

A PRELIMINARY INVESTIGATION INTO FACTORS AFFECTING GAS FORMATION IN MASSECUIE AND MOLASSES

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Abstract

A Maillard type of reaction was investigated in the laboratory and it was found that it occurs in all factory products from syrup to C molasses. Temperature was found to have the greatest effect on the rate of gas evolution followed by total solids and true purity. It was also found that some sucrose, some fructose and a relatively large amount of glucose was destroyed during this reaction.

Introduction

It has been observed that at certain times of the year gas is evolved from massecuite. During the 1977/78 season, tests in the pilot crystalliser at Darnall confirmed that gas formation in massecuite has adverse effects on exhaustions. This exothermic reaction causes increased viscosity¹ of the massecuite and consequently difficulties were experienced with cooling, reheating and nutsching the massecuite. This points to many problems which could be caused by gassing in the boiling house. Amatikulu Boiling House Recovery figures show a two unit increase over the 1977/78 figures. Lowering the boiling temperatures and the resultant reduction in gassing was considered to make a large contribution toward this increase.

The reaction producing gas in the massecuite is believed to be the Maillard reaction. That is the reaction of an amino acid with a reducing sugar to form a complex.²

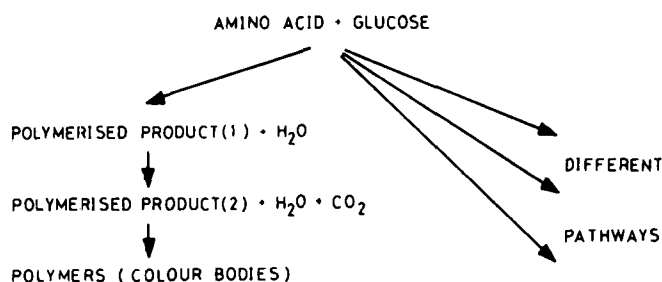


FIGURE 1 Basic diagram of the "Maillard Reaction".

The basic step (see Figure 1) is the formation of a complex which decomposes along a number of different pathways, one of which results in the formation of CO₂, water, polymers and other minor components.

Method

A modified method to that used by Honig² was used to measure the rate of evolution of gas, and so the progress of the reaction.

The apparatus was set up as shown in Figure 2 with the tip of the burette extended to prevent gas escaping. 50 g of massecuite were weighed into the flask, the bung and burette placed in position and the device filled with liquid paraffin to the lowest graduation on the burette. The apparatus was then placed in a water bath and readings of the level of the paraffin were taken periodically. A standard method was developed using this method, where 50 g of massecuite or molasses were gassed for 50 hours at a temperature of 70° C.

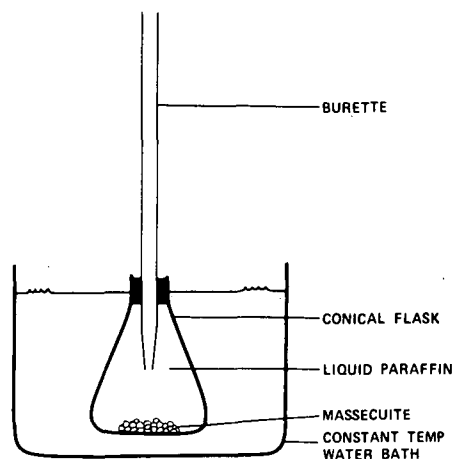


FIGURE 2 Method of measuring gas evolution.

Results

Rate of evolution and quantities of gas formed

Problems caused in factories by the gassing reaction will be related to the extent of the reaction. It was therefore necessary to measure firstly the extent of the reaction and secondly to identify both the controllable and uncontrollable factors that promote it.

Gas evolution by different quantities of the same C-massecuite

Different quantities of the same C-massecuite were tested at 65° C and the quantity of gas evolved measured.

