GAS PRESSURE-VOLUME-TIME RELATIONSHIPS IN FERMENTING DOUGHS. I. RATE OF PRODUCTION AND SOLUBILITY OF CARBON DIOXIDE IN DOUGH

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ABSTRACT

A method for determining the rate of production and solubility of carbon dioxide in a fermenting dough is described. The method is based on measurement of the rate of increase of the external pressure required to hold a dough sample at constant volume, and does not require a value for the absolute pressure of the gas in the dough.

There have been numerous studies of the rheological properties of wheat-flour doughs, but very few of these have been concerned with the behavior of yeasted doughs. However, dough must be considered as a two-phase (gas/viscoelastic solid) system before the mechanical behavior of dough during breadmaking can be fully understood. The relations between pressure, volume, and time in the dispersed gaseous phase are important in any theoretical consideration of fermenting doughs. These relations are determined by several factors, which include the extent and rate of fermentation, gas retention and solubility, and air entrainment during mixing, in addition to the rheological properties of the continuous viscoelastic phase.

The objective of this study is to provide an understanding of the pressure-volume relations for the gas retained in fermenting doughs. Of particular interest is the interaction between the pressure in the gas bubbles, the rate of expansion of the dough, and the rheological properties of the dough as governed by such factors as composition, flour type, and additives.

The methods used to study gas production in fermenting doughs have been reviewed by Bloksma (1) and Bloksma and Hlynka (2). The majority may be classified into one of two categories: (i) measurements of the change in pressure in an airtight container of known volume in which the fermenting dough is sealed, or (ii) measurements of the volume change required to keep the pressure constant in a vessel containing the fermenting dough. Other methods depend on the increase in buoyancy of dough immersed in a fluid as the dough volume increases (3,4). Commercial instruments that have been used to evaluate gas production have been reviewed by Seibel (5).

The procedures described in the literature are used to compare the gassing powers of flours and yeasts in doughs, pastes, or slurries. These methods determine only the evolved gas and neglect the solubility of carbon dioxide in the dough and the effects of the pressure in the bubbles of gas retained by the dough. Such procedures cannot be used to determine the mass of gas produced in a dough without corrections for these effects. Both the solubility of the gas in the dough and the pressure in the gas bubbles in the dough must be known before such corrections can be applied.

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The method described in this paper for measuring the rate of production and solubility of carbon dioxide in dough is based on application of the gas laws to the gas retained in the fermenting dough when the dough is held at constant volume by increasing the external pressure. A knowledge of the gas pressure in the bubbles within the dough is not required. This paper is restricted to a description of the method and the presentation of some preliminary results showing the rate of gas production and the solubility of carbon dioxide for a particular dough.

THEORY

Consider unit mass of dough of total volume V, of which V_d is the volume of the continuous dough phase. The volume of the gas is therefore $V-V_d$. The gas in the bubbles is a mixture of carbon dioxide generated during fermentation, the components of the air entrained during mixing, and water vapor. The gas is considered to be in equilibrium with that dissolved in the continuous dough phase.

From the gas laws the mass of carbon dioxide in the gaseous phase, m_c', is given in terms of its partial pressure, P_c, by

$$m_c' = P_c (V - V_d) \cdot M_c/(RT) \tag{1}$$

where

M_c = molecular weight of carbon dioxide,
R = gas constant, and
T = absolute temperature.

Assuming the solubility of carbon dioxide in the continuous dough phase follows Henry's law, the mass of carbon dioxide dissolved in the dough, m_c'', is given by

$$m_c'' = k_c P_c \tag{2}$$

where k_c is the solubility constant of the carbon dioxide in mass per unit mass of dough per unit pressure.

The total mass, m_c, of carbon dioxide in unit mass of dough is therefore

$$m_c = m_c' + m_c'' = P_c (V - V_d)M_c/(RT) + k_c P_c \tag{3}$$

$$= P_c(V - V_d + V_c)M_c/(RT) \tag{4}$$

where
$$V_c = k_c RT/M_c \tag{5}$$

The term V_c may be considered as the equivalent volume of the carbon dioxide dissolved in unit mass of dough.

Similar equations can be derived for each of the components of the entrapped air. The partial pressure of the ith component is given by

$$P_i = m_i RT/[M_i(V - V_d + V_i)] \tag{6}$$

where
m_i = total mass of the ith component in the dough,
M_i = molecular weight of the ith component, and
V_i = equivalent volume of the ith component dissolved in the dough.

