



Research Paper

Thermodynamic description of the chemical leavening in biscuits

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ABSTRACT

In this paper we describe the chemical reactions of leavening agents in baking biscuits on a sound thermodynamic basis. The model is part in a sequel targetted at physical understanding of biscuit baking with the purpose of reformulation of biscuits with respect to sucrose and sodium levels. The chemical leavening gases, CO₂ and NH₃, originate from the dissociation of sodium and ammonium bicarbonate. Next to water vapour, these produced gases create gas bubbles in the biscuit dough. The concentrations of the leavening agents and added salt lead to high ionic strength. Consequently, the activities of ions participating in the leavening reaction deviate strongly from ideality. The non-idealities are described using the Pitzer equations. The values of many parameters of the Pitzer model and equilibrium constants are obtained from the strong developed field of CO₂ sequestering in ammonia solutions. The model describing the chemical reactions is coupled to a cell model describing the expansion of gas bubbles. Model simulations show that most of the produced gas originates from the bicarbonate, and the ammonium contributes significantly less. The functionality of ammonium as leavening agent is not quite clear, but it may help in reducing sodium levels.

1. Introduction

We are involved in a research program involving the understanding of the baking process of biscuits, and in particular the function of ingredients regarding resulting microstructure, in order to develop reformulation strategies (van der Sman and Renzetti, 2019). Biscuits are high in sugar and sodium levels, with sodium contributed by added salts and leavening agents. Sound reformulation strategies must be based on good understanding of the functionality of ingredients. In an earlier paper we have reviewed the many functions of sucrose in biscuits van der Sman and Renzetti (2019). Here, in this paper we will focus on the functionality of the leavening agents in biscuits, based on the AACC-1053 formulation (Kweon et al., 2009), which we use as a model biscuit in our research. The leavening agents, sodium and ammonium bicarbonate, are involved in a complex of chemical reactions. The function of leavening agents is to generate CO₂ gas, which allows (together with the evaporation of moisture) gas bubbles to be formed during baking. For a good understanding of the leavening action, we aim to develop a multiscale simulation, which is based on a sound thermodynamic description of the driving forces for bubble formation, similar to our previous study on expanding starchy snacks (van der Sman and Broeze, 2014).

In food science the chemical reactions of leavening agents are hardly investigated. In a larger review paper Kweon et al., (2014) have made some remarks on the functionality of leavening agents, but without a

detailed description of experiments. Leavening in bread dough via CO₂ from yeast or chemical leavening agents is better investigated, which is shortly reviewed below.

The studies (Bellido, 2007; Bellido et al., 2008) have investigated the action of chemical leavening agents in bread dough. Leavening agents produce gases via a reaction of a base like sodium bicarbonate and a weak organic acid, as lactic acid, citric acid, or tartaric acid. The sodium bicarbonate reacts quickly with the weak acid. For more slow release of gases one uses also ammonium bicarbonate, which produces both CO₂ and NH₃. Maximal gas production is assumed at $T = 59^{\circ}\text{C}$. Its use is limited to low moisture products like cookies, where one expects maximal decomposition, because residues give off-tastes after baking.

The dissolution of CO₂ in dough is investigated in bakery products leavened by yeast. Earlier models have assumed that during proofing the bread dough is saturated with CO₂ (Shah et al., 1998; Fan et al., 1999). Distinct liquid and gas phase are assumed, exchanging CO₂ and H₂O. During baking the temperature will rise, and the solubility of CO₂ reduces - which is released as gas in the expanding bubble. One assumes no extra generation of CO₂ by yeast. Later models incorporated the action of yeast, but the hydration of CO₂ is not included (Chiotellis and Campbell, 2003; Narsimhan, 2014).

(Aissa et al., 2015) have given a quantitative description of yeast leavening including the hydration of CO₂ solubility. In their model they account for 1) the presence of both a liquid and gas phase, 2) the

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hydration of CO₂ into (bi)carbonate, and 3) the ionic strength of the dough (due to added salts). Data is given of CO₂ solubility as function of NaCl, showing that salt reduces the solubility of CO₂. Dissociation constants for bicarbonate is given as function of temperature, and ionic strength. For the vapour-liquid equilibrium of CO₂ they have considered a temperature dependent Henry constant. We intend to develop a similar model for chemical leavening agents, but one which is based on first principles and sound thermodynamics.

In biscuits there is also a significant amount of salt present, moderating the ionic strength of the aqueous solution phase of the biscuit. As is known from electrochemistry, the ionic strength will significantly change the dissociation of ions from the leavening agents. Hence, we have to take into account the effect of the sodium chloride (NaCl) in the chemical reactions.

In chemical engineering the inverse reaction, the solubilization of CO₂ and NH₃ gases in water, is a strongly developed field. Currently, the problem of CO₂ sequestering is driving this field (Wang et al., 2011; Zhao et al., 2012). It follows that the gases are produced via a complex network of chemical reactions. Furthermore, the high ionic strength requires the use of the Pitzer equation for the computation of the ion activities (Edwards et al., 1978), which enter the expressions for the equilibrium constants. In several (de) protonation reactions water is involved, requiring knowledge of the water activity. Also for the biscuit the water activity must be known, as the moisture content of the biscuit is low, and the sugar content is high. Consequently, the water activity will be considerably lower than unity, which influences the chemical equilibrium of fast reactions.

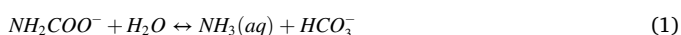
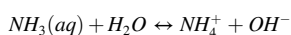
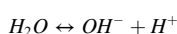
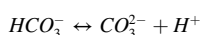
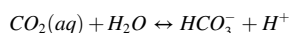
Wang et al., (2011) have studied the sequestering of CO₂ in ammonia solutions. They show a convenient representation of the reaction network, with 3 axes showing 1) proton-transfer, 2) OH transfer, and 3) NH₃ transfer. Reactions involving NH₃ transfer is the least likely, implying very slow reaction kinetics. Hence, there is a wide separation of time scales of the reaction kinetics, making it a numerical stiff problem, which is very challenging to solve. It will be too demanding to incorporate the full model into a biscuit baking model. Hence, we will also investigate the model reduction of this chemical system.

