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Falling film hydrodynamics of black liquor under evaporative conditions

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ABSTRACT

Bubbles were observed in a thin, evaporating, falling film of black liquor (a fluid mixture generated during the pulp production) on the exterior wall of a research evaporator. Because the presence of bubbles could not be explained by nucleate boiling, a combination of turbulent vapour entrainment and effects due to surface-active compounds – surfactants – is proposed. Black liquor contains numerous surfactants, which are likely to enhance bubble formation and stabilization in the fluid and on the film interface. One observed important effect of bubble formation was fluid loss due to bubble-bursting aerosolization (sputtering). Also, bubbles and bubble processes probably alter the film velocity-profile and heat transfer resistance, thereby affecting heat transfer across the film and hence evaporator efficiency.

1. Introduction

This study focused on black liquor, a fluid generated during the production of chemical pulp from wood or annual plants, whose main constituents are lignin and other organic matter separated from the wood, cooking chemicals, and process water [1].

In these experiments, intense bubble formation was observed for conditions where nucleate boiling theory indicates that bubble formation should not have occurred. Likely explanations for this unanticipated behaviour involve a combination of factors, including turbulence, wave-breaking, and the effect of surface-active compounds – surfactants – as well as high dissolved gas concentration.

2. Theory

2.1. Surface tension

A liquid's surface tension is a reflection of the cohesive forces in a liquid that arise from the attractive forces between fluid molecules [2]. At an air–water or an oil–water interface, hydrophilic head-groups tend to be located in the aqueous phase while the lipophilic end-groups attempt to orient themselves into the gas phase. This orientation is energetically more favourable than complete dissolution in the liquid [3].

A liquid's surface tension is related to the energy needed to expand the gas-liquid interface: greater surface tension implies greater requisite energy to increase the surface area. Molecules also experience repulsive forces, which arise from steric forces of an entropic nature. These repulsive forces decrease the energy [4]. Note that surface tension refers to static equilibrium conditions.

When the interface is freshly formed, it has a surface tension close to that of the solvent (water), but then it changes with time to that of the solution. The rate of change is characterized by the dynamic surface tension and depends on the surfactant's adsorption and desorption rates, and the effect of adsorption barriers [5].

Foams always are formed from mixtures [2] with two important requirements for the liquid mixture to foam. First, one component must be surface-active, and second, the foam film must show surface elasticity. Surface elasticity is defined as the increase in surface tension as the surface area is increased [2].

2.1.1. Black liquor

Black liquor is a highly complex mixture of lignin, residual inorganic chemicals, numerous organic extractives in the wood, and other constituents produced due to fragmentation reactions of lignin and its products during the pulping process [6]. Lignin is composed of linked phenylpropane units that form a polymer network, and contains end groups of methoxy radical (CH_3O) [8] and coniferyl alcohol, among others [7]. Lignin has high molecular weight [1] and forms compounds with dissolved salts used in the pulping process.

Organic wood extractives from Kraft pulping primarily contain sodium salts of tall oil soap. Lipophilic organic wood extractives

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Nomenclature

ΔH_{vap}	enthalpy of vaporization (J/kg)
ΔT	temperature difference (°C)
ΔT_{bl}	temperature difference across black liquor film (°C)
ΔT_{ONB}	wall superheat necessary to cause nucleation (°C)
c_p	specific heat (J/kg °C)
DS	dry solid content (%)
h	heat transfer coefficient across black liquor film (W/m^2 °C)
k	thermal conductivity (W/m °C)
$\dot{q}$	heat flux (W/m^2)
$\dot{q}_{\mathrm{ONB}}$	heat flux for the onset of nucleate boiling (W/m^2)
r_c	critical radius (m)
T	temperature (°C)
T_{sat}	saturation temperature (°C)

Greek symbols

Γ	mass flow rate per unit width (kg/m s)
μ	dynamic viscosity (Pa s)
Θ	contact angle
ρ	density (kg/m^3)
ρ_g	gas density (kg/m^3)
σ	surface tension (N/m)
Pr	Prandtl number $\equiv \frac{c_p\mu}{k}$ (−)
Re	Reynolds number $\equiv \frac{4\Gamma}{\mu}$ (−)

of wood (resins) are converted during the pulping process into sulphonated oil soap, or tall oil soap. Tall oil soap is mainly a mixture of resin acid salts and fatty acid salts [9,10] as well as alcohols, fatty alcohols, triglycerides, and sterols. The resin acids and dissolved fatty acids may act as emulsifiers [11]. Black liquor also contains a range of carbohydrates, which generally are present as polymers or oligomers, both in dissolved and colloidal forms [11]. Black liquor has significant compositional differences with respect to wood species [12], heartwood/sapwood ratio – i.e., age [11], and the pulping process conditions [1].

The general trend for surface tension for black liquor is a rapid decrease with increasing dry solid content to a value between 30% and 60% of the surface tension of pure water. The surface tension may have a flat minimum between 15% and 40% dry solid content [1]. In a normal mill, black liquor is evaporated to a dry solid content that ranges from 15% to 80%.

