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ARTICLE *in* JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY · FEBRUARY 2010

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Kinetics of the 5-Hydroxymethylfurfural Formation Reaction in Chinese Rice Wine

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The kinetics of 5-hydroxymethylfurfural (HMF) formation in Chinese rice wine was investigated under different treatment conditions. Samples I and II were the rough rice wine and outflow fraction of the rice wine from the macroporous resin, respectively. Sample III was the fraction derived from sample II loaded through ion-exchange resin. The HMF content of the different samples under a range of temperature values from 323.15 to 363.15 K was measured by high-performance liquid chromatography. The results demonstrated that the kinetics of HMF formation in sample I was determined as first-order [$C_t = C_0 \exp(kt)$], but those for samples II and III were found to be the zero-order reaction [$C_t = C_0 + kt$]. For all three samples, the relationships of reaction rates (k) and temperature (T) were computed as follows: $k_1 = 2.81 \times 10^5 \exp(-43.01/RT)$, $k_2 = 2.33 \times 10^{18} \exp(-123.90/RT)$, and $k_3 = 1.79 \times 10^{13} \exp(-89.16/RT)$. By applying the Arrhenius equation $k = k_f \exp(-E_a/RT)$, the activation energy was 43.01, 123.90, and 89.16 kJ mol⁻¹, respectively. On the basis of these kinetics equations, weak polar components such as phenolic groups may be involved in HMF formation.

KEYWORDS: Chinese rice wine; 5-hydroxymethylfurfural (HMF); kinetics

INTRODUCTION

Rice wine, along with beer and red wine, is one of the three most famous traditional alcoholic beverages in China (1). It contains an abundance of carbohydrates, amino acids, vitamins, minerals, and bioactive substances (2). Comprehensive studies on the functional components, flavor compounds, and chemical reactions within rice wine are limited. Most investigations to date have focused on phenolic compounds (3, 4), functional oligosaccharides (5, 6), amino acids (7), and short peptides (2, 8). In 2007, hydroxymethylfurfural (HMF) was identified in rice wine by the gas chromatography–mass spectroscopy (GC-MS) method (9). HMF can be produced after monosaccharides pyrolysis in many processes such as the Maillard reaction. Thus, HMF has been measured in honey (10), infant dairy products (11, 12), breakfast cereals (13), biscuits (14), and concentrated fruit juices (15).

With special properties, HMF can affect both flavor (16) and appearance (browning) (12, 17). The function of HMF in foods and beverages is controversial. It has been reported that HMF irritates the eyes, mucosa, and skin. In addition, excessive consumption of HMF could cause poisoning, induce striated muscle anaesthetization, and result in crippling of the viscera (18–20). Therefore, the allowed HMF content in honey and concentrated fruit juices is minimal. However, recent studies show that HMF and its derivatives have healthy benefits including improvement of nerve ischemia and hypoxia, amelioration of the dysfunction caused by neurological injury, reduction of nerve cell edema,

increasing the scavenging capacity of free radicals, decreasing the free radical damage, and decrement of the calcium overload of nerve cells (21, 22). It was also found that HMF can play an important role in the treatment of endotoxemia and cutback the death rate caused by multiple organ failure (23). A 53.56 mg L⁻¹ HMF content in Shaoxing rice wine with a brewing age of 3 years was found, but just a 7.69 mg L⁻¹ HMF content in yellow Shaoxing rice wine with a brewing age of 9 months was found. Thus, the mechanism and affecting factors of HMF formation in rice wine should be investigated in the interest of determining HMF effects and safety.

In the present study, the effects of temperature, time isothermal heat treatment, and different components on HMF contents in rice wine are discussed. A kinetic model(s) for HMF formation in rice wine under the heat treatment was also determined.

