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Article de recherche

Formation kinetics of total hydroxymethylfurfural during UHT processing of buffalo milk

R.R.B. Singh and G.R. Patil

Division of Dairy Technology, National Dairy Research Institute, Karnal 132001, India

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Summary — The kinetics of 5-hydroxymethylfurfural (HMF) formation upon UHT processing of buffalo milk over a temperature range of 130—145 °C and exposure time of 3.3—22.7 sec was studied using a pilot scale directly heated UHT plant. The formation reaction of total HMF could be described by a constant *z*-value of 32.5 °C (Q_{10} = 2.03). The reaction rate constants for total HMF formation obtained in this study could be expressed by Arrhenius as well as absolute reaction rate theories. The formation of total HMF had an activation energy of 93.9 kJ/mol. The activation enthalpy (ΔH^*) and free energy of activation (ΔG^*) were 90.5 and 102.9 kJ/mol, respectively, for the temperature range of 130—145 °C. The activation entropy (ΔS^*) was found to be negative and was very small (– 30.2 J/mol.K).

UHT processing – buffalo milk – total hydroxymethylfurfural

Résumé — Cinétiques de formation d'hydroxyméthylfurfural total au cours du traitement UHT de lait de bufflonne. *Les cinétiques de formation du 5-hydroxyméthylfurfural (HMF) au cours du traitement UHT de lait de bufflonne dans une gamme de température de 130 à 145 °C et un temps de séjour de 3,3 à 22,7 sec ont été étudiées sur un équipement UHT pilote à chauffage direct. La réaction de formation du HMF total pouvait être décrite par une valeur de z constante de 32,5 °C (Q_{10} = 2,03). Les constantes de vitesse pour la formation du HMF total observées dans cette étude étaient en bon accord avec celles découlant de la théorie d'Arrhenius et de celle dite des vitesses absolues de réaction. La formation d'HMF total avait une énergie d'activation de 93,9 kJ/mol. L'enthalpie d'activation* (ΔH^*) *et l'énergie libre d'activation* (ΔG^*) *étaient respectivement de 90,5 kJ/mol et de 102,9 kJ/mol pour les températures de 130 à 145 °C. L'entropie d'activation* (ΔS^*) *observée était négative et très faible (– 30,2 J/mol.K).*

traitement UHT – lait de bufflonne – hydroxyméthylfurfural total

Introduction

The Maillard reactions occur as a consequence of a complex series of reactions (Hodge, 1953) which involve a first stage heat-induced condensation reaction between the free aldehyde group of lactose and the ε-amino group of lysine. Various intermediate compounds which are formed in the Maillard reactions can be measured and, since their formation follows similar kinetics, their concentrations are also potential measures of heat treatments (Burton, 1984). The Amadori rearrangement products of Maillard reactions *viz.* the 1-amino-1-deoxy-2-ketoses are readily converted into 5-hydroxymethylfurfural (HMF) upon mild acid treatment (Gottschalk, 1952) which can be quantitatively measured using a sensitive method suggested by Keeney and Bassette (1959).

The kinetics of total HMF formation during UHT processing of cow milk have been determined by several researchers (Konietzko and Reuter, 1980; Mottar, 1981). Such information, however, is lacking for buffalo milk which has a slightly different compositional makeup from cow milk and is, hence, expected to show different kinetics of HMF formation during UHT processing. The present study was, therefore, undertaken to obtain accurate kinetic data of total HMF formation during UHT processing of buffalo milk.

Materials and Methods

Raw buffalo milk for UHT processing was obtained from the bulk supply of the experimental dairy of the National Dairy Research Institute, Karnal.

Unhomogenized milk was processed at 130, 135, 140 and 145 °C temperatures for 3.3, 9.6, 16.2 and 22.7 sec using an experimental direct type UHT plant developed by Anap and Agrawala (1985).

Determination of total HMF

The total HMF was determined using a method developed by Keeney and Bassette (1959). Absorbance was measured in a photoelectric colorimeter (EEL, England). The following regression equation was obtained from the standard curve prepared by using a standard HMF (Sigma) solution.

$$\mu\text{mol / l HMF} = R \times 133.0179 - 0.79767$$

where R is the absorbance for the treated sample—the absorbance for raw sample at 443 nm.

Computation of kinetics

The formation reactions, including formation of total HMF, being mostly complex reactions involving multistage conversion, difficulty is usually encountered in finding out their reaction order. In the interest of computing reaction kinetics of such complex formation reactions, Herrmann (1973) suggested that one should restrict calculations to the lower region of the growth curve where there is slight turnover. Thus, according to him, the order of the reaction can be neglected up to 1/10th of the substances formed and, up to this point, all reactions can be treated as 0 order reactions. Konietzko and Reuter (1980) successfully applied these fundamentals to the computation of kinetics of HMF formation in cow milk. The kinetics of HMF formation in buffalo milk (during UHT processing) therefore was computed accordingly.