The solubility of tall oil soap varies with the dry solid content of the black liquor, gradually decreasing with dry solid content up to ~25% dry solid content. In industrial processes, the tall oil soap normally is skimmed off the black liquor at the dry solid content when the tall oil soap has the lowest solubility. The greater the fraction of dissolved lignin, the lower is the black liquor's surface tension [13]. Surface tension values vary somewhat; Olausson [14] assumed a constant surface tension of 0.029 N/m in his calculations, while Beckwith et al. [15] measured the surface tension of black liquor at 25 °C and 20–40% dry solid content and found 0.032–0.034 N/m. Söderhjelm and Hausalo [16] measured 0.023–0.030 N/m at 55% dry solid content and 90 °C, depending on the type of black liquor and on the mill conditions. Overall, Kraft black liquor's surface tension is significantly lower than water's surface tension, and exhibits a trend with temperature similar to that of water [1]. Water's surface tension decreases from 0.0728 N/m at 20 °C to 0.0589 N/m at 100 °C [17].

As stated earlier, a freshly formed interface of a surfactant solution has a surface tension close to that of the solvent, i.e., black liquor's dynamic surface tension is higher than its static surface tension. The dynamic surface tension increases with greater dry solid content and decreases with increasing temperature [1]. The time scale for dynamic surface tension is ~5 s, and it increases with higher dry solid content [1].

The heat transfer coefficient across the falling black liquor film during evaporation is dependent mainly on the viscosity of the black liquor and the circulation flow in the evaporator. The viscosity is a function primarily of the dry solid content and the temperature of the black liquor [18]. However, according to some studies, the heat transfer coefficient for the fluid in falling film evaporation also depends on the fluid's surface tension [19].

2.2. Bubbles

In the ocean, the turbulence process of wave-breaking entrains air into the water, forming bubbles [20]. Although details of the bubble formation process from breaking waves are poorly understood, it is strongly affected by aspects including temperature [21] and the presence of surfactants (including salt) [22,23]. In both cases, significant changes in the bubble size distribution are observed [24].

After formation, bubbles rise due to buoyancy, and are advected by turbulence and fluid motions [25,26] and the velocity shear (lift force), which results from unequal pressure on the bubble in the flow and results in a transverse motion towards lower shear [27], as well as other forces. The bubble also exchanges gases with the surrounding fluid, which may be supersaturated or undersaturated relative to the bubble, where equilibrium is determined by Henry's law solubility, the bubble partial pressures, and the dissolved gas concentrations [25]. Note that the bubble's internal pressure is greater than the fluid pressure due to surface tension and hydrostatic pressure. This causes gas pressures in the bubble generally to be above equilibrium relative to the dissolved gases in the surrounding fluid [25]. Also, bubbles can grow rapidly due to water vapour, particularly bubbles in a boiling liquid [28]. The literature on the behaviour of bubbles entrained in falling thin films (not nucleating on walls as in [28]) is lacking; thus, aspects will be proposed in Section 5.

Outside ultra-clean laboratory conditions, all bubbles are contaminated with surfactants. Subsurface, a bubble's interface may be partially or completely contaminated with surfactants in a film of thickness varying from submolecular (i.e., interspersed among interface water molecules) to a thick film [29]. Details of the surfactant layer depend upon the various surfactants' chemical properties and the fluid dynamics associated with the bubble motion [30]. Further, bubbles acquire a thin surfactant film at the air-fluid interface that includes both sparged (i.e., collected material from the bulk fluid) and interfacial compounds. These interfacial surfactant concentrations can be significantly enhanced over the bulk fluid concentrations [31]. Surfactants also stabilize thin films [29] and enhance the bubble lifetime subsurface (from formation through bursting at the interface or dissolution [25]) and on the interface [2]. Other fluid properties, including higher viscosity and higher density, also enhance these lifetimes [2,32,33]. Although surfactants significantly affect bubble hydrodynamics and gas exchange rates in quiescent fluid [25], in highly turbulent environments where the turbulence length scale is comparable to the bubble size, the effect of surfactants can be reduced significantly [34].

Bubbles are important to microflotation – the transport of surfactants to a fluid's interface [35], including particles such as algae in the marine environment [36] – and to maintaining the enhanced organic composition of the sea surface microlayer [35]. Needless to say, surfactant particles affect the bubble behaviour differently than surfactant compounds, by decreasing buoyancy and influencing the flow field around the bubble; these particles can be comparable in size to the bubble boundary layer.

Where there are multiple surfactants, each adsorbs onto and desorbs from the bubble interface. Over time, the interfacial surfactant composition evolves towards surfactants with lower solubility, with the equilibrium determined by the bulk concentrations and the adsorption and desorption rates [37]. Further, where there are surfactants and surfactant particles, synergistic effects may result from affinities between the particles and surfactants. For example, bubbles are efficient collectors of algal exudates, which are important binding agents in marine aggregates [38].