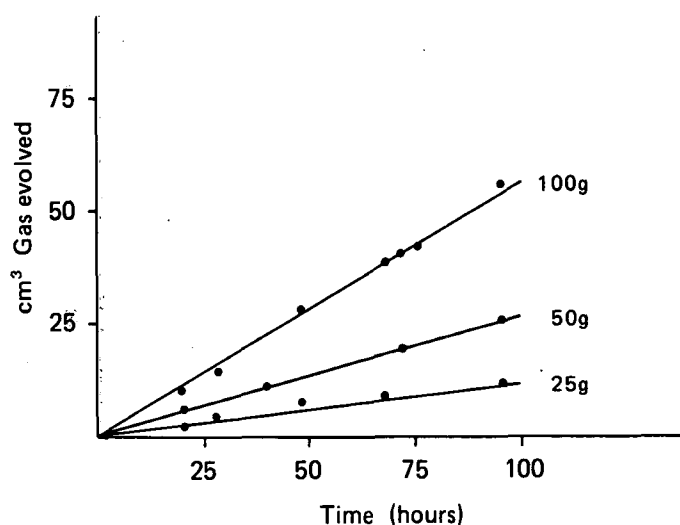


FIGURE 3 The effect of quantity of C-massecuite at 65° C.

After gassing for a 100 hours 100 grams of C-massecuite gassed at a rate of 0,006 cm³ h⁻¹ g⁻¹ 50 and 25 gram samples of the same massecuite showed a rate of 0,005 cm³ h⁻¹ g⁻¹ of gas. This indicates that the gassing rate is independent of the mass of massecuite and could be used to predict quantities of gas formed under factory conditions.

Rate of gas evolution

Two different types of rates, both zero and first order types have been observed. These are shown in Figure 4.

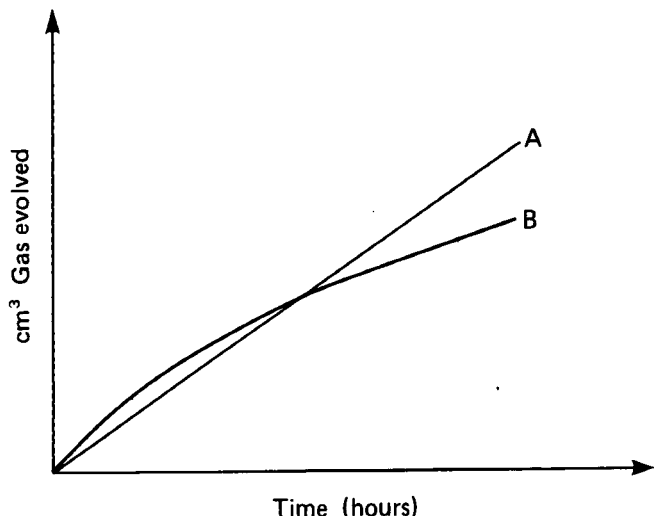


FIGURE 4 Two different rates of gas evolution observed.

Rate (A) which shows a zero order reaction, was only observed with some C-masseccutes.

Rate (B) which shows a first order reaction, (or higher) occurred in both masseccuite and molasses. It is possible that rate (A) represents the first part of a first order reaction which has yet to level off. Honig² also reports that the amount of gas given off decreases with age and that the kinetics of this reaction is a function of concentration.

Gas evolution from different materials

Various materials from the boiling house were tested for gas evolution. The results are shown in Figure 5.

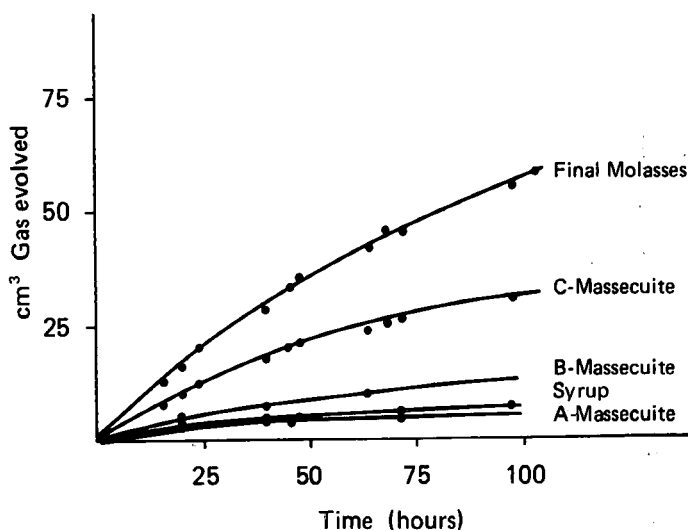


FIGURE 5 Gas evolved from different materials at 70°C. The same mass of solids was present in each material.

This figure shows that at a relatively high temperature, syrup, A and B masseccuite are also capable of generating gas. It is thus possible that the reaction would occur with A and B molasses. The graph indicates that the amount of gas given off increases rapidly with the decrease in purity (higher non-sucrose content).