The partial pressure, P_a, of air in the bubbles is given by

$$P_a = \sum_i P_i = \sum_i m_i RT / [M_i(V - V_d + V_i)] \tag{7}$$

where the summation is for all the components of the air. Thus the partial pressure of the carbon dioxide is given by

$$P_c = P - P_a - P_w \tag{8}$$

where P is the total pressure in the bubbles and P_w is the vapor pressure of water.

Substituting equation 8 in equation 4 gives for the total mass of carbon dioxide in unit mass of dough:

$$m_c = (P - P_a - P_w)(V - V_d + V_c)M_c/(RT) \tag{9}$$

Note that the only parameter which varies with time in the expression P_a, given by equation 7, is the volume V. Thus differentiating equation 9 with respect to time, t, at constant volume gives for the rate of production of carbon dioxide

$$dm_c/dt = M_c/(RT) \cdot (V - V_d + V_c) \cdot (\partial P/\partial t)_v \tag{10}$$

because the total pressure P is the only parameter on the right-hand side of equation 9 which varies with time at constant volume.

The pressure of the gas in the bubbles, P, is related to the external atmospheric pressure P_o, by

$$P = P_o + P_e + p \tag{11}$$

where P_e is the external pressure, above atmospheric, applied to the dough to maintain the volume constant, and p is the pressure exerted on the gas by the dough.

Substituting in equation 10 gives

$$(dm_c/dt) = M_c/(RT) \cdot (V - V_d + V_c) \cdot [(\partial P_e/\partial t)_v + (\partial p/\partial t)_v] \tag{12}$$

because P_o is constant.

The pressure p is a function of both the geometry of the bubble structure and the rheological properties of the dough. The geometry of the bubble structure can be considered to be essentially a function of the specific volume of the dough, and would be expected to change slowly when the volume is kept constant. The rheological properties of the dough also change slowly so that $(\partial p/\partial t)_v$ can be neglected compared with $(\partial P_e/\partial t)_v$. Thus, as a good approximation,

$$dm_c/dt = M_c/(RT) \cdot (V - V_d + V_c) \cdot (\partial P_e/\partial t)_v \tag{13}$$

The experiments described in this paper show that the rate of production of gas is constant over a considerable period and that it is possible to make measurements of $(\partial P_e/\partial t)_v$ for several volumes of the gas bubbles. Rearranging equation 13 gives

$$(V-V_d) \cdot (\partial P_e/\partial t)_v = -V_c (\partial P_e/\partial t)_v + (RT/M_c) \cdot (dm_c/dt) \qquad (14)$$

and, over the period for which dm_c/dt is constant, a plot of $(V - V_d)(\partial P_e/\partial t)_v$ against $(\partial P_e/\partial t)_v$ gives a straight line of slope $-V_c$. When V_c has been determined, the rate of production of carbon dioxide can be calculated from equation 13 and the solubility constant, k_c, from equation 5.

MATERIALS AND METHODS

Doughs were prepared from a range of commercially available Australian flours by mixing for 5 min in a Hobart laboratory mixer. The illustrative results presented in this paper were obtained on doughs prepared from a baker's flour (protein 11.2%; ash 0.62%; moisture 14.0%; diastatic activity 16 mg maltose per 10 g flour; farinograph water absorption 62.9%; farinograph development time 4.3 min) with 2% yeast, 2% salt, 2% fat, 8 ppm potassium bromate, and 58% water absorption.

For the measurements, the dough was held in a stainless-steel cylinder (100 mm diameter, 300 mm long) with one end closed and restricted by a close-fitting steel piston. A CSIRO Maturometer (6) was modified to measure the pressure required to keep the volume of the fermenting dough constant. The instrument is shown diagrammatically in Fig. 1.

A 500-g sample of dough, A, is placed in the bottom of the cylinder, B, in such a manner as to avoid the trapping of any air between the dough and the cylinder. The piston, C, is then pressed down firmly, forcing the air above the dough to escape through the 30 μm clearance between the piston and the cylinder wall. Sufficient light paraffin oil is poured onto the top of the piston to facilitate observation of any gas escaping from the dough and also to act as a lubricant.

A rigid steel rod, D, attached to the piston, passes through the clear plastic guide-sleeve, E. The rod is brought into contact with a plate, F, suspended by four force rings, G, from the fixed plate, H. The force required to prevent the piston from moving, i.e., the force required to prevent the dough from expanding, is calculated from the small movement of the plate, F, compressing the force rings. This displacement is measured by a dial gauge, I, calibrated in divisions of 2.54 μm (0.0001 in.); each division is equivalent to a force of 2.32 Newtons.