2.3. Nucleate boiling

One possible cause of the observed bubble formation which was observed is nucleate boiling. A criterion for the onset of nucleate boiling is the following, according to Collier and Thome [39]:

$$\dot{q}_{\mathrm{ONB}} = \frac{2\sigma T_{\mathrm{sat}} h}{r_c \rho_g \Delta H_{\mathrm{vap}}} \tag{1}$$

where r_c is the critical radius of the cavity mouth at the nucleation site and T_{sat} is in °C. Given the lower surface tension and lower heat transfer coefficient of black liquor compared to water, the onset of nucleate boiling for black liquor from (1) is for a much lower heat flux than for water.

The water to black liquor ratio of the heat flux needed to start nucleate boiling expresses the comparative ease of initiating nucleate boiling for black liquor compared to the more commonly known criterion for water. This ratio can be simplified because many of the parameters in (1) are the same or similar for water and black liquor. The heat transfer coefficient, h, varies with mill conditions – e.g., circulation flow, temperature, and the dry solid content (viscosity) of the black liquor. For typical values, $T_{\mathrm{sat}} = 100$ °C, $h = 2500$ W/m^2 K based on $\Gamma = 1.4$ kg/m s, and $\mu = 0.002$ Pa·s (μ is a function of DS and T of the black liquor [1]), the ratio for black liquor is:

$$\begin{aligned}\frac{(\dot{q}_{\mathrm{ONB}})_{\mathrm{water}}}{(\dot{q}_{\mathrm{ONB}})_{\mathrm{black\ liquor}}} &= \frac{\left(\frac{2\sigma T_{\mathrm{sat}} h}{r_c \rho_g \Delta H_{\mathrm{vap}}}\right)_{\mathrm{water}}}{\left(\frac{2\sigma T_{\mathrm{sat}} h}{r_c \rho_g \Delta H_{\mathrm{vap}}}\right)_{\mathrm{black\ liquor}}} \rightarrow \frac{(\sigma \cdot h)_{\mathrm{water}}}{(\sigma \cdot h)_{\mathrm{black\ liquor}}} \\ &= \frac{0.0589 \cdot 8500}{0.026 \cdot 2500} = 7.7\end{aligned} \tag{2}$$

In (2), the gas density and the enthalpy of vaporization are neglected because they differ little between water and black liquor.

Although the surface tension is largely insensitive to T_{sat}, T_{sat} significantly affects the heat transfer [18]. For lower T_{sat} the heat transfer coefficient, h, is less because of increased viscosity [18] and thus the onset of nucleate boiling occurs at lower heat fluxes for lower T_{sat}. Therefore, nucleate boiling is more probable during evaporation at low T_{sat}. A higher dry solid content implies higher viscosity and thus a lower heat transfer coefficient. Normally, T_{sat} is increased for higher dry solid content in industrial black liquor evaporators [40], which increases the heat transfer because of the lower viscosity.

For evaporators, the wall superheat ratio is more appropriate for comparison, because boiling occurs from superheated walls. In such a case, the tendency to start nucleate boiling for black liquor and water can be compared through the wall superheat ratio. Here, the "nuclei" are defects on the wall and the ratio can be considered solely a function of surface tension. Thus, it is only weakly sensitive to T_{sat}, although because of the solubility of the soap, there is a weak dependence on the dry solid content of the black liquor. The heat flux, $\dot{q}$, is determined by the temperature difference across the black liquor film (wall superheat), ΔT, and the heat transfer coefficient, h [41]:

$$\dot{q} = h \cdot \Delta T \tag{3}$$

From (3), the wall superheat water–black liquor ratio is:

$$\begin{aligned}\frac{\Delta T_{\mathrm{water}}}{\Delta T_{\mathrm{black\ liquor}}} &= \frac{h_{\mathrm{black\ liquor}}}{h_{\mathrm{water}}} \cdot \frac{(\dot{q}_{\mathrm{ONB}})_{\mathrm{water}}}{(\dot{q}_{\mathrm{ONB}})_{\mathrm{black\ liquor}}} \\ &= \frac{h_{\mathrm{black\ liquor}}}{h_{\mathrm{water}}} \cdot \frac{(\sigma \cdot h)_{\mathrm{water}}}{(\sigma \cdot h)_{\mathrm{black\ liquor}}} = \frac{\sigma_{\mathrm{water}}}{\sigma_{\mathrm{black\ liquor}}} = \frac{0.0589}{0.026} \\ &= 2.3\end{aligned} \tag{4}$$

The wall superheat ratio between water and black liquor is smaller than the heat flux ratio, 2.3 versus 7.7, from (2) and (4), respectively. Generally, the wall superheat in an evaporator is a controlled parameter [40].

3. Experimental work

A research evaporator, built in cooperation with Metso Power AB, Göteborg, Sweden (previously Kvaerner Power AB), was used to study the behaviour of falling films. The evaporator is described in detail in [42]. In brief, the heart of the plant is a 4.5-m long vertical tube, 0.06-m outer diameter, with a falling film of black liquor flowing on the outside. An ejector system continuously evacuates air and other non-condensable gases from the system.