Investigation of factors affecting the reaction

To determine which were the most important factors affecting the formation of gas several factorially designed experiments were performed.³ The first experiment was an eight factor factorial screening test using high and low levels of temperature, total solids, purity, glucose, pH, phosphate, amino acids and calcium ions. Of these, temperature, purity and total solids showed a significant effect on gas evolution.

This was followed by a five factor factorial experiment to find the effect of temperature, purity, total solids, phosphate

and glucose. A second factorial with five factors was done to investigate pH, purity total solids, temperature and copper sulphate. Both factorials showed temperature, total solids and purity to have a significant effect on gas formation.

A further experiment was done to investigate the effect of possible inhibitors of the reaction. In this category sodium hydrosulphite (Blankite), Viscaid, sodium sulphite (quoted as being an inhibitor for colour forming reactions⁴) and Complemix were investigated. None of these showed statistically significant effects on gas evolution.

It can thus be concluded that the effect of these factors is very small compared to the effects of temperature, total solids and purity.

Effect of temperature

Temperature was found to be the most important factor. The higher the temperature, the faster was the rate of gas evolution.

Since temperature may be controlled in the factory, its effects were investigated in more detail.

Samples from three different C-masseccutes were kept at 50, 55, 60, 65, 70 and 75°C. The volume of gas evolved in 48 hours was recorded.

The rate of gas evolved, in moles of gas per second was plotted against the temperature (see Figure 6).

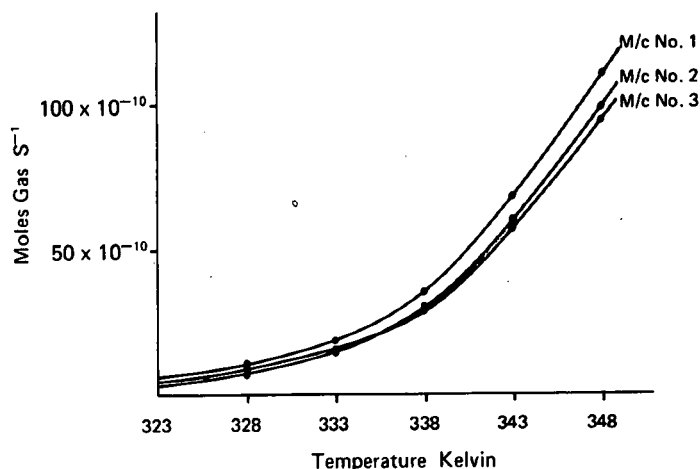


FIGURE 6 Rate of gas evolved plotted against temperature in Kelvin for three different C-masseccutes.

The main findings are:

- (a) There is a large temperature effect particularly when the temperature rises above about 65°C.
- (b) Even at 50°C there is a measurable rate of evolution.
- (c) Different C-masseccuite (No. 1 from Tongaat, No. 2 and No. 3 from Empangeni) show similar temperature dependence.

The expected exponential relationship between rate of gas evolution and temperature was found. In order to calculate the activation energies of the reaction, the Arrhenius rate equation was applied. A plot of $\ln(\text{moles S}^{-1})$ against $(\text{temperature})^{-1}$ produced a straight line.

Given the slopes of the lines in Figure 7, the activation energies can be calculated from the Arrhenius rate equation:

$$K = A \cdot e^{\frac{-E_a}{RT}}$$

$$\text{or } \ln K = \ln A - \frac{E_a}{RT}$$

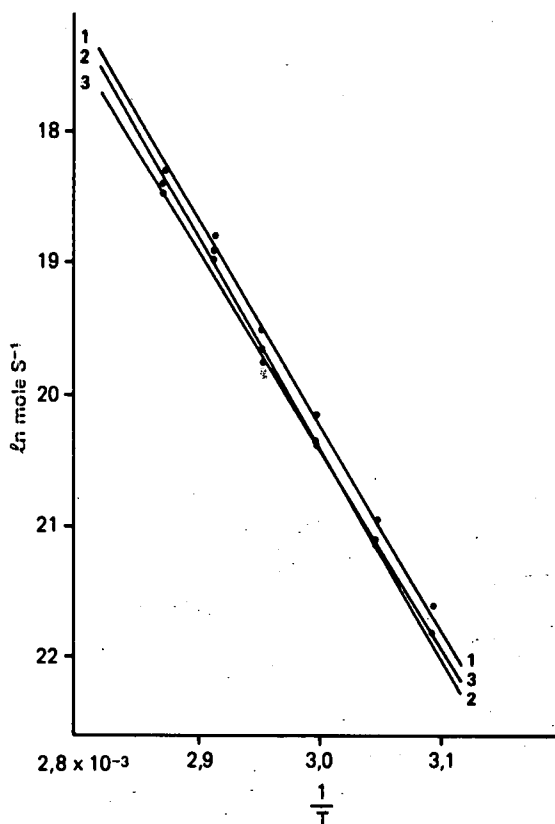


FIGURE 7 \ln (rate of evolution) plotted against reciprocal of temperature.

where K = rate of gas evolution in moles S^{-1}
 A = pre exponential factor (constant)
 E_a = activation energy in joules moles
 R = universal gas constant equal to $8,31 \text{ joules } K^{-1} \text{ mol}^{-1}$
 T = temperature in Kelvin

Activation energies for the reactions were thus calculated and are shown in Table 1.

TABLE 1
Activation energies for the gassing reaction

Masseccuite No.	E_a (kJ mol^{-1})
No. 1	130
No. 2	132
No. 3	127

These values are very close to that reported by C. H. Lea⁵ for the reaction of protein amino groups with glucose, viz. 121 kJ mol^{-1} . This close agreement with the experimental values in Table 1 indicated a similarity between the reactions taking place in the masseccuite and that investigated by Lea.

Effect of total solids and true purity on the evolution of gas

Using figures from the factorial experiments total solids and true purity effects were looked at in more detail. Both were found to have highly significant effects. The total solids was investigated between 88 and 91 percent. The purity was investigated from 53 to 60 percent. The figures are reflected in Table 2.

From this table temperature gives the largest change of volume of gas evolved per unit temperature change. Total solids has the next highest effect, viz. $2 \text{ cm}^3/\text{unit percent change in solids}$ and true purity has $1,4 \text{ cm}^3/\text{unit percent change in purity}$. The change due to total solids and true purity was assumed to be linear over the ranges investigated.

Interactive effects

The statistically designed factorial experiments, used to

TABLE 2
Approximate high and low levels used of the 3 most important factors and the averages of the changes in the volume of gas given off after 50 h from low to high levels

	Low level (L)	High level (H)	Average change in volume (cm^3) of gas given off after 50 h, from low to high levels
Temperature (T)	65	75	+ 25
Total solids (S)	88	91	+ 6
True purity (P)	53	60	- 10

evaluate the various factors, also revealed interactive effects. The implications of the effects have been described elsewhere.³ Briefly, an interactive effect is present if the effect due to one factor is dependent on the level of another factor.

Two such interactive effects were found to be statistically highly significant.

(a) Interaction between temperature/total solids —

The figures on the corners of the square were taken from one of the factorial experiments. They indicate the volume of gas given off after 50 hrs. at high (H) and low (L) levels of temperature and total solids.

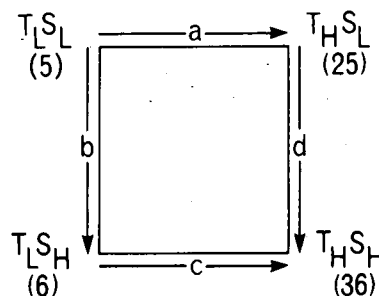


FIGURE 8 Temperature (T) / Total solids (S) interaction.

From this figure 8 we see that if the temperature is low, increasing the total solids causes a 1 unit rise in gas evolution (b). At a high temperature, increasing the total solids the same amount, gives an 11 unit rise in gas evolution (d). At a low total solids, increasing the temperature gives a 20 unit rise in gas evolution (a). At a high total solids, increasing the temperature gives a 30 unit rise in gas evolution (c). It is evident that temperature is the most important factor and should be kept as low as possible in masseccuite and molasses. Lower total solids combined with a low temperature, would reduce the occurrence of gassing still further. However, a compromise will have to be reached between lowering total solids to stop gassing, and increasing total solids to improve exhaustions.

(b) Interaction between temperature/purity —

The figures on the corners indicate the volume of gas given off after 50 h at high and low levels of temperature and purity.