MATERIALS AND METHODS

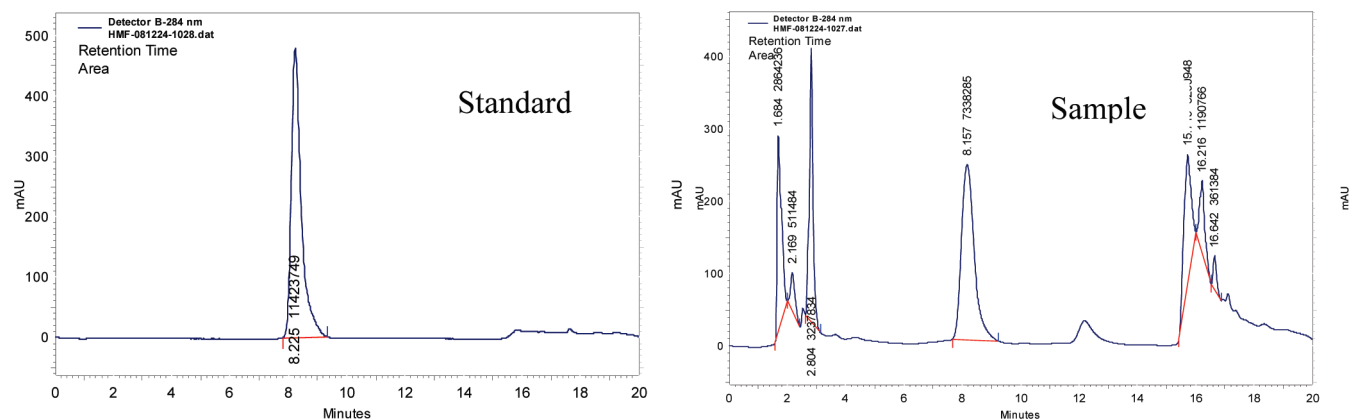
Materials. Nine month aged rough rice wine was purchased from Zhejiang Shaoxing. The AB-8 macroporous resin and 732# ion-exchange resin were obtained from the Chemical Plant of NanKai University (Tianjin, China). Methanol (high-performance liquid chromatography, HPLC) was obtained from Dikma (Dikma Technologies Inc., Lake Forest, CA), and water was distilled in glass and purified using a Milli-Q water purification system (Millipore, Bedford, MA).

HPLC Analysis. A Shimadzu model HPLC system (Shimadzu Corp., Kyoto, Japan), consisting of a communications bus module (CBM-20A), a vacuum degasser (DGU-20A5), a solvent delivery module (LC-20AT) with a double plunger reciprocating pump, a diode array detector (SPD-M20A), a column oven (CTO-10ASvp), and a manual injector with a 20 μ L sampling loop was employed for the HMF analyses.

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Table 1. Sample Treatment

| samples | sample I | sample II | sample III |
|----------------------|-------------------------------------|--|---|
| processing procedure | not treated (i.e., rough rice wine) | outflow solution from the AB-8 macroporous resin | outflow solution from sample II and 732# ion-exchange resin |
| removed components | none | ethanol, phenols, fats, etc. | ethanol, phenols, fats, protein components, etc. |

**Figure 1.** HPLC spectrogram of the HMF for the standard solution and the sample.

The chromatography column [Diamonsil C₁₈ (150 mm × 4.6 mm i.d., 5 μm particle size)] was obtained from Dikma. Data were collected, processed, and analyzed using Class-VP Chromatography Laboratory Automated software (Shimadzu Corp.). The chromatographic separations were carried out at 284 nm and 40 °C. The mobile phase was methanol–water (10:90) with flow of 1.0 mL min⁻¹, and the injection volume was 20 μL. The identification of compounds was achieved by comparing their retention time values and UV spectrograms with those of the appropriate standards. Samples that had been under reaction were filtered through the 0.45 μm PTFE filter only, and 10 μL was immediately injected into the HPLC according to the above conditions. No other sample pretreatment was used.

Sample Treatment. To explore the effects of different chemical constituents on the formation reaction of HMF in Chinese rice wine, different resins were used to remove the affecting factors. AB-8 macroporous resin was used to remove weak polar components, while 732# ion-exchange resin was used to remove protein components (Table 1). The samples for HMF determination were prepared as follows and are summarized in Table 1.