The volume of the dough sample is varied by adjusting the height of the loaded cylinder with the screw jack, J. The change in height of the cylinder is determined from either the number of turns of the screw jack or from measurements of the height of a reference mark on the cylinder with a cathetometer. Because the distance between the piston and the plate is fixed, the change in volume of the sample can be calculated from the change in height of the cylinder and the change in the dial gauge reading. The difference in the dial readings is usually negligible compared with the difference in heights of the cylinder, and the volume of the sample may then be determined from the height of the cylinder.

The temperature of the sample is controlled at 27° C by circulating water from a thermostatted bath through the jacket, K, surrounding the cylinder.

The volume of the 500-g sample, as loaded into the cylinder, includes gas bubbles entrained during mixing. The volume of these bubbles is calculated from the density of a sample determined at the time of loading and the density of a sample of non-yeasted dough which has been degassed under vacuum. The total volume of the gas bubbles at any stage of fermentation is taken as the sum of the volume of these bubbles entrained during mixing and the change in volume as calculated from the change in height of the cylinder.

RESULTS AND DISCUSSION

After an initial induction period, during which the rate of production of
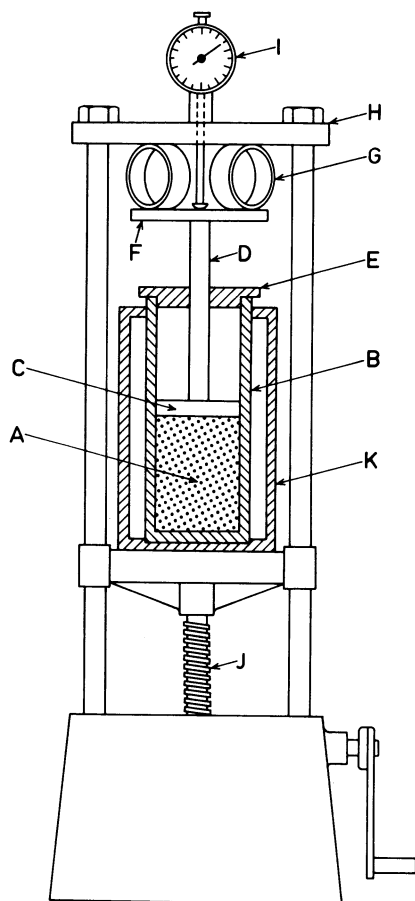

Fig. 1. Schematic diagram of instrument used to make pressure-volume measurements on dough. A, sample; B, cylinder; C, piston; D, steel rod; E, plastic guide; F, plate; G, force rings; H, fixed plate; I, dial gauge; J, screw jack; and K, water jacket.

carbon dioxide is increasing, the rate of increase in the external pressure required to maintain the sample of dough at a given volume is constant for a considerable period. Eventually the rate of increase in pressure again increases.

The change in the rate of increase of pressure at the early stages is illustrated by Fig. 2, in which the pressure required to maintain the dough sample at its initial volume is plotted against the time after completion of mixing. There is obvious curvature in this plot and the rate of increase in pressure rises with time.

At longer times the measured values of pressure and time can be fitted by a linear relationship. This is illustrated by Fig. 3, where the pressure is plotted against time for four specific volumes. The times on the abscissa are measured from the time at which the dough reached the particular specific volume. The straight lines shown in Fig. 3 are the linear regressions of pressure on time.[3] For this dough, the experimental points determined at each specific volume can be fitted by a linear relation between the pressure and the time for the period between 2000 and 7000 sec after completion of mixing. The linear relation between the external pressure at constant specific volume and time indicates that the rate of production of carbon dioxide is constant, and justifies the assumption that the rate of change of the pressure exerted by the dough is small compared with the rate of change of the measured external pressure during this period. The eventual increase in the rate of change of external pressure is discussed later.