Five viewports are located along the evaporator to study the falling film. Two viewports are at the evaporator tube's top, one is in the middle and two are ~0.5 m from the tube bottom. Both falling water and black liquor films were photographed through the lowest viewports with a Nikon D2x.

In most cases, the fluid is slightly subcooled (below the saturation temperature for evaporation) when it enters the evaporator tube; however, the fluid T rapidly increases to its saturation temperature, T_{sat}. For each experiment, the hydrodynamic and thermal entrance lengths were calculated [43] and were less than 1.5 m. In all the studies here, the flow was fully developed before it reached the lowest viewport.

For these studies, the black liquor's dry solid content was ~40%. Experiments were performed both above and below atmospheric pressure and for circulation flows up to 7.78×10^{-3} m^3/s, i.e., highly turbulent flow, which covers typical industrial conditions. Further experimental details are in references [18,42,44]. Results presented are based on experiments which all used the same softwood black liquor from a Swedish Kraft pulp mill.

3.1. Surface tension measurements of black liquor

Static surface tension measurements of the black liquor were performed using a computer-controlled, Sigma 70 tensiometer (KSV Instruments Ltd., Finland) equipped with a du Noüy ring. This technique involves determination of the force needed to detach a ring of wire from the liquid's surface [2]. The ring is hung on a balance and submerged below the surface of the liquid. Thereafter, the ring is moved upwards, forming a rising meniscus, which eventually breaks as the ring detaches from the liquid. The force exerted on the ring reaches a maximum value prior to the breakdown of the meniscus, and the surface tension is calculated from the measurement of this maximum force. The ring was platinum (19.1-mm in diameter) and was flamed prior to each experiment to remove surface contaminants. Ensuring the contact angle between the ring

Table 1
Measured surface tension of black liquor and water using the ring method and the literature values.

Conditions	Surface tension (N/m) 20–25 °C	Surface tension (N/m) 90–100 °C	Comment
Expeimental 28% DS	0.0325	–	Measured at 21.2 °C
Expeimental 35% DS	0.0327	–	Measured at 21.1 °C
Expeimental 40% DS	0.0328	–	Measured at 21.7 °C
Extrapolated expeimental 35% DS	–	0.0265	Extrapolated to 100 °C
Beckwith et al. [15]	0.032–0.034	–	20–40% DS, 25 °C
Söderhjelm and Hausalo [46]	–	0.023–0.030	55% DS, 90 °C
Water	0.0728	0.0589	The literature values at 20 °C and 100 °C

DS is dry solid content.

and the liquid at zero or near-zero is important [45] and was maintained for all measurements. Surface tension measurements (Table 1) were comparable to the literature values [16,15].

The experimentally measured black liquor surface tension was extrapolated to 100 °C by assuming the same temperature dependence for black liquor as for water. This temperature dependence was determined from the program, REFPROP [17].

4. Results

The evaporating black liquor film (Fig. 1) clearly had many large bubbles, which were not observed in the non-evaporating black liquor film for similar conditions. This was in contrast to water falling film, where there were no observed differences between evaporative and non-evaporative conditions.

To better understand this significant difference between falling films of evaporating falling water and black liquor, experiments were conducted to study the effect of heat flux on the heat transfer coefficient during black liquor evaporation.

The observed trend (Fig. 2) showed a weak inverse dependence of the heat transfer coefficient on the heat flux for three different dry solid content levels, DS, with decreasing sensitivity to $\dot{q}$ for higher DS. For nucleate boiling, h should increase with $\dot{q}$ because of contributions to h due to both convection and nucleate boiling. In experiments with black liquor, where they increased $\dot{q}$ and measured h, Müller-Steinhagen and Branch [47] achieved nucleate boiling in some experimental series. In one series of experiments Müller-Steinhagen and Branch [47] demonstrated a significant increase in h for an increase in $\dot{q}$; h increased from 2000 to 5500 W/m^2 K for an increase in $\dot{q}$ from 80 to 120 kW/m^2.

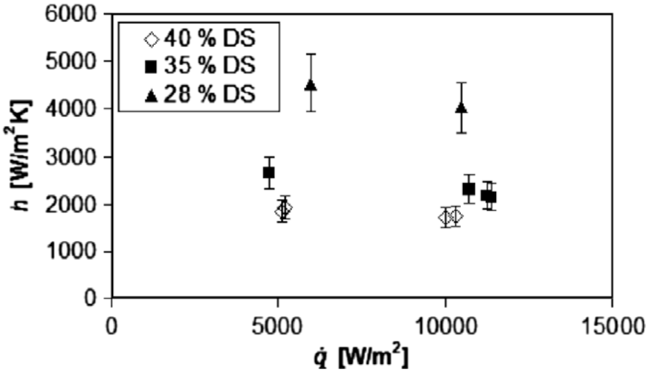

Fig. 2. Heat transfer coefficient, h, versus heat flux, $\dot{q}$. Each data point represents 10 measurements. DS is dry solid content.