The paper is organized as follows. We start with a comprehensive model description, entailing a) the thermodynamics of chemical reactions, b) the Pitzer model, c) the bubble expansion model, and d) the model reduction. As experimental data on the action of leavening agents in food is very scarce, model validation will be performed on sub-problems from chemical engineering. Subsequently, we present the simulation results for the leavening of biscuits, before we end with conclusions.

2. Model description

2.1. Reaction scheme

The leavening system of the AACCC 10–53 biscuit, based on sodium and ammonium bicarbonate, reacts according to the following reaction scheme:



The above set of reactions is identical to that of the CO₂-NH₃-H₂O system, which is well investigated in the field of chemical engineering (Edwards et al., 1978; Wang et al., 2011). NH₂COO⁻ is the carbamate

ion. In studies of CO₂ sequestering it is shown during solubilization of NH₃ and CO₂ in water, more carbamate is formed than ammonium (Wang et al., 2011). Only if CO₂ is depleted more ammonium than carbamate is formed.

The following equilibrium constants are defined:

$$K_1 = \frac{a_{\text{HCO}_3^-} a_{\text{H}}}{a_{\text{w}} a_{\text{CO}_2}}$$

$$K_2 = \frac{a_{\text{CO}_3^{2-}} a_{\text{H}}}{a_{\text{HCO}_3^-}}$$

$$K_3 = \frac{a_{\text{OH}^-} a_{\text{H}}}{a_{\text{w}}}$$

$$K_4 = \frac{a_{\text{NH}_4^+} a_{\text{OH}^-}}{a_{\text{w}} a_{\text{NH}_3}}$$

$$K_5 = \frac{a_{\text{NH}_3} a_{\text{HCO}_3^-}}{a_{\text{w}} a_{\text{NH}_2\text{COO}^-}} \quad (2)$$

with $a_i = \gamma_i m_i$ is the activity of component i , which will be expressed in terms of the molality m_i , and the activity coefficient γ_i .

The temperature dependency of the equilibrium constants has been investigated in multiple papers (Edwards et al., 1978; Bieling et al., 1989), which all follow the generalized relation:

$$\log(K) = A_1/T + A_2 \log(T) + A_3 T + A_4 \quad (3)$$

In Table 1 we have listed the values of A_i that we have used together with references to their source.

2.2. Pitzer model for multiple electrolyte solutions

We use the Pitzer model as used in the study of (Edwards et al., 1978). In the AACCC 10–53 system the total ionic strength is of order unity, and consequently the ternary terms of the Pitzer model are not required.

Hence, the activity coefficient of ion a is defined by:

$$\log(\gamma_a) = -z_a^2 F(I) + 2 \sum_c m_c B_{ac} - z_a^2 \sum_c \sum_{d'} m_c m_{d'} B'_{ac'} \quad (4)$$

In Eq. (4) the subscripts ac represent any anion/cation pair, while $a'c$ represent anion/cation pairs with $a' \neq a$. B_{ca} are called the binary ion-ion parameters.

I is the ionic strength, computed as:

$$I = \frac{1}{2} \sum_i z_i^2 m_i \quad (5)$$

and z_i the valency of the ion.

The first term is the Debye contribution with:

$$F(I) = -A_\varphi \left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right] \quad (6)$$

with $A_\varphi = 0.392$, and $b = 1.2$ (Edwards et al., 1978).

The binary Pitzer coefficients are a function of the ionic strength, via:

Table 1
Temperature dependency of equilibrium constants. K_i

K_i	A_1	A_2	A_3	A_4	ref.
K_1	-12092	-36.8	0.0	235	(Edwards et al., 1978)
K_2	-12431	-35.5	0.0	220	(Edwards et al., 1978)
K_3	-13446	-22.5	0.0	26.9	(Edwards et al., 1978)
K_4	-3336	1.497	-0.03706	2.76	(Edwards et al., 1978)
K_5	-2900	0.0	0.0	8.6	(Edwards et al., 1978)

$$B_{ac} = \beta_{ac}^{(0)} + 2\beta_{ac}^{(1)} \frac{1 - (1 + \alpha\sqrt{I})\exp(-\alpha\sqrt{I})}{\alpha^2 I} \quad (7)$$

and

$$B'_{ac'} = \beta_{ac'}^{(1)} \frac{1 - \left(1 + \alpha\sqrt{I} + \frac{1}{2}\alpha^2 I\right)\exp(-\alpha\sqrt{I})}{\alpha^2 I^2} \quad (8)$$

The constant is $\alpha = 2$.

The water activity in multicomponent electrolyte solution is related to the osmotic coefficient φ , which is given by (Pitzer, 1973; Edwards et al., 1978):

$$(\varphi - 1) \sum_i m_i = -A \frac{2I\sqrt{I}}{1 + b\sqrt{I}} \quad (9)$$

$$+ 2 \sum_c \sum_a m_c m_a \left(\beta_{ca}^{(0)} + \beta_{ca}^{(1)} \exp(-\alpha\sqrt{I}) \right)$$

The water activity is computed via:

$$\varphi = - \frac{\log(a_w)}{M_w \sum_i m_i} \quad (10)$$

with M_w the molar mass of water.

Data on interaction coefficients $\beta_{ca}^{(i)}$ are shown in Table 2, which are taken from (Kim et al., 1993; Meng et al., 1995).

