SHORT NON-REFEREED PAPER

MODELLING OF HARD-TO-BOIL MASSECUITES

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Introduction

Background to the study

The Mathematics in Industry Study Group (MISG) meets annually to consider cases where mathematics can be used to address problems in industry. The hard-to-boil (HTB) massecuite issue was one of the problems considered at the 2017 workshop. This short paper, based on Fowkes *et al.* (2017), describes some of the results that were derived from mathematical modelling of the situation.

Previous work on boiling difficulties

There has been much experimentation and speculation concerning this loss-causing problem. The problem can be mild to severe (Koster *et al.,*1992) and can be so severe that it can bring a factory to a stand-still, which occurred at the New Iberia, Louisiana, USA, factory in 2002 for three weeks (Eggleston *et al.*, 2011).

Saska (2003) measured heat transfer coefficients in a pilot vacuum pan and found that some Louisiana mill samples had less than one tenth of the heat transfer capability of normal samples. Surfactants, lubricants, and soda ash also appeared to have little or no effect on improving heat transfer in the HTB samples and the viscosity of the samples appeared to be unaffected. Eggleston *et al.* (2011) reported a 9-33% lower heat conductivity of HTB massecuite in Louisiana mills in USA. Also, they reported that a highly viscous intermolecular network was present in HTB molasses which would explain the difficulty in removing entrapped water on boiling. Several chemical agents have been tested (such as soda ash and sodium hydrosulfite) to alter the properties of the massecuite (viscosity reduction, sucrose solubility agents and surfactants) to improve its boiling characteristics with very limited success (Duffault and Godshall, 2004).

Saska (2005) gives details of experiments that were conducted to modify the heat transfer coefficient of massecuites. An improvement of 4 to 7 times was achieved with the addition of hydrochloric acid but determining the exact mechanism was not part of the study. Madho (2009) noted that anti-foaming agent had a positive effect on evaporation rate. When a HTB problem occurs, there appears to be little information about the mechanisms involved that can assist a mill to decide on corrective action.

Rein (2014) reported on experiments primarily done by Echeverri (2007) using a vertical plastic tube arrangement such as that in an industrial pan. The tube was filled with corn syrup and air was injected at the bottom of the tube causing the syrup to move up and out of the tube, later returning to the bottom of the tube through a return pipe. The viscosity of the syrup was varied by varying the brix and crystal content. Echeverri also used the experimental laboratory rig and trials on a full-scale pan to examine the overall convection pattern developed in the pan and used the results to calibrate a computational fluid dynamics (CFD) model. All the above experimental results, from laboratory work, were performed using liquids whose viscosity was significantly less (0.2 to 3.9 Pa.s) than that of massecuite (1-14 Pa.s) in the pan. However, the results obtained are consistent with results for two-phase flow, reported by many other authors.

A calandria tube flow model

Transitions described between flow regimes have been observed by Rouillard (1985) in pilot and experimental pans, and Echeverri (2007) and Rein (2014) in factory pan experiments. Echeverri observed fluctuations in pressure over periods of about two seconds with bubble explosions at the free surface. Observations suggest a greatly reduced heat transfer rate under HTB conditions, so this strongly suggests that the effect of impurities is to change the flow regime from a saturated flow boiling regime through to a subcooled flow regime or even a liquid forced convection regime. Such changed behaviour could occur either because of viscosity changes under HTB conditions, or because of a reduced bubble production rate in HTB massecuites.

Atkinson *et al.* (2000) presented a detailed one-dimensional analysis of the forces that drive the circulation of massecuite through a tube in a pan. The driving force is the rate of change of pressure, p, with distance along the tube, x. The pressure gradient, and hence the movement of the massecuite, is dependent on the volume fraction of vapour bubbles that are formed in the tube as well as viscous and drag effects. The authors used numerical techniques to model the volume fraction, temperature and pressure through the tube.

