reactions for liquid systems.

Peterson (1994) studied the flavor formation in a model system, consisting of L-proline, D-xylose, and

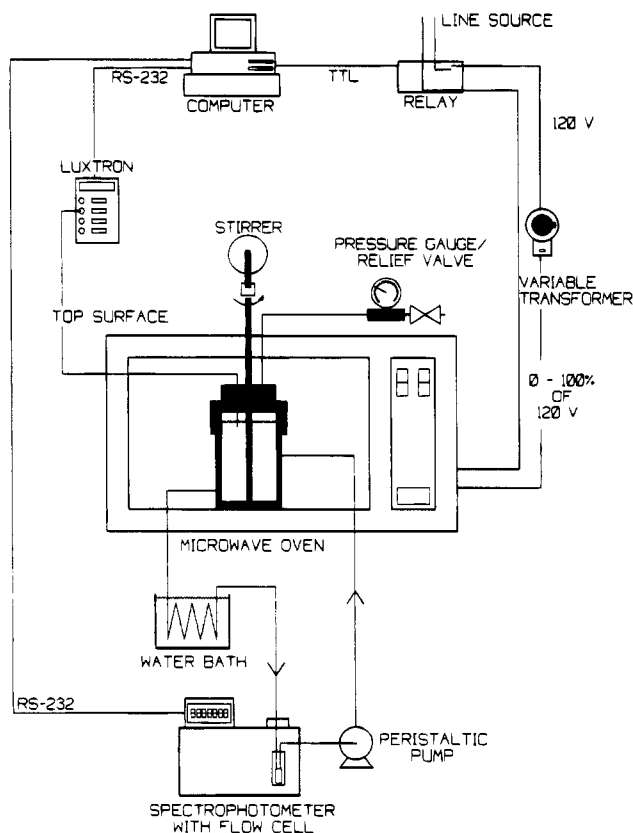
propylene glycol, by microwave heating. Propylene glycol was found to be a good vehicle for a browning/flavor agent as reacting L-proline and D-xylose in propylene glycol (0% added moisture) produced a strong aroma and a rich flavor profile. It was further shown by the author that the addition of a small amount of water (2.5%) dramatically decreased the flavor and color formation. The browning reaction kinetics as affected by water content under microwave environment have not been studied, due to the lack of an appropriate apparatus. Therefore, the second objective was then to use the developed on-line system to study the effect of moisture content on the browning reaction kinetics of this same system.

## MATERIALS AND METHODS

**Sample Preparation.** L-Proline (Sigma Chemical Co., St. Louis, MO) was weighed and dissolved in propylene glycol (Sigma) in a volumetric flask by mechanical stirring for 24 h to give a 0.02 M solution. Samples with 0, 2.5, and 5% added moisture content were prepared by replacing the propylene glycol with different amounts of deionized distilled water. D-Xylose (Aldrich Chemical Co. Inc., Milwaukee, WI) solutions were prepared to a concentration of 0.02 M in the same manner.

**Apparatus.** The apparatus consists of three major components: a modified microwave oven with a feedback temperature control system, a microwave kinetics reactor (MWKR), and a spectrophotometer. A schematic of the apparatus is shown in Figure 1. The temperature feedback control system has been described in detail by Tong et al. (1993); however, a larger capacity oven rated at 900 W (Model MQS 1403W, Quasar Co., Elk Grove, IL) was modified and used in this study. The operation of the feedback control features has been demonstrated by Welt et al. (1992). In review, a fiber optic temperature sensing unit (Model 755, Luxtron Corp., Santa Clara, CA) measured the temperature of the sample and fed this information to an IBM/AT compatible computer through an RS-232 cable. A feedback temperature control software program determined whether the temperature sample was above a user-supplied upper temperature limit or below a user-supplied lower temperature limit. When the sample temperature was below the lower limit, the computer activated a relay in the magnetron power supply circuit, which caused the sample to heat. When the sample temperature was above the upper limit, the relay was deactivated, which allowed the

\* Author to whom correspondence should be addressed (e-mail woody@caft1.rutgers.edu).



**Figure 1.** Schematic diagram of the on-line system for measuring browning reaction kinetics for liquids during microwave heating.

sample to cool. Welt et al. (1992) showed that the feedback temperature control system was capable of maintaining a desired set-point temperature to within  $\pm 0.5$  °C.

A detailed description of the design and operating characteristics of the MWKR was provided by Welt et al. (1993). Briefly, the MWKR is a completely sealed microwavable pressure vessel made from ULTEM 1000 (GE Plastics, Pittsfield, MA). The vessel was designed with the following features: (i) an internal volume of approximately 500 mL, (ii) a completely sealed mechanical mixing assembly using of O-rings, and (iii) penetrations equipped with Teflon compression fittings to provide access for fiber optic temperature probes, pressure gauge, over-pressure safety relief valve, and tubing for continuous flow. For this experiment, one large anchor-type impeller was used for mixing. The impeller was mounted at the bottom of the mixing shaft such that it would scrape the floor and the walls of the vessel.

