MAILLARD REACTION IN MOLASSES STORAGE TANK

[1]L WONG SAK HOI AND [2]JC CHASTEAU DE BALYON

[1]*Mauritius Sugar Industry Research Institute, Reduit, Mauritius*
[2]*Flacq United Estates Ltd, Union Flacq, Mauritius*

Abstract

The Maillard reaction was observed in a molasses storage tank in a Mauritian sugar factory near the end of the 1994 crushing season. The remedial action taken is detailed and the economic loss due to the incident is assessed. The mechanisms of the Maillard reaction and measures for its prevention are reviewed.

Keywords: Froth fermentation, foaming, Maillard reaction, molasses cooling.

Introduction

With the advent of the continuous C-centrifugal, which enables the curing of more viscous massecuites than had hitherto been possible by the batch machines, either the massecuites are re-heated to a high temperature or steam is used generously to lower the massecuite viscosity, with the result that the temperature of the final molasses is above 40°C, and may reach 55-60°C. If the hot molasses is not cooled before being pumped to the storage tank, a Maillard type reaction may occur in the tank, with catastrophic consequences.

Occurrence of the incident

Near the end of the 1994 crushing season, it was noticed on 28 November at Flacq United Estates Ltd (FUEL) sugar factory that it took longer than usual to fill a 24 ton molasses tanker. The molasses was darker in colour than normal, it was 'froth fermenting' with evolution of carbon dioxide and its temperature was 63°C. The 7 000 ton capacity mild steel tank, 12 m high and 23 m diameter, was hot and vapour was coming out of the air vent. The tank was about half full at the time the incident was reported. A sample of the molasses was analysed and it was found that the sucrose content was already down from 37,8% to 12,7%, and the reducing sugars up from 12,93% to 17,3% (Table 1). Neither re-circulation of the molasses to a second tank, nor the addition of ice or water through the air vent, were possible at the time. Nothing much could be done to save the molasses. Trends in brix, sucrose and reducing sugar contents are shown in Table 2.

Table 1

Comparison of deteriorated with undeteriorated molasses

Component	Molasses	
	Deteriorated	Undeteriorated
Brix %	51,72	83,46
Pol %	1,85	30,40
Reducing sugars %	15,95	12,93
Sucrose %	2,17	37,80
Total sugars %	18,12	50,73
Carbonated ash %	8,19	10,27
Calcium %	0,50	1,02
Magnesium %	0,41	0,43
Nitrogen %	0,34	0,64
Phosphorus %	0,08	0,10
Potassium %	3,38	1,27
Sodium %	1,18	1,18

Table 2

Trends in brix, sucrose and reducing sugar contents in the deteriorated molasses

Day	Date	Brix %	Sucrose %	Reducing sugars %	Temperature °C
1	28.11.94	86,4	12,7	17,3	63
2	29.11.94	86,2	13,3	17,1	63
3	30.11.94	84,7	13,5	20,8	64
12	09.12.94	84,2	10,2	21,1	69

When evolution of the carbon dioxide had subsided, most of the molasses had turned into a dark brown carbonaceous mass, with only a small proportion remaining in the liquid state. This liquid portion was analysed and the analytical data are compared in Table 2 with those of the undeteriorated molasses obtained just before the occurrence of the incident.

It can be seen that there is a marked decrease in brix, pol, sucrose and total sugars, and a gain in reducing sugars. This is consistent with the findings of earlier workers (Fromen and Bowland, 1961; Tseng, 1965). As the potassium present in the deteriorated molasses was not negligible and had certain fertiliser value, the molasses was therefore discharged into a canal, pH adjusted to 6,8 with milk of lime, and mixed with river water for surface irrigation of cane. This was a very slow operation as the manhole of the molasses tank was partially blocked by solid carbonaceous mass and it took a fortnight to dispose of all the fluid contents of the storage tank.