Fig. 1. Photograph of a black liquor falling film during evaporation. The photograph shows the evaporator tube (60-mm outer diameter) with black liquor falling film on the outside of the tube wall. The black liquor had a temperature of ~110 °C and the circulation flow was 5.56×10^{-5} m^3/s (Re number of ~600). The temperature difference between the heating steam and the evaporating black liquor film was ~8 °C. (The red dot in the top of the picture is a mark associated with the viewport glass. The lighter part to the right in the photograph is from the flash located inside the evaporator jacket.)

The experimental temperature difference, ΔT_{bl}, for the black liquor film was varied from 1.3 to 5.4 °C (see Table 2). For comparison, the calculated temperature difference needed for the onset of nucleate boiling from wall superheat, ΔT_{ONB}, using Eqs. (1) and (3) was significantly greater (see Table 2); $\Delta T_{\mathrm{ONB}} = 7.3–7.6 \pm 20\%$, $\Delta T_{\mathrm{ONB}} = 9.2–9.6 \pm 20\%$ for the welding seams and the overall tube, respectively.

Here, the critical radius, r_c, was determined experimentally with water in the research evaporator. Specifically, water was evaporated for a range of heat fluxes and the onset of nucleate boiling was determined from visual observations of the film on the overall tube walls and also at the welding seams. For the overall tube, r_c was 1.39×10^{-6} m, and for the welding seams it was ~25% greater ($r_c = 1.75 \times 10^{-6}$ m).DS is the dry solid content, $\dot{q}$ is the experimen-

Table 2
Summary of heat flux and superheat.

DS (%)	$\dot{q}$ (kW/m^2)	ΔT_{bl} (°C)	ΔT_{ONB} (°C) (tube)	ΔT_{ONB} (°C) (seams)
28	9.6	2.5	9.2	7.3
28	5.5	1.3	9.2	7.3
35	10.3	4.9	9.2	7.3
35	10.4	4.9	9.4	7.5
35	4.3	1.8	9.4	7.5
35	9.8	4.4	9.4	7.4
40	9.1	5.4	9.4	7.5
40	4.7	2.7	9.6	7.6
40	4.7	2.6	9.5	7.6
40	9.4	5.3	9.5	7.6

Fig. 3. The left photograph shows a black liquor falling film during evaporation for a low circulation flow where bubbles are created in a surge or wave front. The middle image shows wave-breaking and bubble formation on a beach; the right image shows wind-stress, wave-breaking at sea.

tal heat flux, ΔT_{bl} is the temperature difference across the black liquor film, ΔT_{ONB} is the calculated wall superheat from Eqs. (1) and (3) necessary to cause nucleate boiling for the overall tube ($r_c = 1.39 \times 10^{-6}$) and welding seams ($r_c = 1.75 \times 10^{-6}$), and r_c is the critical radius of the cavity mouth at the nucleation site.

Fig. 3 shows bubbles initially created in the film at a wave front, similar to a tidal bore or surge, wherein the upper layers of the fluid override deeper layers. We propose that bubble formation in thin, evaporating falling films has similarities to the wave-breaking bubble formation process, a ubiquitous marine phenomenon shown in Fig. 3. Naturally, there are notable differences, such as the gravitational force being parallel to the fluid motion in the falling and evaporating film, as well as fluid properties and driving forces, among other aspects. Nevertheless, it is illustrative to focus on similarities.

Bubble formation and flow non-linearities increased with increasing circulation flow (Fig. 4). At low flow, the film could be described as wavy-laminar (left image), with a few large bubbles, which often were observed close to surface waves. At higher circulation flows (middle image), a range of bubble sizes was observed and the film liquid-vapour interface was rough (turbulent). At even higher flow rates, many bubbles burst (or vented) in the field of view, sometimes leading to the formation of bubble jets (right image). As a result, black liquor droplets separated from the film (Fig. 5). Droplet formation is part of the process called sputtering.

5. Discussion

Possible explanations for bubble formation in the falling, evaporating black liquor film include nucleate boiling, desorption of other volatile dissolved gases, and turbulence and wave-breaking. Also of likely importance are the effects of black liquor surfactants. Each is discussed below.

5.1. Nucleate boiling

Experiments over a range of heat fluxes and dry solid contents (Fig. 2) strongly suggest that bubble formation was not due to nucleate boiling. For nucleate boiling, the heat transfer coefficient normally should increase for increasing heat flux. In the experi-