Thus, the reaction rate constant k for total HMF formation at any given constant temperature could be expressed by 0 order reaction as:

$$\frac{\text{d}\,HMF}{\text{d}\,t} = k\,(T = \text{constant}). \qquad (1)$$

The reaction rate constant k was then related to 1/10th of the HMF formed, in order to eliminate the effect of reaction order on k, using the following relationship :

$$k = \frac{1}{10.\,H} \qquad (2)$$

where H is the new value given by Herrmann, which gives the time required for 10% of the substances formed.

The relationship between total HMF and the H-value was obtained using the following expression :

$$H = \frac{t}{10 \times HMF\,(\mu\text{mol/l})} \quad (T = \text{constant}). \quad (3)$$

A time-temperature curve for total HMF formation was obtained by plotting log H against T, from which the z-value (which is reciprocal to the slope of the curve) for the said formation reaction was derived.

The activation energy for the formation of total HMF was obtained from the Arrhenius relationship by plotting log k against $1/T$.

$$k = A \cdot e^{-E_a/RT} \qquad (4)$$

where, A = Arrhenius constant; Ea : activation energy; R = gas constant.

The enthalpy (ΔH^*), entropy (ΔS^*) and free energy (ΔG^*) of activation were calculated from the experimentally obtained reaction rate constants as suggested by Emmanuel and Knorre (1969).

The enthalpy was calculated from activation energy obtained from the experimentally determined reaction rate constant using the following relationship :

$$\Delta H^* = E_a - RT. \qquad (5)$$

The entropy of activation was obtained from the following well known absolute reaction rate theory.

$$k = \frac{k_B \cdot T}{h} \; e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \qquad (6)$$

where k_B = Boltzmann's constant; h = Plank's constant.

The free energy of activation was obtained from the following relationship

$$\Delta G^* = \Delta H^* - T \cdot \Delta S^*. \qquad (7)$$

Results and Discussion

Formation of total HMF

The temperature dependence of total HMF formation in buffalo milk at various holding times is depicted in Fig. 1. The minimum amount of total HMF (2.04 µmol/l) was formed at 130 °C/3.3 sec. With increases in time and temperature, the concentration of total HMF increased steadily and at the maximum time—temperature combination (145 °C/22.7 sec), formation was as high as 19.34 µmol/l.

Wide variations in the reported values of total HMF formed during UHT processing of milk have been reported in the literature. Töter (1979) reported that the HMF concentration in commercial UHT milks immediately after processing varied from trace to 9.2 µmol/l, whereas Mottar *et al.* (1979) obtained 4—16 µmol/l

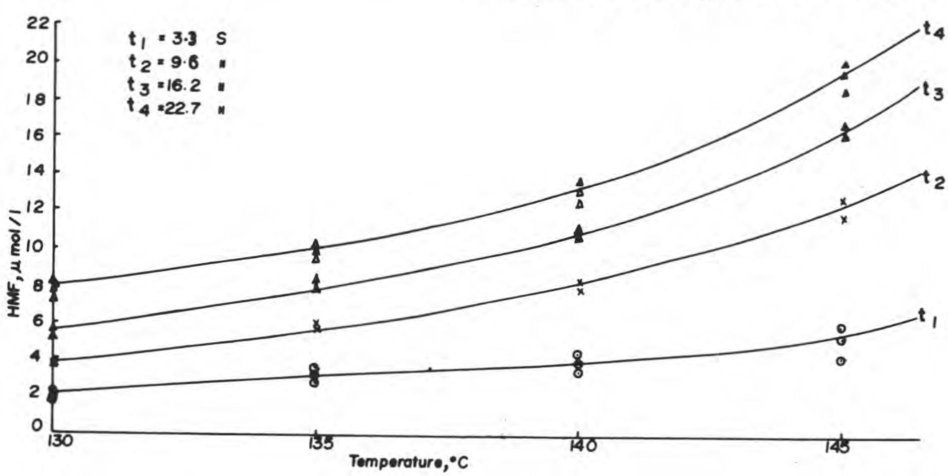

Fig. 1. Effect of time and temperature on HMF formation (total) during UHT processing of buffalo milk.

total HMF in different commercially processed UHT milks. Absolute values of total HMF formed during UHT processing of buffalo milk were comparatively higher and this could be ascribed to the higher levels of protein and lactose in buffalo milk. In addition, a number of components, such as phosphates, dissolved oxygen, active sulfhydryl groups, *etc.*, have been shown to influence the reaction in model systems. The contents of these components, therefore, significantly determine the rate of formation of HMF in milk (Nickerson, 1972).

Kinetics of total HMF formation

H-values were calculated from the available data and log *H* plotted against processing temperatures (Fig. 2) which gave a straight line. The *z*-value obtained for UHT processing of buffalo milk was 32.5 °C (Q_{10} = 2.03) which was comparatively close to the value obtained by Mottar (1981), who described the reaction kinetics of total HMF formation by *z* = 27.8 °C (Q_{10} = 2.29). When compared with *z* = 20.7 °C (Q_{10} = 3.04) as described by Horak (1980) and with *z* = 23.7 °C (Q_{10} = 2.64) as obtained by Konietzko and Reuter (1980), the *z*-value for buffalo milk was higher.