The brown solid was found to contain 30,9% moisture and the analytical data on the dried solid (Table 3) show that it consists mainly of organic material and can be easily burnt away. Anon (1953) reported that the porous material left after a similar incident in Egypt has a thermal value of 5 336 calories (1 270 J).

Table 3

Composition of brown carbonaceous mass from deteriorated molasses

Loss of ignition %	82,8
Solids insoluble in HCl %	0,57
Silica %	0,38
Mixed oxides %	0,94
Sodium %	2,00
Calcium %	1,82
Magnesium %	0,81

When the reaction in the tank had subsided and the temperature had dropped, large sections of the molasses tank wall were cut off to enable a rock breaker to move into the tank to break the solid mass into small pieces for transportation to the bagasse storage area, where spontaneous combustion took place before the solid pieces could be used as fuel in the boilers.

The loss of the molasses was estimated at 2,0 M roupies and the cost of the clean-up operation and repairs to the storage tank amounted to 1,2 M roupies.

Discussion

Molasses storage tank

The molasses tank storage conditions at the factory are summarised in Table 4.

Table 4
Molasses storage conditions at FUEL sugar factory before modification

Tank no	1
Height of tank	12 m
Diameter of tank	23 m
Type of tank	mild steel
Capacity of tank	7000 tons
Method of filling	from above
Method of emptying	from below
Temperature control	nil
Facilities for re-circulation	nil
Facilities for ventilation	two air vents of 15 cm ö each
Facilities for air injection	not operational
Facilities for inhibitor dosing	nil
Average length of storage period	4 weeks maximum
Temperature of molasses entering storage	± 60°C

A well-designed molasses tank should be equipped with the facilities of re-circulation, for pumping the molasses from one storage tank to another. It should have an air injection system and, most important of all, adequate ventilation on the roof top. After the incident, the two air vents have been enlarged from 15 to 75 cm diameter at FUEL sugar factory.

The retrieval of molasses from the tank should be on a first-in, first-out basis so that its storage period would not be unduly long.

The design of one of the storage tanks at the molasses terminal is described below. It is 25 m in diameter, 12 m high, and has a cone roof with four air vents of 40 cm diameter each and two manholes of 60 cm diameter each. At about 20 cm above the base of the tank there is an air injection system whereby air from a compressor unit is led by a 6,3 cm diameter pipe to the centre of the tank, where the air is distributed into six 3,8 cm diameter branch pipes equidistant from each other. The pipes are open-ended and are situated 1 m from the periphery of the tank wall, as illustrated in Figure 1. The air compressor is electrically driven, water-cooled and operating at 600 rpm and 100 psi. The temperature of the exit air is about 30°C. Compressed air is introduced into each tank for two hours a day with the objective of breaking through the upper surface of the molasses to enable the hot gases, if any, to be carried away into the atmosphere.

Trivett (1953) first claimed that foaming can be controlled to a certain extent by introduction of compressed air into the mass of the molasses and Parsons (1958) described an air injection and a calcium hypochlorite dosing system in a tank at the molasses terminal in the Philippines to control molasses foaming.

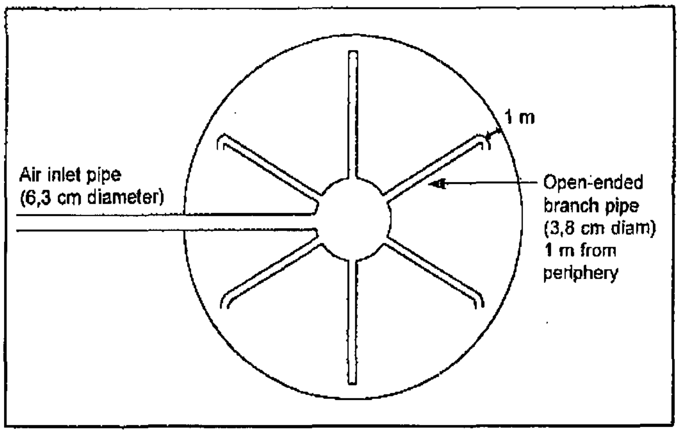

FIGURE 1: Top view of the air injection system 20 cm above the base of a molasses storage tank

Mechanism of Maillard reaction

Back in the 1950s, when incidents of froth fermentation were reported, it was recognised that the change was chemical and not biological as there was an absence of yeast, mould, bacteria or other micro-organisms. It was a spontaneous exothermic chemical change with evolution of carbon dioxide and the formation of volatile acids, mainly acetic. The decomposition is essentially a reaction between amino acids and reducing sugars (Maillard, 1912a, 1912b).