2.3. Relaxation scheme

The full model is solved via a relaxation scheme. We have defined pseudo reaction rates:

$$\begin{aligned} r_1 &= k_1(-K_1 a_{CO_2} a_{H_2O} + a_{HCO_3} a_H) \\ r_2 &= k_2(-K_2 a_{HCO_3} + a_{CO_3} a_H) \\ r_3 &= k_3(-K_3 a_{H_2O} + a_{OH} a_H) \\ r_4 &= k_4(-K_4 a_{NH_3} a_{H_2O} + a_{NH_4} a_{OH}) \\ r_5 &= k_5(-K_5 a_{NH_2COO} a_{H_2O} + a_{HCO_3} a_{NH_3}) \end{aligned} \quad (11)$$

This renders the following relaxation scheme:

$$\begin{aligned} \partial_t m_{CO_2} &= -r_1 \\ \partial_t m_{NH_3} &= -r_4 + r_5 \\ \partial_t m_{NH_4} &= +r_4 \\ \partial_t m_{NH_2COO} &= -r_5 \end{aligned}$$

Table 2
Pitzer interaction coefficients (Kim et al., 1993; Meng et al., 1995).

ion-pair	$\beta^{(0)}$	$\beta^{(1)}$
NaCl	0.0765	0.2664
Na ₂ CO ₃	0.0399	1.389
NaHCO ₃	0.0277	0.0411
NaOH	0.0864	0.253
NH ₄ HCO ₃	-0.038	0.070
(NH ₄) ₂ CO ₃	-0.105 + 0.000375 T	0
NH ₄ Cl	0.0457	0.204
NH ₄ NH ₂ COO	0.4162-0.00125 T	0
HCl	0.1775	0.2945

$$\begin{aligned} \partial_t m_{CO_3} &= +r_2 \\ \partial_t m_{HCO_3} &= -r_2 + r_1 \\ \partial_t m_{OH} &= +r_3 + r_4 \\ \partial_t m_H &= +r_1 + r_2 + r_3 \end{aligned} \quad (12)$$

Not all equations need to be solved, as there are three algebraic equations for the balance of carbon, nitrogen and charge. The two mass balances for total nitrogen and total carbon in the liquid phase hold:

$$\begin{aligned} N_T &= m_{NH_3} + m_{NH_4} + m_{NH_2COO} \\ C_T &= m_{CO_2} + m_{HCO_3} + m_{NH_2COO} + m_{CO_3} \end{aligned} \quad (13)$$

and the electroneutrality condition is:

$$m_{NH_4} + m_H = m_{HCO_3} + 2m_{CO_3} + m_{OH} + m_{NH_2COO} \quad (14)$$

m_{NH_4} , m_{HCO_3} and m_{OH} are computed via the nitrogen balance, carbon balance, and electroneutrality condition.

The relaxation scheme needs initial conditions for its solution. For the biscuit system the amount of water, the amounts of bicarbonate m_{HCO_3} and ammonium m_{NH_4} are given, rendering also the values for C_T and N_T . m_H and m_{OH} follow from the assumption of neutral pH. The initial value of other compounds is assumed to be zero.

2.4. Bubble formation

During baking there is growth of bubbles due to released gases from the leavening agents. The amount of CO₂ and NH₃ in the gas bubble are extracted from solution phase, which is accounted for in the carbon and nitrogen balance. The sum in the nitrogen and carbon balance C_T and N_T account for the compounds in the solution phase.

Assuming that the biscuit dough behaves as a viscous liquid before thermosetting, the growth of gas bubbles can be described by the Amon and Denson cell model (Amon and Denson, 1984; van der Sman and Broeze, 2014):

$$p_{gas} - p_0 = \frac{4\eta(1 - \varphi_{gas})}{R_b} \frac{dR_b}{dt} \quad (15)$$

η is the dough viscosity, φ_{gas} is the porosity of the dough, and R_b is the bubble radius. Initially the air bubble is of order $R_b(0) = O(10^{-6})$ m. We assume a linear ramp of temperature, representing baking conditions - up to the point of gluten thermosetting (95°C). Biscuit dough viscosity in the temperature range 20 – 40°C is about $\eta = 1 - 5 \times 10^3$ Pa.s (Charun et al., 2000). The number of bubble nuclei N_0 is computed from the assumed initial bubble radius and initial porosity. The gas contains CO₂, NH₃, H₂O, and air:

$$p_{gas} = p_{CO_2} + p_{NH_3} + p_{H_2O} + p_{air} \quad (16)$$

The partial pressures of CO₂ and NH₃ follow Henrys law, cf. (Kawazuishi and Prausnitz, 1987):

$$p_{vap,i} = K_{H,i} \gamma_i m_i \quad (17)$$

with its temperature dependency following:

Table 3
Temperature dependency of Henry constants $K_{H,i}$ (Kawazuishi and Prausnitz, 1987).

Gas	B_1	B_2	B_3	B_4
CO ₂	-17060	-68.3	0.0660	430
NH ₃	-7579	-13.6	0.0086	96.2

$$\log(K_{H,i}) = B_{1,i}/T + B_{2,i}\log(T) + B_{3,i}T + B_{4,i} \quad (18)$$

The coefficients $B_{j,i}$ are listed in Table 3. The Henry constant as function of temperature are shown in Fig. 1.

The water vapour pressure follows from the (total) water activity, which includes the effects of salt and sugar:

$$p_{H_2O} = a_{w,tot} p_{sat}(T) \quad (19)$$

with p_{sat} the temperature dependent saturated vapour pressure. We use the Tetens relation:

$$p_{sat}(T) = p_{ref} \exp\left(17.27 \frac{T - T_{ref}}{T - 35.86}\right) \quad (20)$$

with $T_{ref} = 273.15$ K, and $p_{ref} = 610$ Pa.

To compute the partial gas pressures, we have 3 mass balances describing the change in amount of gas molecules in the gas phase:

$$\begin{aligned} \partial_t n_{CO_2} &= \frac{1}{\tau_{gas}} \frac{K_{H,CO_2} m_{CO_2} - p_{CO_2} A_{gas}}{RT} \\ \partial_t n_{NH_3} &= \frac{1}{\tau_{gas}} \frac{K_{H,NH_3} m_{NH_3} - p_{NH_3} A_{gas}}{RT} \\ \partial_t n_{H_2O} &= \frac{1}{\tau_{gas}} \frac{a_w p_{sat}(T) - p_{NH_3} A_{gas}}{RT} \end{aligned} \quad (21)$$

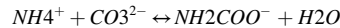
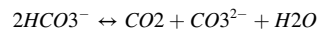
with $n_i = p_i/RT$ the molar concentration of gas i in the gas phase. A_{gas} the surface area of all gas bubbles. τ_{gas} is a relaxation constant, representing the rate of mass transport in the dough matrix. In this simple model we keep it fixed to a small value, such that the gas pressures remain close to the equilibrium values, but fast expansion of the gas bubble will be damped. This damping is also required from a numerical point of view, because Eq. (15) can imply explosive growth of the bubble if $p_{gas} \gg p_0$ at too small values of τ_{gas} (van der Sman and Broeze, 2014). Hence, the value of τ_{gas} is determined via trial simulations. The amount of air molecules remains equal to the initial amount: $n_{air} RT_0 = p_0 V_{gas}$, with V_{gas} the total volume of the gas phase, and T_0 the initial temperature.