Atkinson *et al.* (2000) derived the following equation to estimate the driving force on the massecuite noting that the effect of the two-phase mixture is approximated by the proportional contribution from each phase:

$$\frac{dp}{dx} = -\bar{\rho}g - \frac{fG^2}{\bar{\rho}R} - G^2\frac{d}{dx}\left[\frac{\alpha^2}{\beta\rho_v} + \frac{1-\alpha^2}{(1-\beta)\rho_l}\right] \quad (1)$$

where $\bar{\rho}$ is the density of the liquid-solid mixture, g is acceleration due to gravity, f is the Fanning friction factor, G is the liquid mass velocity, R is the pipe radius, α is the mass fraction of vapour, β is the volume fraction of vapour, ρ_v is the density of vapour and ρ_l is the density of the liquid portion.

An analysis presented by Fowkes *et al* (2017), using simplifying assumptions, yields the relationship for the vapour volume fraction, α:

$$\frac{d\alpha}{dx} = h\,\xi, \quad (2)$$

where h is the non-dimensional heat transfer coefficient based on the advective heat transfer coefficient and massecuite velocity up the tube, $\xi = \frac{2\,h_0\,[T_w - T_b]}{RV_0\,\rho_l\,\mathcal{L}}$ is essentially a thermodynamic performance indicator. h_0 is the effective convective heat transfer coefficient, T_w is the tube wall temperature, T_b is the bulk fluid temperature, $V_0 = \sqrt{\alpha g L}$, L is the tube length and $\mathcal{L}$ is the latent heat of vaporisation.

These analyses highlight that the increase in vapour volume fraction, α, is essential to driving the process, that is, heat must be transferred to the massecuite resulting in the formation of bubbles which must expand.

Explanations for changed massecuite behaviour

Eggleston *et al.* (2011) carried out a comprehensive set of experiments that examined the physical characteristics of normal and HTB massecuites. These experiments showed that HTB massecuite (i) has significantly reduced thermal conductivities (by up to 30%) and heat transfer coefficients, and (ii) can exhibit viscoelastic rheology due to the presence of an intermolecular gel-like network that is formed by long-chain polysaccharides. This can influence the energetic requirements for the nucleation of a vapour bubble, and vapour bubbles can be entrapped within the polysaccharide matrix, thus making it appear as if the massecuite is not boiling.

Thermal modelling

The industrial pan tube is a cylindrical system which heats massecuite radially as a result of heat input from steam condensing on the cylindrical wall. Craig *et al.* (1996), Echeverri (2007) and Eggleston *et al.* (2011) report that the composition of the massecuite can significantly alter the overall heat transfer coefficient from the steam to the massecuite. It is therefore of interest to model the thermal transfer and investigate the time to boil for a set of conductivity and heat transfer parameters.

Model development

The temperature variation from conductive heat flow in a cylindrical tube of radius *R* full of massecuite and with steam on the outer surface is governed by the differential equation

$$\rho\, c_p \frac{\partial T}{\partial t} = \frac{k}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right), \tag{3}$$

with boundary conditions: $$k\frac{\partial T}{\partial r} = h(T_s - T),\ r = R,$$

where ρ is the massecuite density, c_p is the thermal heat capacity at constant pressure, k is the thermal conductivity of massecuite, h is the advective heat transfer coefficient with the steam, and T_s is the steam temperature. The boundary conditions use a symmetry condition $T_r = 0$ at $r = 0$ and an application of Newton's law of cooling to the steam contact region.

The influence of the reduction in thermal conductivity of massecuite under HTB conditions was estimated by considering the time taken for the temperature of the massecuite to increase from its entrance temperature, T_a, to the vaporisation T_v assuming purely conductive heat transfer.

Using values from Asadi (2006), Echeverri (2007) and Eggleston *et al.* (2011), as detailed in Fowkes *et al.* (2017), the time taken for the massecuite temperature to reach the vaporisation temperature T_v (i.e. when it starts boiling) from the initial massecuite temperature $T(r, 0) = T_a$ is of the order of 20 to 40 minutes, which is consistent with the typical heating times for massecuite.