A Stedfast laboratory stirrer (Model 14-505-1, Fisher Scientific, Springfield, NJ) was attached to the drive shaft to rotate the coupling and mixing shaft. The motor was mounted above the microwave oven and connected to the drive shaft through a hole drilled through the roof of the oven.

A modification was made in the original design of the MWKR to facilitate the on-line measurement of browning kinetics by a spectrophotometer (Spectronic 301, Milton Roy Co., Rochester, NY). Using a Masterflex L/S peristaltic pump (Model 7520-00, Cole-Palmer Instrument Co., Chicago, IL) the sample was pumped from the vessel through a Teflon tube to a stainless steel cooling coil immersed in a room temperature water bath outside the microwave oven. The cooling coil was used to lower the temperature of the sample before it reached the spectrophotometer to avoid any possibility of damaging the detector. Via Masterflex (Pharmed) tubing, the sample continued to a quartz flow cell (Fisher Scientific Co., Pittsburgh, PA; 0.6 mL, 1-cm path) sitting in the spectrophotometer and then through the pump back to the MWKR in the microwave oven by connecting another section of Teflon tubing. The total volume of the tubes and coil was 9 mL. The pump was adjusted to give a flow rate of 3 mL/min for all trials in this study.

**Table 1.** Experimental Conditions for Kinetic Studies

temp (°C)	moisture content (% H <sub>2</sub> O)	temp (°C)	moisture content (% H <sub>2</sub> O)	temp (°C)	moisture content (% H <sub>2</sub> O)
110	0	130	2.5	130	5
120	0	140	2.5	140	5
130	0	150	2.5	150	5

The spectrophotometer, set at 420 nm, was connected to the computer with an RS-232 cable, and the same custom computer program that controlled the temperature feedback system continuously read the data from the spectrophotometer and saved it onto a disk, thus facilitating on-line data acquisition.

**Experimental Procedure.** The initial temperature of the reactants was maintained at room temperature. Reaction temperature studies are shown in Table 1. Before each experiment, the optical fiber temperature measurement system was calibrated at 100 °C with boiling distilled water. Each trial was performed by mixing 100 g of proline and xylose solutions immediately prior to the start of the reaction to give a final concentration of 0.01 M. After the sample was placed in the reaction vessel and the system closed, the peristaltic pump was turned on to achieve a flow of 3 mL/min. The mechanical stirrer was adjusted to give a rotation rate of 240 rpm.

Magnetron power was set at the maximum of 120 V by setting the variable transformer to 100%. After come-up (to the desired reaction temperature), magnetron power was reduced by using approximately 80% of the maximum available voltage. Magnetron power was handled in the same manner for each trial. The absorbance or optical density (OD) was recorded continuously, and the reaction was terminated when the absorbance reached a maximum of approximately 1.200. Duplicate experiments were performed for each reaction temperature.

**Kinetic Studies.** Numerous studies have applied a pseudo-zero-order model to successfully describe the rate of browning in a food or in a model system when reactant concentrations are not limiting for the rate of formation of brown pigment (Mizrahi et al., 1970; Warmbier et al., 1976; Waletzko and Labuza, 1976; Franzen et al., 1990), as

$$dB/dt = k_b = \text{rate of browning} \quad (1)$$

where  $B$  is a measurement of browning expressed in OD and  $t$  is time. Assuming no induction period, a plot of  $B$  (OD) versus time should give a straight line where the slope is equal to  $k_b$ .

The Maillard browning reaction, as with other chemical reactions, has been successfully described with respect to temperature dependence by the Arrhenius relationship

$$k_b = k_{b0} e^{-E_a/RT} \quad (2)$$

where  $k_b$  is the rate constant at a temperature  $T$ ,  $k_{b0}$  is the rate constant at a reference temperature  $T_0$ ,  $E_a$  is the activation energy (kcal/mol),  $R$  is the gas constant (1.986 cal/mol K), and  $T$  is the absolute temperature (K) (Labuza and Saltmarch, 1981). In a plot of  $\ln k$  versus  $1/T$ , the slope is equal to  $-E_a/R$ .

## RESULTS AND DISCUSSION

To measure the rate of browning of proline/xylose in propylene glycol as a function of moisture content during microwave heating, it was necessary to have a reaction system that would give reproducible results as well as to satisfy the requirements of a steady state system. The come-up time to the desired temperature for each trial was very quick (under 2 min) and, with the use of the MWKR and its stirring capability, the temperature gradient was negligible ( $\pm 0.5$  °C). Therefore, given this quick come-up time and constant temperature capability, the system was well suited for kinetic studies.