The Amon-Denson cell model is solved numerically using a simple explicit time integration scheme, but with an adaptive scheme for the

time step. The time step will be proportional to $\Delta t \sim (1 - \varphi_{gas})^2 (p_r / (p_r + p_{gas} - p_0))^2$, with p_r a reference over-pressure of $O(100)$ Pa. It follows that for $\Delta t / \tau_{gas} = 0.01$ stable numerical simulations are obtained. For values larger than $\Delta t / \tau_{gas} \geq 0.025$ we obtain unstable simulations with numerical oscillations in bubble size.

2.5. Model reduction

Preliminary simulations have shown that proton transfer reactions are very fast. Some effective reactions are quite slow, which becomes apparent after elimination of the fast proton transfer:



Their effective equilibrium constants are:

$$\begin{aligned} K_a &= \frac{K_2}{K_1} = \frac{a_{CO_2} a_{CO_3} a_w}{a_{HCO_3}^2} \\ K_b &= \frac{K_3}{K_5 K_4 K_2} = \frac{a_{NH_2COO} a_w}{a_{NH_4} a_{CO_3}} \\ K_c &= \frac{K_3 K_5}{K_4 K_1} = \frac{a_{NH_3}^2 a_{CO_2}}{a_{NH_4} a_{NH_2COO}} \end{aligned} \quad (23)$$

The equilibria of these reactions will be computed using a similar relaxation scheme as used for the full model. Again balances hold for the total carbon, total nitrogen and charge. Effectively, we solve the reduced model via relaxation for m_{CO_2} , m_{NH_3} , m_{NH_2COO} and m_{CO_3} :

$$\partial_t m_{CO_2} = r_a + r_c$$

$$\partial_t m_{NH_3} = 2r_c$$

$$\partial_t m_{NH_2COO} = r_b - r_c$$

$$\partial_t m_{CO_3} = r_a - r_b$$

$$r_a = k_a (K_a a_{HCO_3}^2 - a_{CO_2} a_{CO_3} a_w)$$

$$r_b = k_b (K_b a_{NH_4} a_{CO_3} - a_{NH_2COO} a_w)$$

$$r_c = k_c (K_c a_{NH_4} a_{NH_2COO} - a_{NH_3}^2 a_{CO_2}) \quad (24)$$

3. Biscuit leavening system

We perform our calculations for the AACC-10-53 biscuit system (Kweon et al., 2009), which is often taken as a reference system for

Table 4
Formulation of the reference biscuit, according to AACC-10-53 method.

Compound	Weight (g)
Soft Wheat Flour (13% moisture)	225
Sucrose	94.5
Shortening	90.0
High-fructose corn syrup (42%)	3.4
Skimmed milk	2.3
NaCl	2.8
Sodium Bicarbonate	2.3
Ammonium bicarbonate	1.1
Total water	49.5

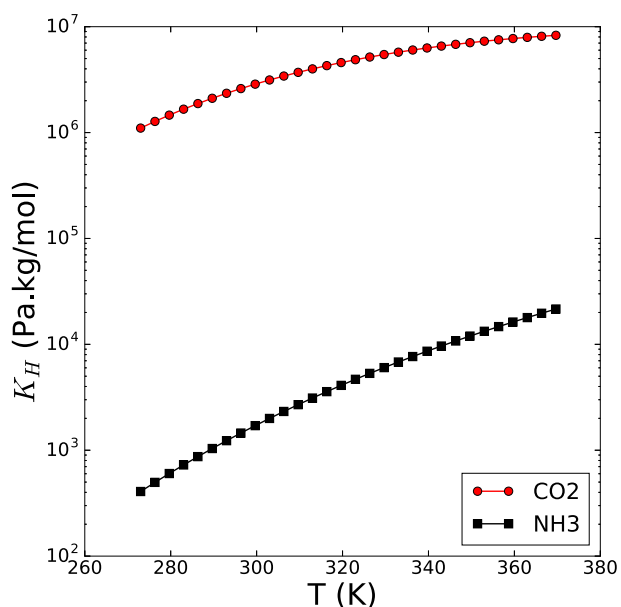


Fig. 1. Henry constant for CO_2 and NH_3 as function of temperature, cf. (Kawazuishi and Prausnitz, 1987).

biscuits in scientific literature. Hence, a significant amount of data is available for this system. The to-be-developed biscuit baking model will be based on this same system.

The composition of the AACCC-10-53 biscuit system is shown in Table 4. Given the molar weights of NaCl (58.4 g/mol) NaHCO₃ (84.0 g/mol), and NH₄HCO₃ (79.0 g/mol) and the amount of water available in the formulation, we can compute the following molalities: $m_{\text{NaCl}} = 0.61$ M, $m_{\text{NaHCO}_3} = 0.35$ M, and $m_{\text{NH}_4\text{HCO}_3} = 0.18$ M. If the leavening agents fully dissociate, 0.18 M of NH₃ and 0.35 M of CO₂ will be produced. Given the weight of water and the amount of moles of gas produced, using the ideal gas law and assuming the gas is at atmospheric pressure p_0 , we can compute the volume of gas, $V_{\text{gas}} = n_{\text{gas}}RT/p_0$. The amount of dry matter in the biscuit dough is about 450 g, which is assumed to have same density as polysaccharides $\rho = 1550$ kg/m³ (van der Sman and Meinders, 2011). Consequently, we expect that the maximal porosity of the biscuit will be about 0.8.