To establish the accuracy of the linearity, the measurements presented in Fig. 3 were taken over longer time periods than necessary to measure the rate of increase of the pressure. Consequently, the pressure of the carbon dioxide in the

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[3]The inclusion of a quadratic term in the regression analysis marginally improves the fit, and shows that the slope of the pressure-time curves changes by less than $\pm 0.6\%$ for cases A, B, and C, and by less than $\pm 1.6\%$ for case D. The slight increase in the slope of curve D at longer times indicates that some points from the region where the rate of pressure change has begun to increase have been included.
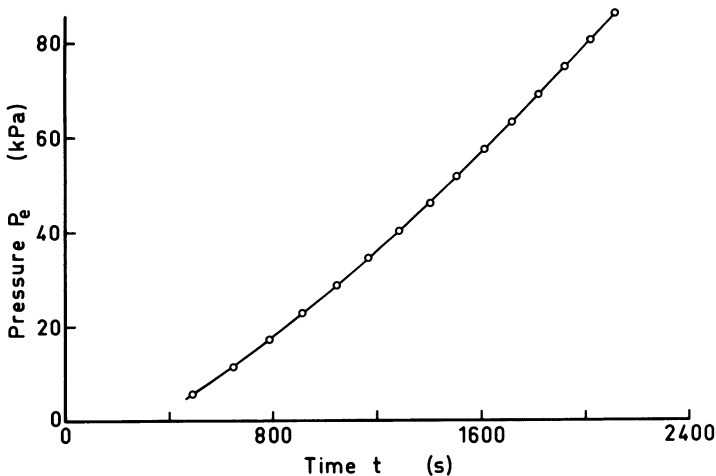

Fig. 2. External pressure required to maintain dough sample at constant volume plotted against time after completion of mixing. The change in slope reflects the change in the rate of production of carbon dioxide at the early stages of fermentation.

bubbles rose to relatively high values, reaching up to 86 kPa above that attained when the dough was allowed to expand without additional restraint. There is no evidence that the rate of production of carbon dioxide is reduced because of the high pressure of the carbon dioxide.

The rates of increase of the external pressure required to maintain constant specific volume have been determined for a range of specific volumes by observing the pressure as a function of time for fixed volumes of the dough sample. At the end of each set of readings, the volume was increased with a corresponding fall in the pressure. When the volume was again held constant, there was a relatively rapid rise in the pressure before the rate of increase in pressure became constant. This rapid rise in pressure can be attributed either to carbon dioxide coming out of solution in the continuous dough phase to equilibrate with the lower pressure of carbon dioxide in the bubbles, or to a change in the pressure exerted on the gas by the dough because of changes in the geometry of the bubble structure and the rheological properties of the dough.

The equivalent volume, V_c, for the carbon dioxide dissolved in unit mass of dough can be determined from the slope of the plot of $(V - V_d) \cdot (\partial P_e / \partial t)_v$ against $(\partial P_e / \partial t)_v$ in accordance with equation 14. A typical plot is shown in Fig. 4. The points plotted are those within the time range for which the rate of increase of pressure at a fixed specific volume is constant. The fit of the experimental points to the straight line again confirms that the rate of production of carbon dioxide is constant and that the rate of change of p is small.

The equivalent volume, V_c, determined from the slope of the line in Fig. 4, is 0.81 ml/g of dough which, from equation 5, corresponds to a solubility constant of 1.44×10^{-3} g/atm/g of dough for carbon dioxide in dough at 27°C.

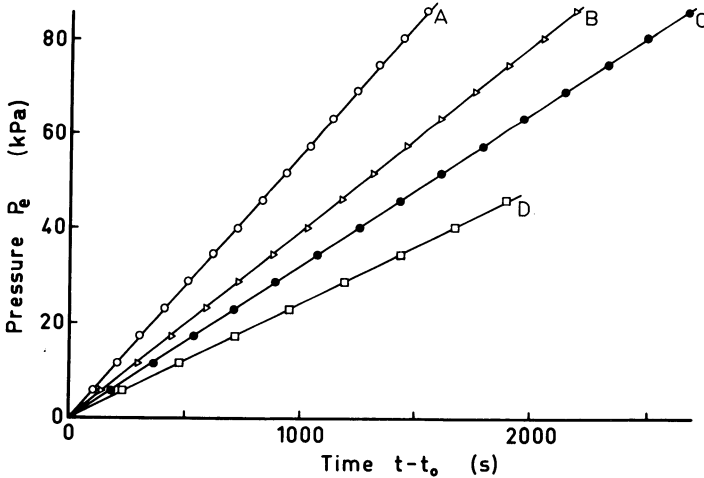The solubility of carbon dioxide in the dough is of great importance at two

Fig. 3. External pressure required to maintain dough sample at constant volume plotted against time after reaching selected volume.