Sample I. The untreated rice wine with 9 months of aging time was regarded as sample I.

Sample II. Two liters of 9 month aged rice wine was condensed by rotary evaporation under vacuum below 45 °C to remove the alcohol. The condensed solution was allowed to flow through the AB-8 macroporous resin until the outflow of the fluid did not have a refractive index. Then, the outflow solution regarded as sample II was collected and condensed to the original 2 L by vacuum evaporation at 45 °C.

Sample III. Sample II was prepared as above and then was allowed to flow through a 732# ion-exchange resin until the outflow of the fluid did not have a refractive index. Eventually, the outflow solution regarded as sample III was collected and condensed to the original 2 L by vacuum evaporation at 45 °C.

Kinetic Detection of HMF Formation. The reflux devices and superthermostat water bath (temperature control precision, ±0.1 °C) were used to place the samples under isothermal heat treatment at 323.15, 333.15, 343.15, 353.15, and 363.15 K at the definite, respective time (0, 2, 4, 6, 8, and 10 h). Samples were subsequently obtained every 2 h and immediately cooled to room temperature and injected into the HPLC to determine their HMF contents. Every detection point was determined by triplicate measurement.

Mathematical Modeling. Nonenzymatic browning reactions present an initial induction period that corresponds to the stage of HMF formation. After this induction period, which can be fast, the content of the product can increase linearly with time (zero-order kinetics) or can

increase exponentially with time (first-order kinetics) (17).

$$C_t = C_0 + k \cdot t \quad (\text{zero-order kinetics}) \quad (1)$$

$$C_t = C_0 \exp(k \cdot t) \quad (\text{first-order kinetics}) \quad (2)$$

$$k = k_f \exp(-E_a/RT) \quad (\text{Arrhenius equation}) \quad (3)$$

Regression analysis (curve fitting) and the calculation of kinetic rate constants were performed using the Microcal Origin v 8.0 software. All statistical analyses were carried out at a 95% level of confidence.

Data Analysis. Graphic displays were used to illustrate the regression of rice wine HMF content over the time of heat treatment. The graph ordinate represents the content of HMF, and the abscissa represents the time of heat treatment, with the ordinate values being given as the natural logarithm of the reaction velocity constant and the abscissa values being determined as the reciprocal of the heat treatment temperature. The relationship between the reaction velocity constant and the temperature of the heat treatment was then determined. For all equations, C_0 is the initial content of HMF, while C_t is the HMF content, with mg L⁻¹ as the unit of measure; T is the thermodynamic temperature, with K (Kelvin) as the unit; R is the molar gas constant; t is the time of heat treatment, with h as its unit; k is the rate constant, with h⁻¹ as its unit; k_f is the frequency factor; E_a is the activation energy; and the number of subscripts stands for the type of samples.

RESULTS AND DISCUSSION

HMF Chromatography for Samples and the Standard Solution.

The HMF peak for the standard solution and the samples appears at about 8.2 min and shows a well-defined shape under the presented chromatographic conditions (Figure 1). This can help to achieve determination and qualitative analysis for HMF based on the use of both retention time and an UV spectra.

Kinetics of the HMF Formation Reaction. Result of Sample I.

During the isothermal heat treatment process, the formation rate and content of HMF in sample I were enhanced as the processing time and temperature increased as depicted in Figure 2 (sample I) and Table 2. These results indicate that the kinetics of HMF formation complied with eq 2. The initial content of HMF in sample I is C_0 , which is equal to 7.69 mg L⁻¹. Figure 3 shows that the logarithmic relational expression with regard to the reaction