The amount of sugar will also lower the water activity, which can be computed using the Flory-Huggins theory ([van der Sman, 2017]). In systems consisting of a mixture of salts, carbohydrates and/or biopolymers the Ross equation is a reasonable approximation to compute the water activity for total system (van der Sman, 2012). The Ross equation states that the contributions of different components can be determined independently, which need to be multiplied with each other:

$$a_{w,\text{tot}} = a_{w,\text{sugar}} \times a_{w,\text{salts}} \quad (25)$$

The water activity of salts $a_{w,\text{salts}}$ will be computed via the above Pitzer model, and $a_{w,\text{sugar}}$ follows from the Flory-Huggins theory (van der Sman, 2017). If the amount of water in the dough remains about constant, it follows from the biscuit composition that $a_{w,\text{sugar}} \approx 0.9$.

The AACCC-10-53 standard has also defined baking conditions. Baking should be done in 11 min in an oven at 200°C. An important step in the baking process is the rupturing of the gas bubbles, which is due to the thermosetting of gluten (van der Sman and Renzetti, 2019). One should mind that gluten has not developed into an extensive network as in bread dough, which is due to the high sugar concentrations (Kweon et al., 2014; van der Sman and Renzetti, 2019). However, they are thought to absorb on the interface of the expanding gas bubble. Gluten will denature around 95°C (van der Sman and Renzetti, 2019), and aggregate with neighbouring gluten proteins. The dough stiffens due to this thermosetting of gluten. This stiffening and the reduced adhesion of gluten to the matrix result in the rupture of the gas bubbles. In our modelling we assume that the bubble rupture is a discrete event, happening when the dough temperature has reached the thermosetting temperature of gluten, being 95°C.

4. Model validation

The full model will be tested and validated using the following subproblems:

- (Water) activity of salt solutions,
- Dissolution of CO₂ in salt solutions as function of temperature and ionic strength,
- Speciation of ions in the NH₃, CO₂, H₂O system.

Subsequently, the full model is run using initial conditions holding for the biscuit system. From these trial simulations followed how the system of reactions can be simplified. This reduced model is explained in section 2.5.

4.1. Test of Pitzer model on NaCl

The Pitzer model is tested against experimental data on water activity a_w and mean activity coefficient γ_{\pm} for NaCl at room temperature. We have used the model from the above section, and the listed parameter values. Results are shown in Fig. 2, where it is shown that the Pitzer model indeed describes the experimental data quite well, and even beyond the concentration range, that is relevant for biscuits (where $m \leq 1$ mol/kg) (Chirife and Resnik, 1984). have shown that a_w is quite independent of temperature in the range of 15–60°C. We also assume that this holds for the activity coefficients.

4.2. Dissolution of CO₂ in salt solutions

A further test of the model is the dissociation of solubilized CO₂ in saline water. Experimental data is available by Thurmond and Millero (1982). Their data are expressed in stoichiometric (dis)association constants:

$$K_1^* = \frac{[\text{HCO}_3][\text{H}]}{[\text{CO}_2]}$$

$$K_2^* = \frac{[\text{CO}_3][\text{H}]}{[\text{HCO}_3]} \quad (26)$$

$pK_1^* = -\log(K_1^*)$ and $pK_2^* = -\log(K_2^*)$ values are given for different molalities of NaCl. For the dataset of Thurmond and Millero (1982) holds that the total amount of carbon is small: $C_T \ll 1$.

We will compare

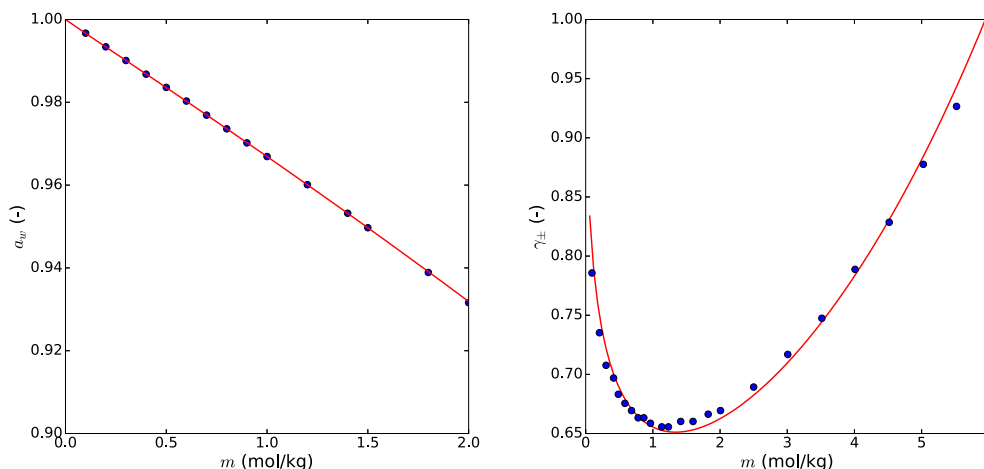


Fig. 2. a) Water activity a_w and b) Mean activity coefficient γ_{\pm} of NaCl solution at $T = 25^\circ\text{C}$ as function of molality m , with predictions made by Pitzer model (solid lines). Symbols represent experimental data by Robinson and Stokes (2002).

$$K_1^* = K_1 \frac{a_w \gamma_{CO_2}}{\gamma_{HCO_3} \gamma_H}$$

$$K_2^* = K_2 \frac{\gamma_{HCO_3}}{\gamma_{CO_3} \gamma_H} \quad (27)$$

with the activity coefficients computed using the Pitzer model, and the given interaction coefficients. We assume a_w is fully determined by NaCl. We have performed calculations with $C_T = 10^{-1} M$, for which holds that $\gamma_{CO_2} \approx 1$. Results are given in Fig. 3. For the range of salt concentrations relevant to biscuit system ($m_{NaCl} \leq 1 M$), the model predictions are well in line with the experimental data.