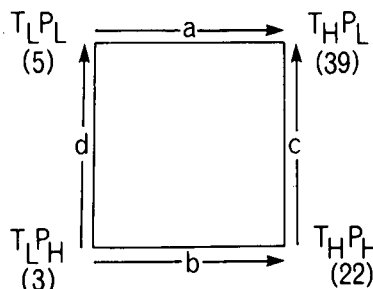


FIGURE 9 Temperature (T) / True purity (P) interactions.

Figure 9 shows that decreasing the purity at a high temperature (c) has a 17 unit increase, as against 2 units at a low temperature (d). Increasing the temperature at a low purity (a) has a 34 unit increase, as against a 19 unit increase at a high purity.

Practically, it is better to run at a low temperature and a high purity in the factory, to reduce the occurrence of gassing. Again, the effect of purity on exhaustion must be considered and a compromise reached.

Change in composition of C-masseccutes during the gassing reaction

Twelve different samples of C-masseccute were analysed by gas chromatography before and after the gassing reaction. The masseccute was reacted for 110 h at a temperature of 65° C with an average volume of 28 cm³ of gas given off. The results of the analysis are shown in Table 3.

TABLE 3

Showing percent total solids, sucrose, fructose and glucose before and after the gassing reaction on C-masseccute

	Before Gassing	After Gassing	% Drop
Masseccute total solids	93,1	91,3	1,8
Sucrose %	51,1	48,8	4,5
Fructose %	6,36	5,79	9,2
Glucose %	5,03	3,46	31,2

To allow for the effect of the drop in total solids, the percentage ratios of sucrose/total solids, fructose/total solids and glucose/total solids, before and after gassing have been tabulated in Table 4.

TABLE 4

Showing the percentage ratios of sucrose, fructose and glucose to total solids on C-masseccute before and after gassing

	Mean			Statistical analysis		
	Before	After	% diff. Before/After	t	n	Significance
Sucrose/Total solids	54,9	53,5	2,55	3,48	12	0,01
Fructose/Total solids	6,83	6,35	7,03	7,20	12	0,001
Glucose/Total solids	5,41	3,79	29,9	10,54	12	0,001

There is statistically, a highly significant difference between the means, independent of the drop in total solids.

Sucrose, fructose and glucose are thus destroyed, approximately, 4, 9 and 31 percent being destroyed respectively, in the 110 h tests.

Inversion must have occurred during the reaction period, as the masseccute had an acidic pH and it was left for over 100 hours at 65° C. Stadler's Table⁶ shows about a 0,9% sucrose loss under these conditions. This is much smaller than the values measured.

The amount of glucose destroyed is so large that experimental errors are negligible.

Standard gassing tests done on C-molasses during the season have confirmed these findings. The gassing was done at 70° C for 50 hours on a total of 77 samples, which came from all five Hulett's mills throughout the season. The average results of these tests are reflected in Tables 5 and 6.

These tables show a significant drop in sucrose and the sucrose chloride ratio. There is also a significant loss of glucose

TABLE 5

Showing average percent sucrose, fructose and glucose on C-molasses before and after gassing

	Before Gassing	After Gassing	% Drop
Sucrose %	30,2	27,9	7,6
Fructose %	7,63	7,61	0,3
Glucose %	5,38	4,82	10,4
Total Solids %	76,6	76,5	0,1

TABLE 6

Showing average sucrose chloride, fructose chloride, and glucose chloride ratios before and after gassing

	Mean			Statistical Analysis		
	Before	After	% diff. Before/After	t	n	Significance
Sucrose/chloride	13,4	12,8	4,5	11,5	77	0,001
Fructose/chloride	3,38	3,49	-3,3	-2,6	77	0,01
Glucose/chloride	2,38	2,21	7,1	9,0	77	0,001

and a drop in the glucose chloride ratio. The fructose shows a slight decrease but an increase in the fructose chloride ratio. This indicates that some fructose is formed and only a small amount of it destroyed.

Morel du Boil and Schäffler⁷ measured a large drop in glucose, and an increase in fructose from syrup to molasses.

Conclusions

The formation of gas is most prevalent in C-molasses and C-masseccute but it can occur in syrup and A/B-masseccutes, although at relatively high temperatures. Temperature had the greatest effect on the rate of gas evolution followed by total solids and purity. A high temperature and total solids and a low purity promoted gas evolution.

It is also evident that when the gassing reaction takes place some sucrose, some fructose and a relatively large amount of glucose is destroyed. This together with other factors mentioned in the text suggest that the reaction taking place is a Maillard reaction.

Acknowledgments

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