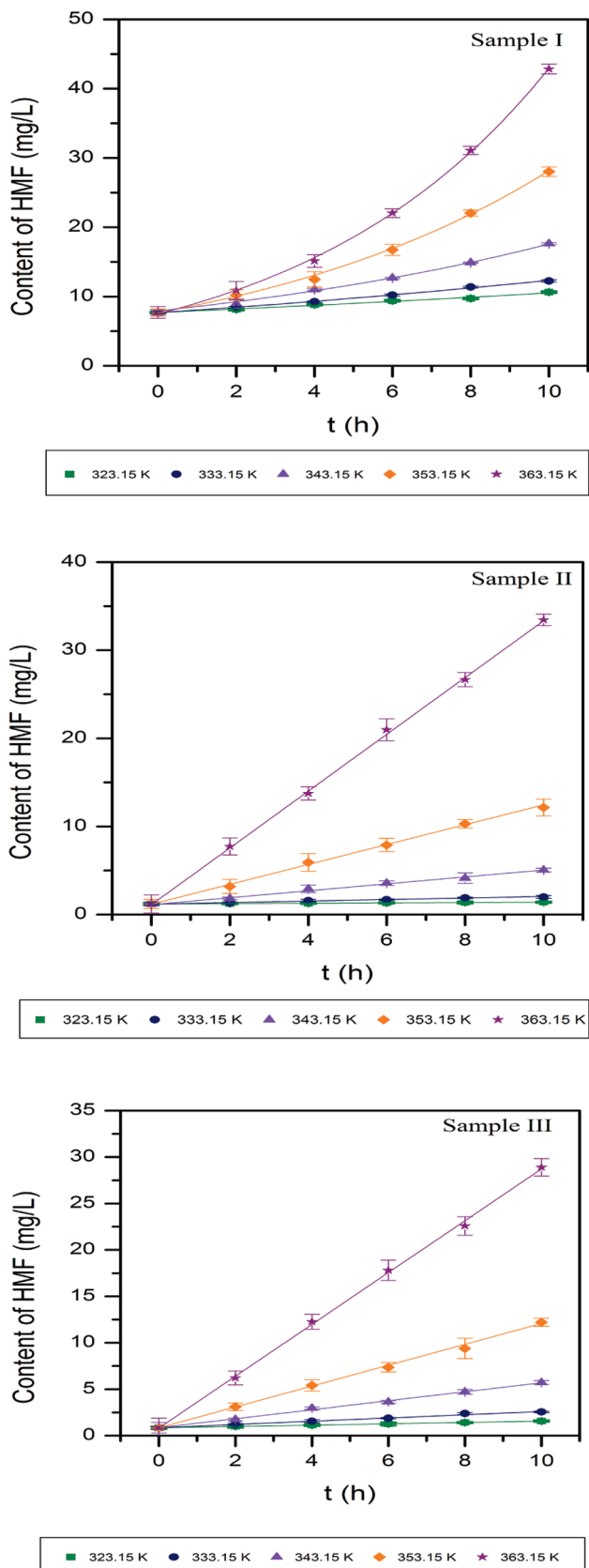


Figure 2. HMF content at different temperatures.

velocity constant and the temperature of the heat treatment is in accordance with the equation $\ln k_1 = -5173.5(1/T) + 12.55$. Then, the corresponding exponential expression is $k_1 = e^{12.55} \exp(-5173.5/T) = 2.81 \times 10^5 \exp(-43.01/RT)$, which is in compliance with eq 3. The apparent frequency constant is $k_f = 2.81 \times 10^5 \text{ h}^{-1}$,

and the apparent activation energy is $E_{a1} = 43.01 \text{ kJ mol}^{-1}$ (Table 3).

Result of Sample II. As shown in Figure 2 (sample II) and Table 2, the HMF content in sample II also had a tendency to increase during the isothermal heat treatment process. However, the change in HMF content, apparently in accordance with eq 1, where C_0 is the initial content of HMF in sample II, was measured in a concentration of 1.21 mg L^{-1} . Figure 3 shows that in sample II, the logarithmic relational expression with regard to the reaction velocity constant and the temperature of the heat treatment is in accordance with the equation $\ln k_2 = -14902(1/T) + 42.29$. Then, the corresponding exponential expression is $k_2 = e^{42.29} \exp(-14902/T) = 2.33 \times 10^{18} \exp(-123.90/RT)$, which is in compliance with eq 3. The apparent frequency constant is $k_f = 2.33 \times 10^{18} \text{ h}^{-1}$, and the apparent activation energy is $E_{a2} = 123.90 \text{ kJ mol}^{-1}$ (Table 3).