Honig (1965) summarised the mechanism of the Maillard reaction as follows:

1. Amino acid + hexose amino acid-hexose compound (colourless)
2. Amino acid + amino acid – hexose compound polymerised product (I) with dehydration (yellow)
3. Polymerised product (I) undergoes decarboxylation and internal combustion

   C02 + dehydration product (II) (brown melanoidin)
4. Polymerisation product (II) humic acid + insoluble non-sugars (dark reddish- brown).

Ducatillon *et al.* (1985) reported that, during the froth fermentation, the pH drop provokes sucrose hydrolysis to reducing sugars, which in turn react with amino acids to produce more brown melanoidin and eventually humic acid.

Hucker and Brooks (1942) found that molasses instability depends on morphological history. Molasses that had been heated produced more gas than that which had not, and inferred that the higher the temperature the molasses had been subjected to in the factory process, the lower the critical foaming temperature and the greater the foaming on subsequent storage.

Newell (1979) studied the factors affecting Maillard reaction occurring in massecuites and molasses, and found effects of high temperature, high brix and low purity to be significant.

Preventive measures

After the incident at FUEL sugar factory, molasses after curing is cooled in an air cooling tower followed by further cooling in a crystalliser (Figure 2). Molasses at 60°C is pumped to the distributing compartment of the cooling tower at the rate of 6-7 t/h. It overflows under gravity from one inclined plate to another, and is cooled by air to about 55°C. It