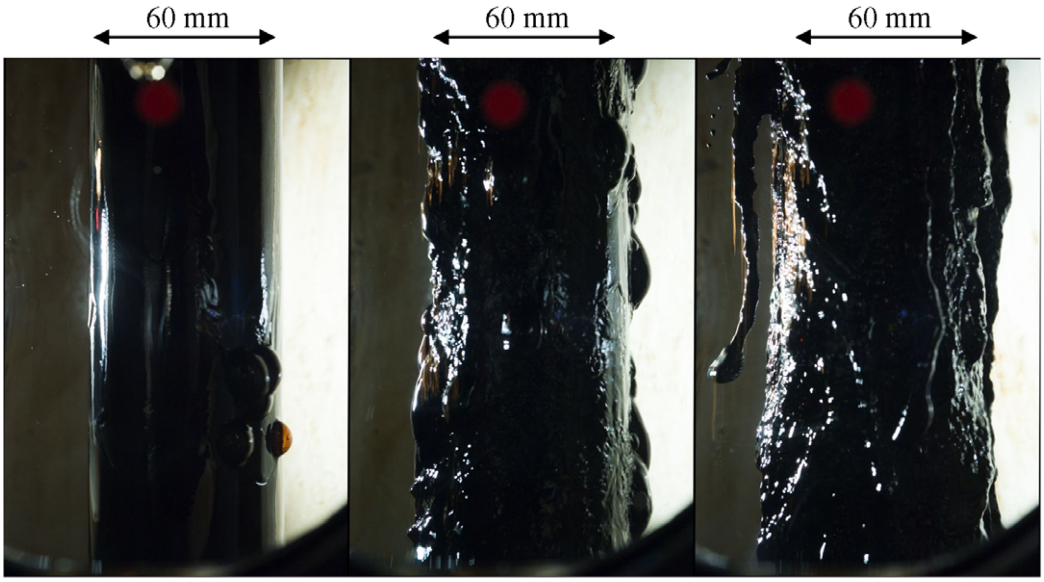

Fig. 4. Photographs of evaporating black liquor falling film for three different circulation flows: 2.87×10^{-5} m^3/s (Re ~ 300), 1.11×10^{-4} m^3/s (Re ~ 2400) and 3.61×10^{-4} m^3/s (Re ~ 3800) for the left, middle, and right images, respectively. The temperature was ~110 °C and the temperature difference between the heating steam and the evaporating black liquor film was ~8 °C.

Fig. 5. Bubble bursting on the falling film. Prior to bursting (left) and after (right).

ments, the heat transfer decreased by 11–19% for an increase in the heat flux of 84–140%. Further, the heat flux (Fig. 2) was between 40% and 500% too low to achieve nucleate boiling. This conclusion is conservative because the heat flux (or superheat) needed is probably even higher than in the calculation, since the surface tension in the falling film is dynamic and thus greater than the static surface tension used in Eq. (1).

The evaporator tube is a commercial cold-rolled duplex steel tube with some welding seams that cause local differences in the wall surface structure. In previous evaporating water experiments, local nucleate boiling occurred in areas on the evaporator tube where the surface structure is rougher (in the welding seams) than the rest of the tube. Nucleate boiling at the welding seams started for water at lower temperature differences because of the greater r_c for cavities on the seam. Therefore nucleate boiling should first occur at seams; however, the measured heat flux still was too low to initiate nucleate boiling for these study conditions.

5.2. Other volatile gases in the black liquor

Bubbles could arise because gases other than water vapour in the black liquor "effervesce", creating small bubbles which then would serve as water-vapour bubble nucleation sites. In black liquor, condensates from the evaporation process include methanol, hydrogen sulphide, methyl-mercaptan, dimethyl sulphide, and dimethyl disulphide [10]. These gases evaporate during the black liquor evaporation process. In the research evaporator, however, most experiments were made with black liquor that was degassed by repeated evaporation. Thus, this explanation is unlikely, although gas desorption probably contributes to bubble growth.

5.3. Turbulence and wave-breaking, and the effect of surfactants in black liquor

In falling films, instabilities develop, leading to the generation of waves and turbulence structures that potentially could lead to wave-breaking [48–50] and thus gas entrainment. Marine wave-breaking leads to the formation of a broad bubble-size spectrum [51]. Further, surfactants enhance bubble formation and affect the bubble size distribution [52], although the mechanism is not understood. One factor that could be critical to the surfactant effect on bubble formation is that surfactants reduce the requisite energy to increase the surface area. In addition, bubbles at the film interface should have enhanced lifetimes due to surfactants in the black liquor.

Breaking-wave bubble formation is a widely known phenomenon [20,24,29,51,52]; however, there are few published studies of bubble formation for evaporating falling films. Publications include a master thesis using the same research evaporator [53] and studies by Holmberg et al. [54], although there are numerous studies about nucleate boiling [28,55]. This master thesis studied the evaporation of CTMP-liquor (a fluid mixture generated from Chemi-Thermo-Mechanical Pulp production), which contained surfactants, where bubbles were photographed in the falling film. Holmberg et al. [54] observed severe disturbances of the film in their experimental study of the heat transfer in a falling film of lithium bromide-water evaporation. These disturbances caused small "explosions" in the film, which sent droplets onto the glass column that surrounded the evaporator tube. Again, small bubbles were observed in the film, for which Holmberg et al. [54] argued that "the most obvious explanation for this would be nucleate boiling but in view of the fact that a falling film of water needs a heat flux of more than 70 kW/m^2 in order to initiate nucleate boiling, this explanation seems unlikely but needs to be further investigated."