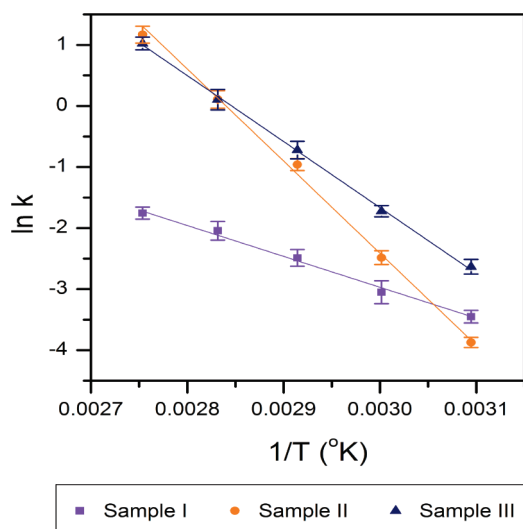
Result of Sample III. The HMF behavior in sample III was the same as in sample II, as seen in Figure 2 (sample III) and Table 2. The kinetics of HMF formation complied with eq 1, with C_0 being equal to 0.85 mg L^{-1} . Figure 3 shows that in sample III, the logarithmic relational expression with regard to the reaction velocity constant and the temperature of the heat treatment is in accordance with the equation $\ln k_3 = -10724(1/T) + 30.51$. Then, the corresponding exponential expression is $k_3 = e^{30.51} \exp(-10724/T) = 1.79 \times 10^{13} \exp(-89.16/RT)$, which is in compliance with eq 3. The apparent frequency constant is $k_f = 1.79 \times 10^{13} \text{ h}^{-1}$, and the apparent activation energy is $E_{a3} = 89.16 \text{ kJ mol}^{-1}$ (Table 3).

For the three different samples, the apparent frequency constant and the activation energy were different, which may be a reflection of inherent differences in the compounds in each sample. Thus, the treatment methods and the sample composition are crucial for consideration of HMF formation. As Table 1 shows, sample II was the outflow fraction from the AB-8 macro-porous resin. Therefore, Sample II contained the protein components (A), carbohydrate (B) and other trail materials (D), without interference from weak polar components(C) (e.g., phenols, fats, etc.), since the resin was applied to absorb phenols and nonpolar substances. Sample III was the outflow fraction from the 732# cation-exchange resin for sample II, which can eliminate nitrogenous substances (A) (e.g., amino acid, protein, etc. detected by Bradford assay), since they are primarily absorbed in the ionic state. Consequently, sample III only contained B and D components, or in other words, it contained primarily B components, since D represents residual material. This can be concluded from the data in Table 3.

The E_{a1} of sample I is the lowest (see Table 3), so the formation of HMF was the most rapid. This indicates that in the natural state, HMF in rice wine can be easily produced. It may result in the color of the rice wine yellow, because the diluted HMF itself is yellow. Nevertheless, as a result of removing the C component, the E_{a2} of sample II is much higher than in sample I, and the formation of HMF decreased significantly. That shows that perhaps the C components, especially the phenolic compounds, can accelerate the formation of HMF. Previous research indicated that phenolic compounds could form oligomers with HMF (24), but whether phenols can accelerate the formation of HMF should be further confirmed. In sample III, after the A components (which can advance the Maillard reaction) were removed, the E_{a3} should have been higher, whereas it was, in fact, lower, and the formation of HMF was more rapid. This observation does not conform with the theory that HMF is a product of the Maillard reaction and should be promoted by the A category of substances (25, 26). Hence, the factor that accelerates HMF