4.3. Speciation of ions in the NH₃, CO₂, water system

A final check of our model is the dissociation of dissolved CO₂ and NH₃ gases in ions. This problem has been investigated in chemical engineering for CO₂ sequestering via Raman spectroscopy (Wen and Brooker, 1995; Zhao et al., 2011; Halstensen et al., 2017). In these systems carbamate (NH_2COO^-) will be formed, next to bi-carbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. We have compared our simulation results of the full Pitzer model with experimental data from Ref. (Halstensen et al., 2017), as shown in Fig. 4. While using values for all parameters from literature, we observe that the Pitzer model still captures the experimental data reasonably well. Given the many binary interaction coefficients required in the full model, see Table 2, it can be expected that some of these parameters are not very accurate, and explain the discrepancy between predictions and experimental data. Furthermore (Edwards et al., 1978), have stated that their model is not very sensitive to the value of K_5 , which has been fitted simultaneously with some binary coefficients like $\beta_{NH_4NH_2COO}^{(i)}$. We expect further experimental analysis for increasing the accuracy of $\beta_{NH_4NH_2COO}^{(i)}$ would increase the accuracy of our model.

5. Gas leavening in biscuit dough

After having validated the full model, as discussed in the previous section, we have performed trial simulations with the full model using initial conditions as stated in the biscuit formulation, as shown in Table 4.

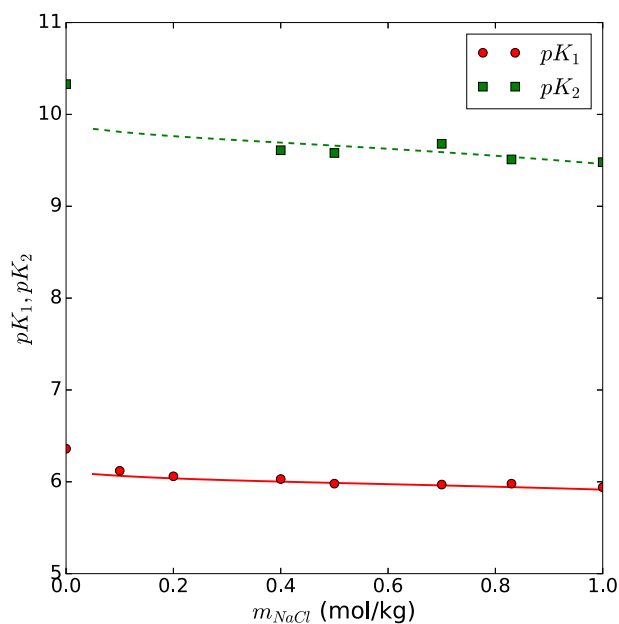


Fig. 3. Effective pK_1 and pK_2 of aqueous solutions at 25 °C with 0.1M NaHCO₃ and NaCl at molality m_{NaCl} . Symbols represent data from (Thurmond and Millero, 1982), and lines are predictions using the Pitzer model.

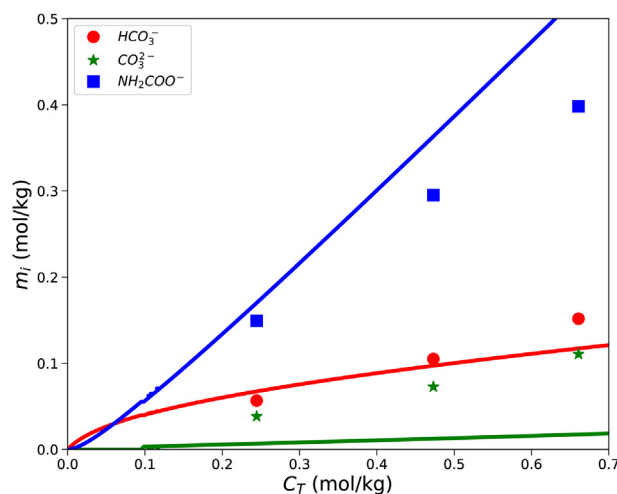


Fig. 4. Speciation of ions in solution of ammonium carbonate in comparison with experimental data of (Halstensen et al., 2017).

From the trial simulations we have learned that there are three dominant (slow) reactions, which can be constructed from the full model via elimination of the very fast proton transfer reactions. This has led us to the reduced model, as given in section 2.5. The reduced model is coupled to the gas bubble model of Amon and Denson, as given in section 2.4.

We have made some simplifying assumptions, as the main focus of this study has been the development of a model describing the chemistry of the leavening agents, using a sound thermodynamic basis. Our assumptions are:

- the dough temperature rises linear in time, from 30°C to 95°C in 5 min,
- the viscosity of the dough remains constant at $\eta = 5 \times 10^3$ Pa.s,
- air pockets are already present in the dough, as a consequence of the dough mixing,
- gas bubbles will grow from these initial air pockets, having an initial radius of $R_{init} = 1 \mu m$ and initial porosity of $\varphi_{gas} = 0.002$,
- there is no leavening gas escaping from the dough (also there is negligible evaporation), and
- the expanding bubbles do not rupture.

We will perform simulation up to the point that the gas bubbles will rupture, which is due to the thermosetting of gluten. Before rupture of the bubble, the escape of the gases to the baking oven is negligible, compared to after rupturing. After rupturing the structure can be assumed to be fixed, which is an open foam structure allowing easy escape of the leavening gases. At the end of baking oven it can be assumed that the chemical leavening agents have fully dissociated, and little gas is dissolved in the remaining moisture, which is also present in low amounts. Development of the model after bubble rupture will be pursued in future research.

In Fig. 5 we show how the molalities of various compounds change during heating of the biscuit dough. Note that the changes in the molalities are due to several effects: 1) the temperature dependency of the equilibrium constants, 2) the temperature dependency of the solubility of dissolved gases, 3) the slow dynamics in the bubble growth via the high viscosity, and 4) the extraction of dissolved gases via the expanding bubble. In Fig. 6 we show how the partial gas pressures and porosity change during heating.