As shown in Fig. 4, conditions that generated only small waves and interfacial movements in the falling film were accompanied by bubble creation. For higher flow rates, there was greater uneven surface deformation and greater bubble formation. Flow irregularities and turbulence arise not only by the high flow, but also from the bubbles in the falling film and from bubble bursting.

Once bubbles grow comparable to the film thickness (giant), their growth is distinct from earlier phases. Specifically, it is entirely dominated by transient heat conduction [28]. Cerza and Sernas [28] found that for bubbles from wall nucleation, the free-stream growth period after detachment is the major bubble-growth period. Due to the film thinness under the bubble's base, these large free-stream bubbles efficiently remove heat locally from the superheated liquid film underneath [28].

The role of surfactants was studied through experiments in the research evaporator for a solution of 0.0013% surfactant (dishwashing detergent) in distilled water. In the evaporator, the behaviour of this surfactant solution falling film showed similarities in terms of bubble formation (Fig. 6) to the black liquor falling film, although foam formation developed more quickly even for this (weak surfactant) solution. Absent the surfactant (pure water), bubbles were not observed. Bubble formation also increased with increasing circulation flows. Given the absence of bubbles for similar non-contaminated water films, this strongly supports the hypothesis that surfactants significantly enhanced bubble forma-

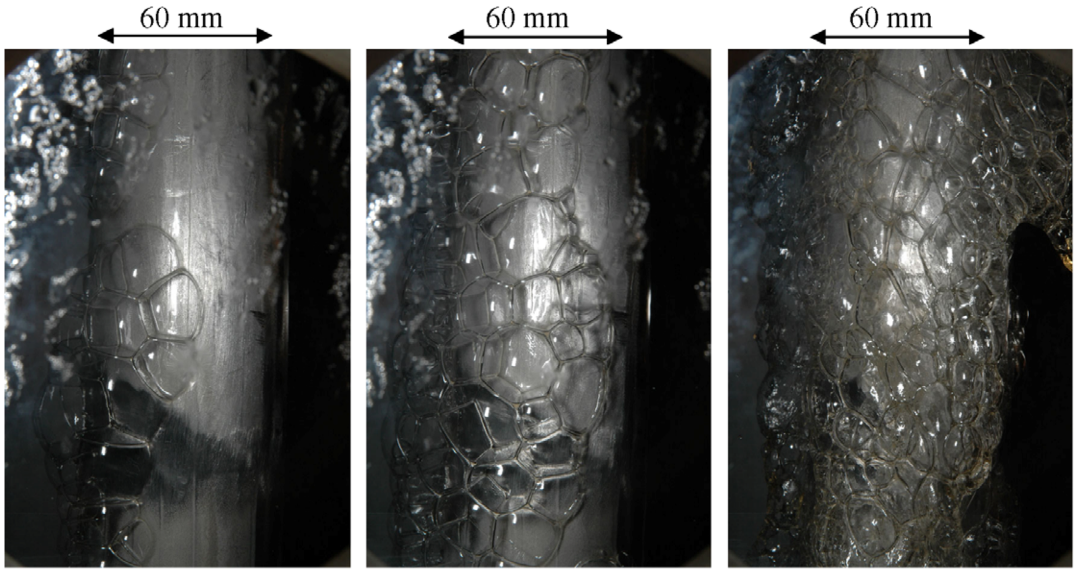

Fig. 6. Photographs of evaporating water falling film with surface-active compounds for three different circulation flows: 6.94×10^{-6} m^3/s (Re ~ 450), 5.56×10^{-5} m^3/s (Re ~ 3600), and 2.78×10^{-4} m^3/s (Re ~ 18000), for the left, middle, and right images, respectively. The water temperature was ~92 °C and the temperature difference between the heating steam and the evaporating water film was ~8 °C.

tion in this study. For giant bubbles, surfactants probably prevent free motion or exchange of fluid from the surrounding film interface onto and off the bubble's interface. Surfactant accumulation would probably continue on the bottom portions of the bubble's film cap, but would be more analogous to the process of surface adsorption.

While completely submerged, the effect of surfactants on bubble behaviour in the film most likely has similarities to bubbles in the dense portions of the bubble plume rather than outside the plume; specifically, the effect is significantly reduced compared to a single bubble in a static fluid. This is because the intense turbulence generated by the falling film (which is forming bubbles) probably has significant energy at size scales comparable to that of the bubble. In a salt-water bubble plume, larger ($r > 500$ μm) bubbles behave clean [56] even though as isolated bubbles in static water they would show contamination effects [57]. Among possible reasons for this effect is intense turbulence. Specifically, bubble wakes generate turbulence at length scales comparable to the bubble's boundary layer (as does the initial wave-breaking event) and thus, where the bubble density is high, bubble-wake interactions are frequent. Because surfactant effects depend on the bubble interface having surfactant concentration gradients (i.e., surface tension) imposed by an external flow, such small-scale turbulence is not conducive to generation of surfactant gradients (see Fig. 7). A decreased surfactant effect in bubble plumes has been observed [34]. Thus, we propose that surfactants enhance the subsurface bubble lifetime for tiny bubbles and also for bubbles that are large compared to the film turbulence, and of course for giant bubbles (larger than the film thickness).