A, $V-V_d = 0.174$ ml/g, $t_o = 2128$ s   C, $V-V_d = 0.860$ ml/g, $t_o = 3750$ s
B, $V-V_d = 0.550$ ml/g, $t_o = 2963$ s   D, $V-V_d = 1.372$ ml/g, $t_o = 5133$ s

stages of breadmaking. First, when shaping the dough pieces between rollers, high pressures will occur as the dough is "pinched" between the rollers and some carbon dioxide will be forced into solution only to come out into the bubbles as the pressure is released. Therefore, rolling cannot eliminate all the gas and there will always be a significant volume of gas bubbles in the dough even after severe treatment. Secondly, because the solubility of a gas falls as the temperature rises, the dissolved gas will be forced out of solution in the oven and this gas will make an important contribution to the increase in loaf volume during the early stages of baking.

The rate of production of carbon dioxide can be calculated by substituting values for the rate of increase of the external pressure, $(\partial P_e/\partial t)_v$, and the corresponding volumes into equation 13. Over the period of the measurements plotted in Fig. 3, the rate of production of carbon dioxide is constant. At earlier times, the rate of production is increasing as shown by Fig. 2. The rate of production of carbon dioxide can still be calculated by substituting, into equation 13, values for the rate of increase of the external pressure derived from the slope of the tangent to the pressure *vs.* time curve.

Figure 5 is a plot of the rate of production of carbon dioxide calculated from equation 13 from measurements covering the entire fermentation period, including the regions where the pressure *vs.* time plots are not linear. The apparent rise in the rate of production of carbon dioxide, at times longer than about 7000 sec, probably results from neglecting the changes in the pressure exerted on the gas by the dough. The rate of gas production should be calculated from equation 12, but the value of the term $\partial p/\partial t$ is not known. At long times and with large bubble volumes the pressure, p, could be falling because of changes in the gas cell structure of the dough. At large bubble volumes, the rate of change of the external pressure, $\partial P_e/\partial t$, is lower and changes of the pressure exerted on the gas by the dough are more important.
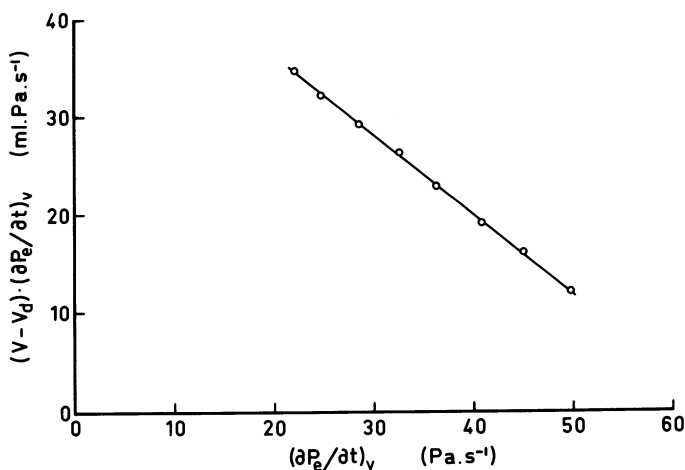

Fig. 4. Plot of $(V-V_d) \cdot (\partial P_e/\partial t)_v$ against $(\partial P_e/\partial t)_v$ in accordance with equation 14. From the slope of line, $V_c = 0.81$ ml/g of dough.
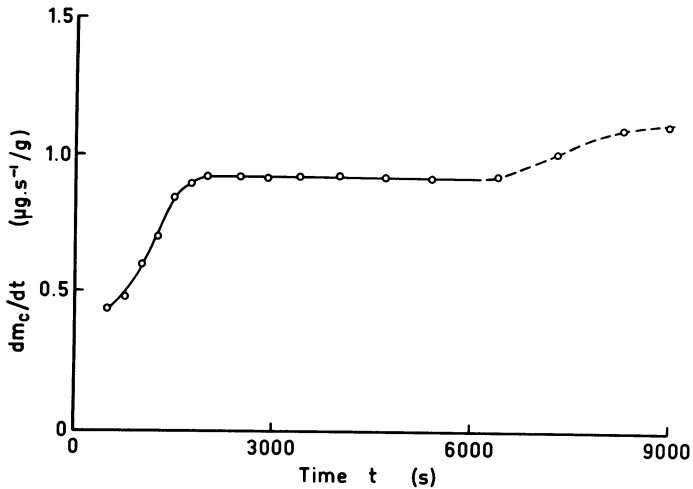
Fig. 5. Rate of production of carbon dioxide (calculated using equation 13) plotted against time after completion of mixing.

The determination of the absolute pressure of the gas in the bubbles in a fermenting dough will be discussed in a later paper in this series.

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