Our simulations show a clear leavening of the biscuit, leading to a final porosity of about $\varphi_{gas} = 0.9$, which is slightly larger than our estimated value of the maximal porosity ($\varphi_{gas} = 0.8$). This discrepancy is due to the facts 1) that we have not taken into account the contribution of the evaporated water to the gas phase, and 2) that more than half of the bi-

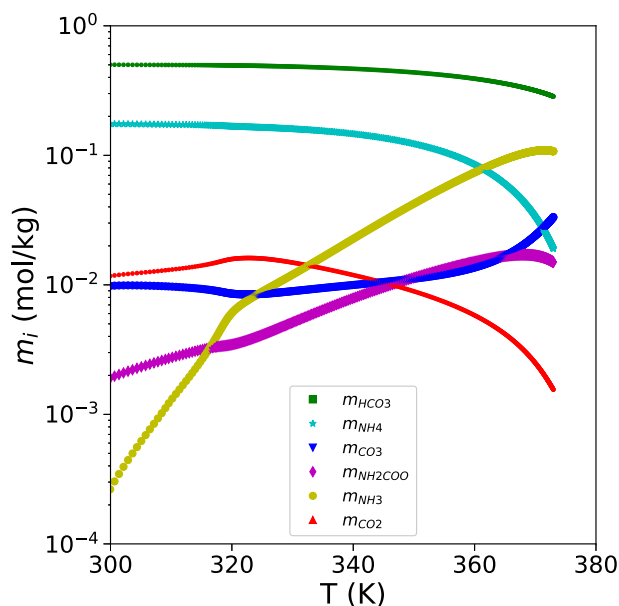


Fig. 5. Development of the molalities m_i of various ions and dissolved gases during the baking of the AACC 10–53 biscuit as computed by the reduced Pitzer model, coupled to the Amon-Denson cell model for the expanding gas bubble.

carbonate has dissociated. A significant amount of carbon in the liquid phase is present as carbamate (NH_2COO^-) instead of carbonate (CO_3^{2-}). Their difference in charge allows more CO_2 to be produced. We observe that most of the ammonium ions are dissociated, but the solubility of NH_3 is still quite high near the thermosetting temperature. Hence, little NH_3 has entered the gas phase, as evidenced its low partial pressure.

The computed porosity is also higher than found in literature. The study of (Pareyt et al., 2009) shows a porosity of about 45%, as obtained via X-ray tomography. In the study of (Fustier et al., 2009) the AACC 10–53 formulation has been used, showing a porosity in the order of 50–60%. These lower values are likely due to the fact that the leavening gases also escape to the environment during heating, which is not taken into account in the current model. Gas escape is particularly significant if the bubble wall ruptures. In the current model all gas bubbles would rupture simultaneously, leading to an abrupt change in porosity. In reality, the bubble rupture would be more distributed over time, leading to a gradual decrease in porosity at the end of baking. If the dough viscosity

is higher than estimated, the bubble growth will be slower than predicted by the current model, and the porosity at the end of baking would also be slower. The model definitely needs improved in this aspect, but our objective of the model was to provide the thermodynamic framework of the leavening agents, and how it can be coupled to gas expansion models. Hence, improvements of the prediction of porosity is for future versions of the model.

Up to $T = 350$ K most of the gas in the bubbles originates from the bicarbonate, as indicated by the high partial gas pressure of CO_2 . At higher temperatures the partial pressure of CO_2 drops, while that of H_2O and NH_3 increases. The total gas pressure remains around atmospheric values during the whole simulation. From our simulation results it follows that the functionality is of ammonium bicarbonate as leavening agent is not clear. The bicarbonate-ions do contribute to the production of leavening gas, but the ammonium ions do not. The use of ammonium ions helps to reduce the level of sodium ions, if compared to the case where bicarbonate is provided purely by NaHCO_3 .

To get better insight in the latter case we have performed simulations with biscuit dough having a different composition for leavening agents, namely 0.50 M sodium bicarbonate and 0.02 M ammonium bicarbonate (corresponding with 3.3g sodium bicarbonate and 0.1g ammonium bicarbonate added to a modified AACC 10–53 recipe). Results are shown in Fig. 7. The simulation shows that of course less NH_3 gas is produced, but the final value of the porosity is lower (0.7) than in the case of the AACC 10–53 biscuit. The temporal evolution of leavening gases is somewhat different, with the gas production delayed until $T = 340$ K, while in the AACC 10–53 biscuit the leavening start more or less immediately. Due to the late start of the gas production the final porosity is lower at gluten thermosetting temperature, $T = 95^\circ\text{C}$.

6. Conclusions

We have developed a thermodynamic model for the action of leavening agents in biscuits. The level of ions in biscuits demands the use of thermodynamic theories like the Pitzer model to compute the deviations of the compounds activities from ideality. The studied leavening agents, sodium bicarbonate and ammonium bicarbonate, are involved in a complex network of chemical reactions. Fortunately, these reactions are also occurring in CO_2 sequestering, which is widely studied in the field of chemical engineering. This has allowed us to construct a sound thermodynamic model with known model parameters, describing the complete set of chemical reaction.