**Table 2. Change of OD of a Preheated Sample as a Function of Time When Measured at Room Temperature**

time (min)	OD (420 nm)	time (min)	OD (420 nm)	time (min)	OD (420 nm)
0 <sup>a</sup>	0.243	10	0.230	30	0.217
		20	0.222	40	0.210

<sup>a</sup> Zero time is 5 min after the sample was taken and cooled to room temperature.

Furthermore, there is no loss of water due to vaporization due to the seals on the vessel.

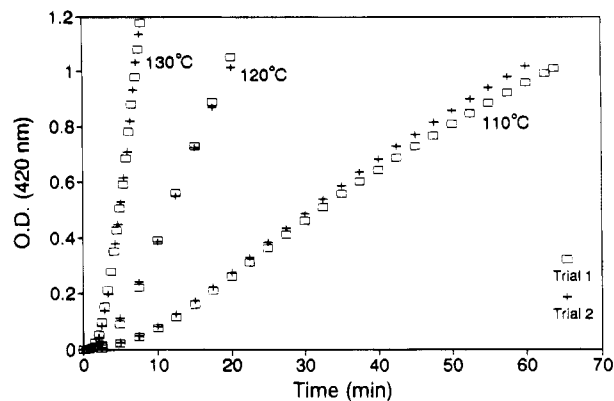
Initially, an off-line method was followed to measure the rate of browning in the model system where the reaction had to be stopped for a sample to be withdrawn from the MWKR. The sample was then cooled in an ice bath before its OD was measured at 420 nm in the spectrophotometer. However, this method proved most inconvenient, especially when the reaction time was short.

The need for development of an on-line system to measure browning kinetics at high temperatures can best be demonstrated by the decrease in absorbance with time of a sample measured at room temperature (Table 2). The sample was heated at 120 °C for 10 min and cooled immediately in an ice water bath before measurement. After 20 min, a decrease of 10% in OD was observed. Therefore, the OD measured off-line did not reflect the OD in the reaction vessel at the moment in question. There is certainly a need to standardize the procedure to measure the OD at consistent time intervals after exposure to heating. This problem has never been addressed previously in the literature as almost all researchers have assumed that the browning reaction is negligible once the temperature is low and the OD would then remain the same. This decrease in the OD may be attributed to the decrease in solubility of the colored compounds in propylene glycol, but the chemistry of these pigments is unknown.

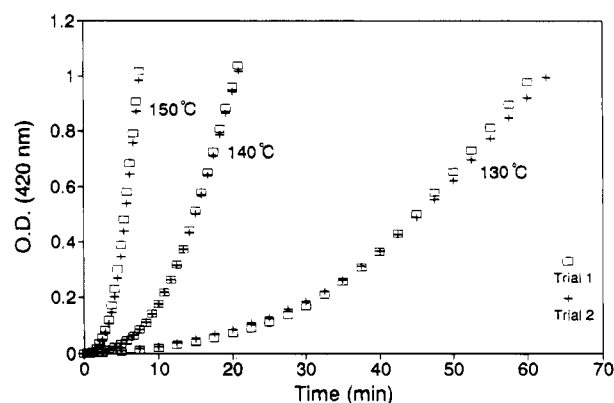
Other advantages of the on-line measurement system are (1) convenience (no arresting of the reaction or physical handling of the sample), (2) reproducibility (The standard deviations were much higher for the off-line method. Though there was still a time delay for the solution to exit the vessel and reach the flow cell in the on-line method, this time difference was very short and was identical at each measurement for each trial.), and (3) accuracy (More data points could be collected, allowing for complete representation of the increase in browning.).

**Maillard Browning Rate Constants and Activation Energies.** The plot of optical density (OD) at 420 nm versus time for 0, 2.5, and 5% moisture contents is shown in Figures 2, 3, and 4, respectively. An induction period was observed for each moisture content and decreased with increasing temperature. The browning rates at each temperature then followed zero-order reaction kinetics after the induction period, as shown by the linear plot of OD versus time, for all three moisture contents studied. Similar phenomena, with respect to induction period and reaction order, have been shown by many researchers (Mizrahi et al., 1970; Warmbier et al., 1976; Singh et al., 1983; Franzen et al., 1990). Rate constants were calculated from the linear portion after the induction period. The slope of these lines was calculated using the least-squares fit method.