Although reducing massecuite conductivity of the order typically occurring under HTB conditions will change the processing time from 28 mins to about 38 mins, this change is not as large as observed in practice; this is unlikely to be the complete explanation for the problem.

Bubble nucleation in a viscoelastic medium

For a vapour bubble to grow, the radius of the nucleated bubble must be sufficiently large that the energy that is released from the phase transformation can offset the energy that is required to form a liquid-vapour interface plus the elastic energy that is required to compress the viscoelastic medium.

Consider the growth of a spherical vapour bubble from radius R_i to radius R. Since mass is conserved during the phase transformation, the radius of the vapour bubble can be calculated as

$$R = (\rho_l / \rho_v)^{1/3} R_i, \tag{4}$$

where ρ_l and ρ_v denote the densities of the liquid and vapour, respectively. Thus, material points surrounding the vaporising liquid are displaced by an amount

$$u_b = R - R_i = [1 - (\rho_v / \rho_l)^{1/3}]R. \tag{5}$$

The energy change that occurs upon nucleating a spherical bubble of radius *R* can be written as

$$\Delta E = -U_{vap} + U_{surf} + U_e, \tag{6}$$

where U_{vap}, U_{surf}, and U_e correspond to the vaporisation, surface, and elastic energies, respectively.

Assembling the various energy components (see Fowkes *et al.,* 2017):

$$\frac{3}{4\pi}\Delta E = -R^3 \left[\rho_v \mathcal{L} - 6\,\mu\,[1 - (\rho_v/\rho_l)^{1/3}]^2 \right] + 3\,R^2 \gamma_{lv}. \tag{7}$$

The critical bubble radius, R_c, corresponds to the radius at which it becomes energetically favourable (i.e., ΔE decreases) for a bubble to grow rather than shrink. This critical radius is given by:

$$R_c = \frac{2\gamma_{lv}}{\rho_v \mathcal{L} - 6\mu\,[1-(\rho_v / \rho_l)^{1/3}]^2}, \tag{8}$$

The effect of an increase of elastic resistance is to increase the critical radius required for bubble growth, with this result becoming infinite when the elastic resistance exceeds μ_{crit} given by:

$$\frac{6\,\mu_{crit}\,[1 - (\rho_v / \rho_l)^{1/3}]^2}{\rho_v \mathcal{L}} = 1, \tag{9}$$

Using the values $\rho_v = 0.1$ kg/m^3, $\rho_l = 1 \times 10^3$ kg/m^3, $\mathcal{L} = 2.3 \times 10^6$ J/kg, gives an approximation of the critical shear viscosity:

$$\mu_{crit} \approx \rho_v\,\mathcal{L}/6 = 0.38 \times 10^5 \text{ Pa}$$

This can be compared to shear resistance values for massecuite presented by Eggleston *et al* (2011) of the order of 1×10^5 Pa (76.5 Brix 20°C) for HTB molasses and between 1×10^3 Pa and 1×10^4 Pa for normal molasses (63.8 Brix 20°C).

The critical shear modulus values are exceeded for hard-to-boil massecuite, in other words, bubbles will not grow.

Conclusions

There are many recipes suggested in the literature for addressing the hard-to-boil massecuite problem encountered at specific mills. The outcomes of this study suggest what properties can be manipulated to influence the boiling behaviour of HTB massecuites. It now remains to test what links there are to the actions proposed in the literature and these properties.

The results from modelling flow of heat from the tube wall into the bulk indicate that the boiling time is not sufficiently affected by reductions in the thermal conductivity and heat transfer coefficient of HTB massecuite to fully explain the HTB phenomenon.

The results do suggest that viscoelastic effects associated with polysaccharide contamination can prevent bubbles from forming and in fact the available data indicate that bubbles will not grow in HTB massecuite.

Other effects may also play a role, but the strong indications are that bubble suppression is dominant.

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