The zero order reaction rate constant (*k*) was calculated for each corresponding *H*-value using eqn. 2. The temperature dependence of the reaction rate constant has been depicted in an Arrhenius plot (Fig. 3). The relationship between log *k* and the reciprocal of absolute temperature (1/*T*) was found to be linear. The standard error of least square fit was found to be (±0.02). The activation energy and Arrhenius constant obtained from the Arrhenius plot were 93.9 kJ/mol and 6.3464 x 10^{11} sec^{-1}, respectively.

The thermodynamic parameters activation enthalpy *(ΔH*)*, activation entropy *(ΔS*)* and free energy of

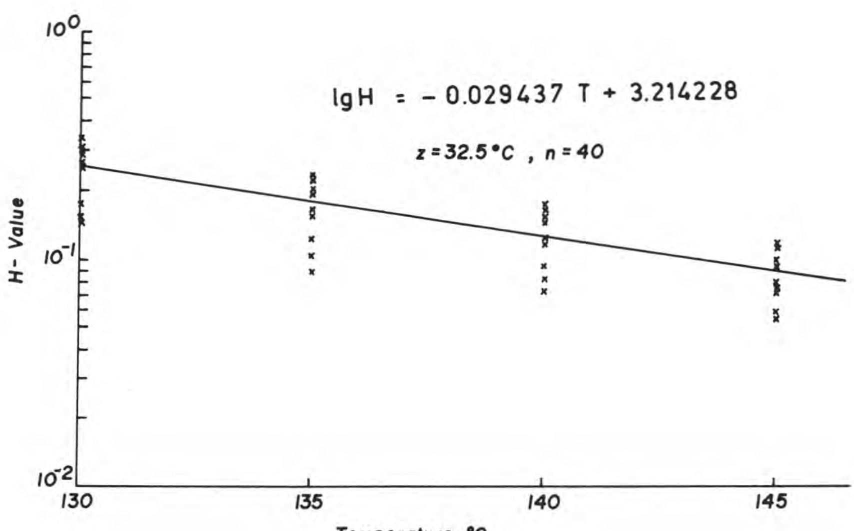

Fig. 2. The relationship between temperature and *H*-value for HMF formation (total) during UHT processing of buffalo milk.

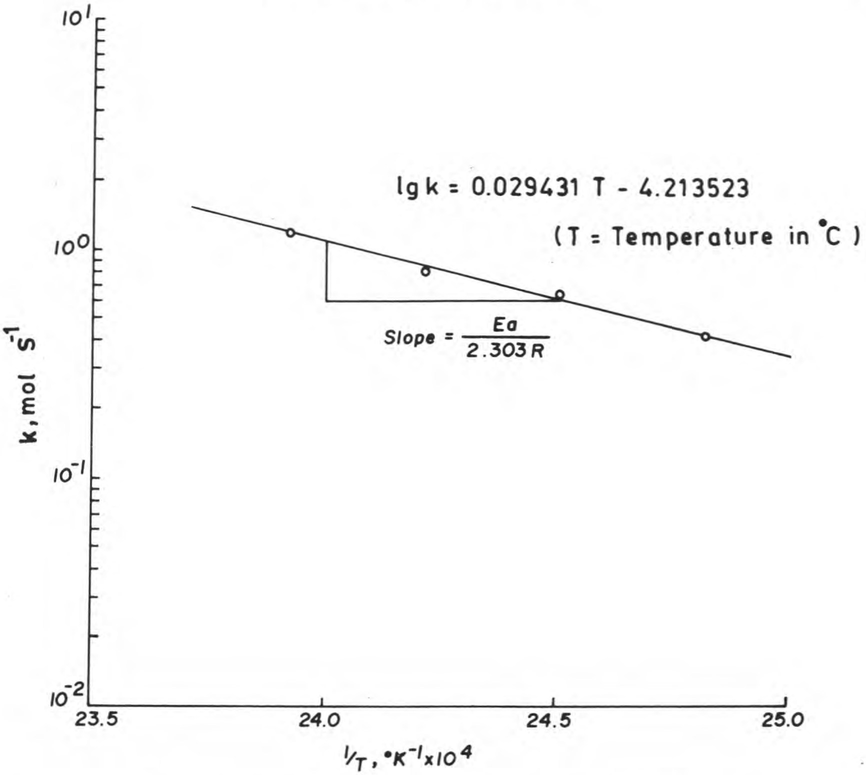

Fig. 3. Arrhenius plot for HMF formation (total) during UHT processing of buffalo milk.

activation *(ΔG^*)* were obtained for the formation ot total HMF using equations 5, 6 and 7, and were 90.5 kJ/mol, –30.2 J/mol.K and 102.9 kJ/mol, respectively. The activation entropy for the HMF formation reaction was negative and was very small.

Conclusion

The experimental results obtained in the present investigation provide useful information as to the thermal load on buffalo milk during UHT processing. It is hoped, therefore, that these results will help to control the severity of heat-treatment given to buffalo milk and hence to optimize the UHT process.

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