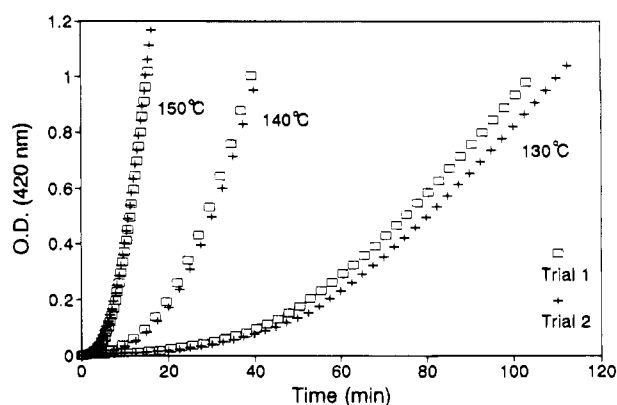
It was noticed that both temperature and moisture content influenced the induction period. The lag time



**Figure 2.** Maillard browning rates of 0.01 M proline and 0.01 M xylose in propylene glycol as a function of temperature at 0% moisture content.

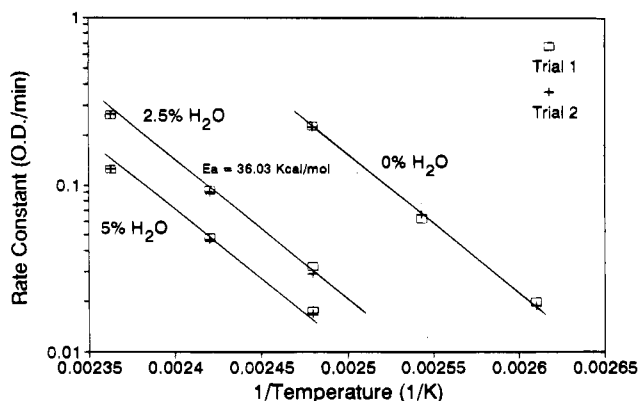


**Figure 3.** Maillard browning rates of 0.01 M proline and 0.01 M xylose in propylene glycol as a function of temperature at 2.5% moisture content.



**Figure 4.** Maillard browning rates of 0.01 M proline and 0.01 M xylose in propylene glycol as a function of temperature at 5% moisture content.

was found to decrease as temperature increased, as also reported by Warmbier et al. (1976). It has been suggested that at higher temperatures the induction period should decrease or disappear altogether (Labuza and Baisier, 1992). In fact, Nelson (1948) reported that at temperatures of 121 °C or higher, an induction period could not be detected. In this study, however, an induction period was seen at temperatures up to 150 °C. Since the induction periods for these types of reactions were very short at high temperatures, other researchers' claims of no induction period at high temperatures could be attributed to the fact that their off-line method could not generate data points quickly enough at the beginning to enable an induction period to be seen.



**Figure 5.** Arrhenius plot of Maillard browning of 0.01 M proline and 0.01 M xylose in propylene glycol at different moisture contents.

With respect to moisture content, Labuza et al. (1970) reported that the lag time decreased as moisture increased, which is the opposite of what was found in this study. However, their system was dehydrated skim milk, so a 0% moisture content would give a system that has no medium in which the Maillard reaction can occur, and therefore an increase in moisture would increase the rate of browning and decrease its induction. In this study it is apparent that propylene glycol was a medium for the Maillard browning reaction and the addition of a small amount of water diluted the reactants and thus lowered the rate of reaction. The inhibitory effect of moisture content on the induction period in the model system at 130 °C can be deciphered from Figures 2–4.

It can also be seen from Figures 2–4 that a small amount of water dramatically lowered the rate of browning. Similar results, but not as dramatic, were found by Eichner and Karel (1972) using a glucose–glycine–glycerol–water model system. It is difficult to compare the results as glycine has been reported to be 3 times more reactive than proline (Wolfrom et al., 1974). In general, the length of the induction period is inversely proportional to the browning rate, regardless of the moisture content.

The temperature dependence of the Maillard browning reaction as a function of moisture content during microwave heating followed the Arrhenius relationship, as shown in Figure 5. Although the rate constants were strongly affected by the addition of water, the activation energies were independent of moisture content, as shown by the parallel lines in Figure 5, suggesting that the addition of water did not change or affect the rate-limiting step of the Maillard browning reaction in this system. An average activation energy of  $36.03 \pm 1.73$  kcal/mol was obtained in this study, and it is within the range (20–40 kcal/mol) reported in foods and model systems (Labuza and Saltmarch, 1981).

#### ACKNOWLEDGMENT

This is Publication D-10209-1-94 of the New Jersey Agricultural Experiment Station. B.I.P. was partially supported by a Teaching Assistantship from the Department of Food Science, Rutgers University.

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Received for review March 3, 1994. Accepted June 13, 1994.\*

\* Abstract published in *Advance ACS Abstracts*, August 1, 1994.