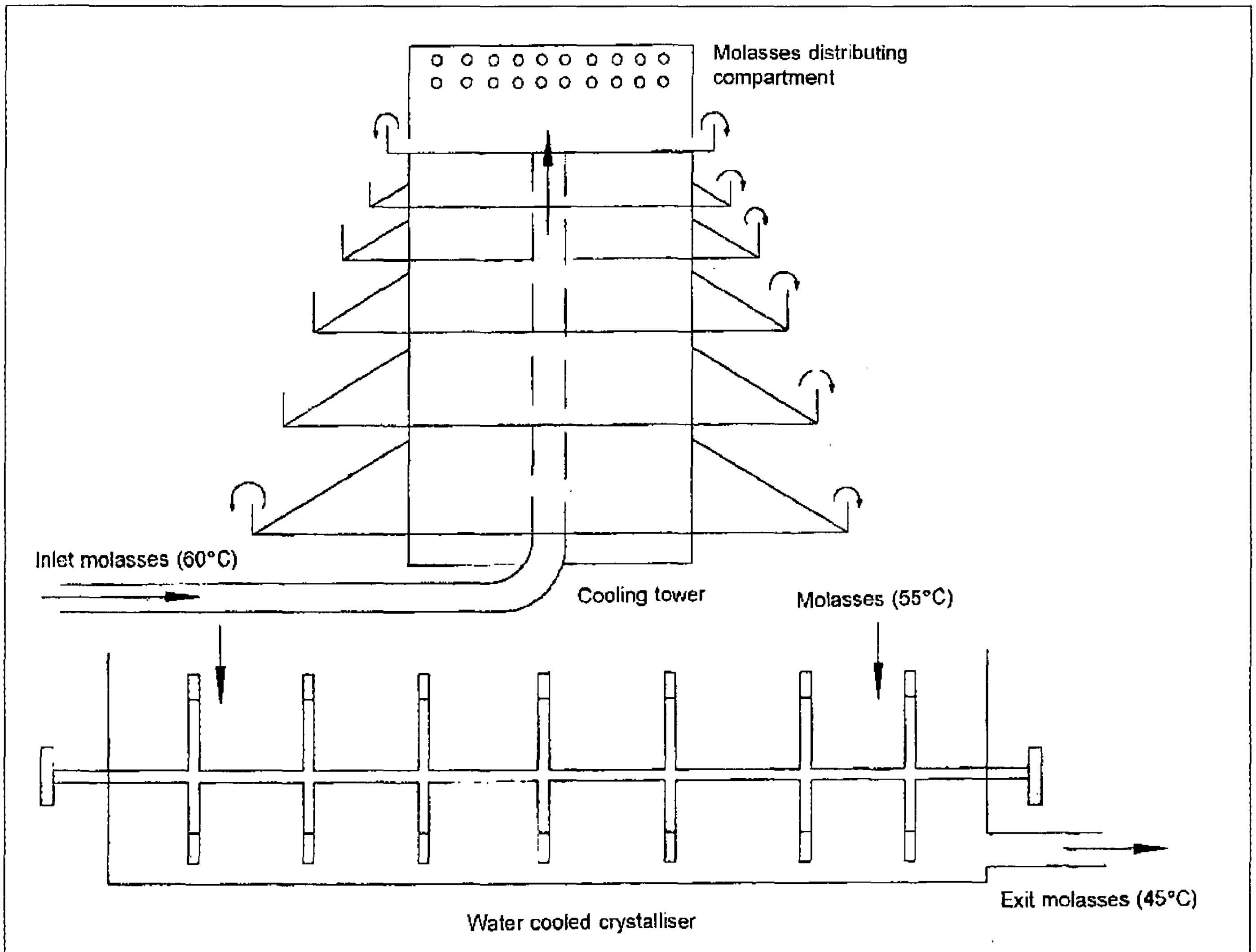

FIGURE 2: Molasses cooling system at FUEL factory after modification

then falls into the water-cooled crystalliser, where a further temperature drop to 45°C is achieved.

Tubular and plate heat exchangers had been used by Julli-enne and Munsamy (1981) for molasses cooling. Broadfoot *et al.* (1990) converted a discarded rotary mud filter to a full scale scraped rotary drum molasses cooler. The temperature of the molasses dropped from 60 to 38°C when the cooler operated at a speed of 2,6 rpm, processing 10 t/h molasses with a molasses film thickness of 1,1 mm on the drum. Quinan and de Viana (1991) used a plate heat exchanger to cool molasses from 57 to 37°C with water at 30°C.

Antifoam chemicals such as sulphur dioxide, sodium sulphite and related compounds have been used in the sugar industry, and their inhibitive action on the Maillard reaction was reported by Trivett (1953). Anet and Igles (1964) showed that bisulphite addition compounds are relevant in the inhibition of browning by sulphur dioxide.

At MTMD, molasses is now diluted to 83° brix, and cooled before being sent to the storage tank, which is now equipped with systems of molasses re-circulation, level control and temperature control. When the molasses temperature exceeds 55°C an alarm is triggered off. A molasses first-in, first-out system is adopted and a close watch is maintained on the amount of steam injected in the centrifugals.

Conclusions

To avoid the Maillard reaction occurring in the storage tank, the molasses must be cooled to below 40°C. It is therefore essential that after the centrifugal station molasses should not be heated to lower its viscosity to facilitate pumping. The molasses storage tank should be well equipped with facilities for ventilation and re-circulation with an air injection, and preferably an inhibitor dosing system.

Acknowledgements

The authors wish to thank the Director of the MSIRI and the Manager of FUEL sugar factories for permission to publish the paper, Mr J Deville, Senior Assistant Director at the MSIRI for review of the paper, Mr JC Ng of the Mauritius Molasses Co Ltd for information on molasses storage tank design, and the staff in the Sugar Technology Division of the MSIRI for their valued assistance in carrying out the sample analysis.

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