Table 2. Summary of HMF Formation in Three Different Samples

| temperatures T (K) | sample I | | | sample II | | | sample III | | |
|-------------------------|------------------------------|--|----------------|--------------------------|--|----------------|--------------------------|--|----------------|
| | regression equation | velocity constant k (h^{-1}) | variance R^2 | regression equation | velocity constant k (h^{-1}) | variance R^2 | regression equation | velocity constant k (h^{-1}) | variance R^2 |
| 323.15 | $C_1 = 7.6924 \exp(0.0317t)$ | 0.0317 | 0.9905 | $C_1 = 0.0208t + 1.2064$ | 0.0208 | 0.9919 | $C_1 = 0.0719t + 0.8457$ | 0.0719 | 0.9993 |
| 333.15 | $C_1 = 7.6924 \exp(0.0473t)$ | 0.0473 | 0.9985 | $C_1 = 0.0834t + 1.2064$ | 0.0834 | 0.9854 | $C_1 = 0.1783t + 0.8457$ | 0.1783 | 0.9922 |
| 343.15 | $C_1 = 7.6924 \exp(0.0831t)$ | 0.0831 | 0.9982 | $C_1 = 0.3830t + 1.2064$ | 0.3830 | 0.9927 | $C_1 = 0.4853t + 0.8457$ | 0.4853 | 0.9968 |
| 353.15 | $C_1 = 7.6924 \exp(0.1296t)$ | 0.1296 | 0.9983 | $C_1 = 1.1145t + 1.2064$ | 1.1145 | 0.9977 | $C_1 = 1.1084t + 0.8457$ | 1.1145 | 0.9975 |
| 363.15 | $C_1 = 7.6924 \exp(0.1730t)$ | 0.1730 | 0.9996 | $C_1 = 3.2174t + 1.2064$ | 3.2174 | 0.9994 | $C_1 = 2.7843t + 0.8457$ | 2.7843 | 0.9991 |

**Figure 3.** Arrhenius plots for HMF accumulation.**Table 3.** Components That Affect the Formation of HMF in Three Samples

| sample | E_a (kJ mol^{-1}) | reactant ^a | reaction order | irrelevant factors |
|--------|-----------------------------------|-----------------------|----------------|---------------------------------------|
| I | $E_{a_1} = 43.014$ | A + B + C + D | 1 | uncertainly |
| II | $E_{a_2} = 123.900$ | A + B + D | 0 | the concentration of A, Bm and D |
| III | $E_{a_3} = 89.163$ | B + D | 0 | 1, A; 2, the concentration of B and D |

^a A, protein components; B, carbohydrate; C, phenols, fats, etc.; and D, trace material that cannot be determined.

formation is the unknown trace material (D), rather than the A component.

Moreover, the reactions in both samples II and III were zero order. The compounds that affect the speed of formation of HMF should not be the concentrations of the A, B, and D components, because the concentration of reactants is not the decisive factor in zero-order reactions. Thus, the factors that affect the formation of HMF in samples II and III must be further investigated. On the basis of the kinetic equations, weak polar components (C), such as phenols, may be implicated in HMF formation, where the concentrations of the nitrogenous compounds and carbohydrates may not be important factors in HMF formation in Chinese rice wine.

ABBREVIATIONS USED

HMF, hydroxymethylfurfural; GC-MS, gas chromatography–mass spectrography; HPLC, high-performance liquid chromatography; C_0 , the initial content of HMF; C_t , the HMF content; T , thermodynamic temperature; K, Kelvin; R , molar gas constant; t , the time of heat treatment; k , the rate constant; k_f ,

the frequency factor; E_a , activation energy; A, protein components; B, carbohydrate; C, phenols, fats, etc.; D, trace material, which cannot be determined.

ACKNOWLEDGMENT

We thank William W. Riley and Chi-Wei Lan for excellent writing assistance.

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Received for review November 21, 2009. Revised manuscript received February 3, 2010. Accepted February 5, 2010.