The full model has been validated against experimental data available

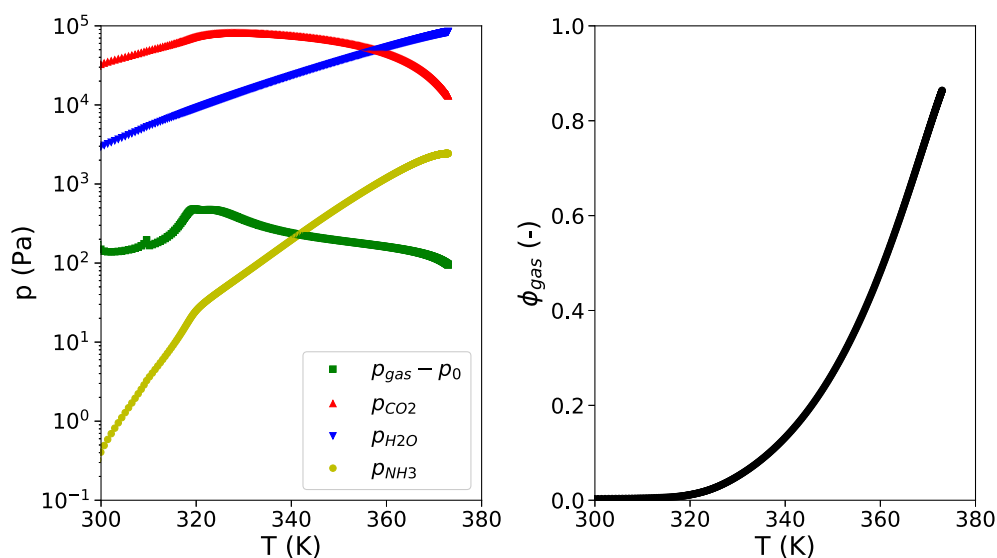


Fig. 6. Development of the gas pressures p_i and the porosity ϕ_{gas} as function of temperature T during the baking of the AACC 10–53 biscuit as computed by our model.

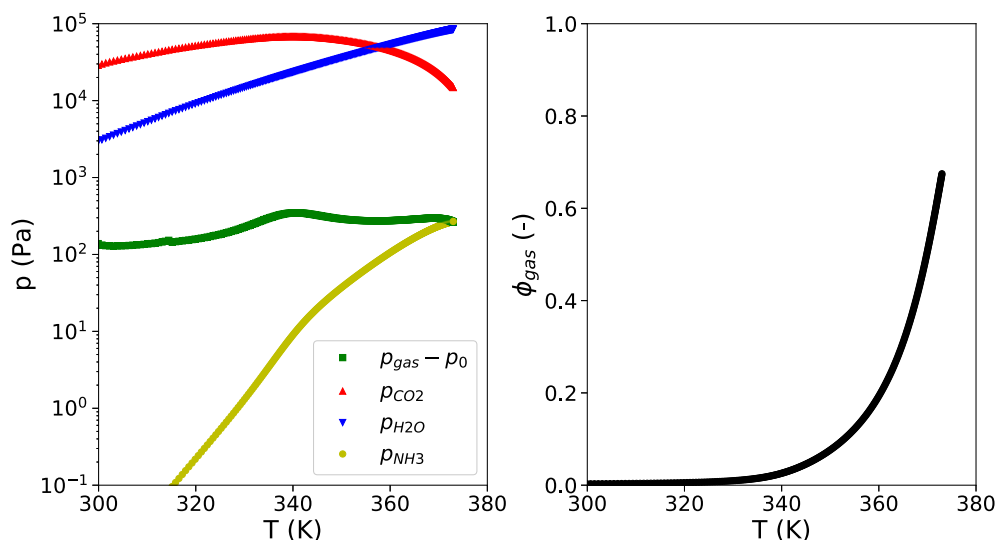


Fig. 7. Development of the gas pressures p_i and the porosity ϕ_{gas} as function of temperature T during the baking of the biscuit with 0.50 M sodium bicarbonate and 0.02 M ammonium bicarbonate.

from the field of chemical engineering. Subsequently, the full Pitzer model has been reduced in complexity via elimination of the fast proton transfer reactions. The reduced model is coupled to the Amon-Denson cell model, which describes the expanding gas bubble in the biscuit dough. This coupled model shows how the chemical equilibria shifts with temperature and expanding gas phase. A final porosity of about 90% is developed in the biscuit dough.

The low level of NH_3 in the gas phase puts question marks at the functionality of ammonium bicarbonate as leavening agent. In the stage before bubble rupture, it is only the bicarbonate ion that contributes to the produced gas. Ammonia gas escapes from the biscuit only after bubble rupture, but the escape will be complete at the end of baking. The synthesis of carbamate makes the leavening gas production already start at the initial temperature, and it is more evenly distributed over time. From a personal communication with Harry Levine, a well-known expert in biscuit manufacturing (Kweon et al., 2009), it follows that ammonium bicarbonate is also well appropriate for fine-tuning the spreading of the biscuit, such that they well fit into the prescribed packaging.

The use of ammonium bicarbonate might also be functional from the viewpoint of the reduction of sodium level. In literature as ammonium chloride has been proposed as salt replacer (Batenburg and van der Velden, 2011; Busch et al., 2013; Israr et al., 2016), but there is a potential of off-odours and off-taste. Also the impact of the compound to acrylamide needs to be evaluated in this issue of sodium replacement in bakery products (Amrein et al., 2006).

The developed framework of the Pitzer model coupled to the Amon-Denson cell model is general enough to encompass biscuit systems containing other leavening agents, for example with reduced sodium levels using potassium bicarbonate instead of sodium bicarbonate. As sodium is not involved in the reaction, the model is easily adapted to capture the action of potassium bicarbonate. It requires knowledge of the Pitzer interaction coefficients between potassium and the other ions in the leavening formulation, which can be found in literature (Roy et al., 1984).

In other biscuit formulations the leavening contains only sodium bicarbonate, or sodium bicarbonate with a weak organic acid, such as sodium acid pyrophosphate, calcium phosphate, lactic acid, citric acid or tartaric acid. For several of these weak acids the dissociation equilibrium is known (Achard et al., 1994; Velezmore and Meirelles, 1998; Corey, 2003). Furthermore, it can be also used to describe the dissolution of CO_2 produced by yeast in other bakery systems cf. (Aissa et al., 2015), provided that the gas production by the yeast is known.

In a subsequent study we will couple the presented model to heat and

mass transfer at the product level, making it a multiscale model, as we have developed for expanded snacks (van der Sman and Broeze, 2014). For this model the thermodynamics needs to be extended towards the effect of moisture removal on water activity, and the thermosetting of gluten. For the latter we will apply our theory of effective solvents for biopolymer melting (van der Sman, 2016), due to the high content of sucrose in biscuits. This multiscale model will be the vehicle to further pursue reformulation strategies, regarding both sugar and sodium levels.

CRediT authorship contribution statement

R.G.M. van der Sman: Writing – original draft, As the sole author, I have written the paper, and developed the model and performed the simulations.

Declaration of competing interest

The author declares there is no conflict of interest.

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