We therefore suggest that the bubble formation and stabilization processes involve turbulence wave-breaking, growth from water vapour, and acquisition of surfactants and surfactant particles, shown schematically in Fig. 7. This process probably reflects the surfactant compounds in the black liquor, whose concentrations will evolve on the bubble interface. Stable foam and enhanced bubble lifetime require components with both high and low molecular weights. Black liquor contains a range of low and high molecular weight compounds, lignin and its derivatives and tall oil soap, which we propose stabilize bubbles and foam. Lignins are "sticky" biopolymers that also may bind other organic compounds on the bubble interfaces, as well as enhancing colloidal adhesion to bubble interfaces. We propose that this organic matrix enhances the bubble's interfacial lifetime. Foam lifetime is increased by decreasing film drainage.

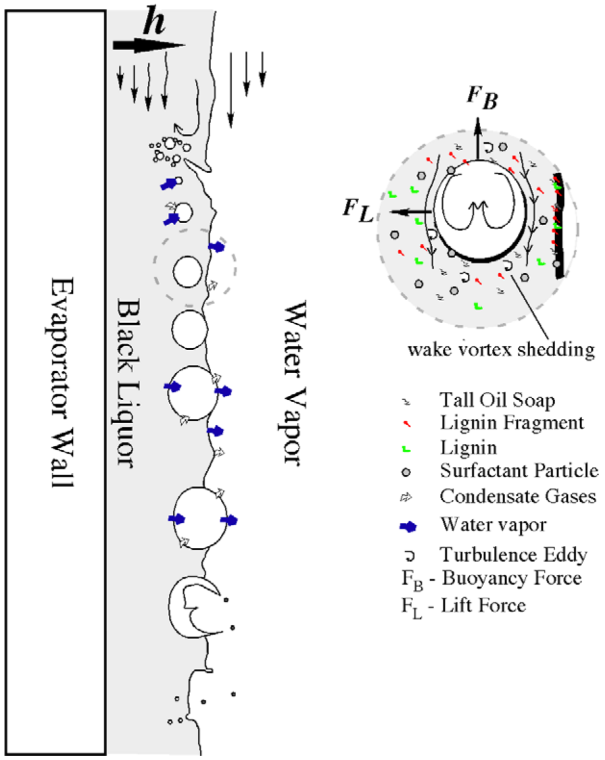

Fig. 7. Detailed schematic of the bubble formation process in an evaporating, falling black liquor film. Bubbles form from breaking waves and rapidly grow from water vapour and gas desorption until eventually they burst, creating small aerosols and bubbles. The inset shows how surfactants and particles attach to the upper surface of a submerged bubble, where a fresh interface is formed that is swept to the bottom of the bubble, forming a thicker surfactant cap. Symbol key in figure.

Black liquor contains dissolved salts, which also are likely to affect the bubble formation and stabilization processes. Cui et al. [58] investigated the effect of dissolved salts in water droplet boiling, and found that the dissolved salts promoted bubble formation and also reduced the evaporation rate by lowering the water vapour pressure. This led to droplet break-up during impact [58]. Thus, inorganic salts probably affect bubble formation in thin films, just as breaking waves have far fewer bubbles in fresh water than in seawater [59].

In the Kraft pulping process, black liquor is formed from the addition of salts that react with lignin. Thus, it is highly likely that black liquor contains ionic surfactants. The presence of multiple surfactants (including ionic surfactants) in the presence of water-soluble polymers enhances the foamability of a mixture compared to a single surfactant system, by increasing surface viscosity and thus decreasing the film drainage time [60].

Given the complex range of surfactants in black liquor, there likely is an evolution in the surface composition of the bubble surfactant layer with time, from the smaller (more mobile) and more soluble compounds towards more lipophilic compounds, which are probably bound into colloidal structures in the black liquor. Bubble surfaces are known to be nucleation sites [61] and plausibly lead to the formation of larger polymers and particles, some of which will desorb due to lower surface activity, turbulence vortex shedding, and bubble bursting (see Fig. 7).

5.4. Implications of bubble formation

Bubble formation has a number of implications for the evaporation process. For example, bubbles are likely to enhance the film–gas interfacial surfactant concentration, which would slow evaporation. Once bubbles become giant (large compared to film thickness), they also provide cooling points that efficiently transfer heat and increase evaporation due to an increase in the surface area. Bubbles transport surfactants from the bulk to the surface of the falling film. Surfactants decrease the interfacial mobility, which generally increases the mass transfer resistance, and thus the heat transfer resistance in the falling film. Also, bubbles are likely to slow the falling film because of their buoyancy and by immobilizing portions of the film due to surfactants. Slower film velocity implies less turbulence in the film and slower heat transfer. Also, small entrained bubbles in the falling film will increase the heat transfer resistance due to the lower heat conductivity of water vapour. All these processes generally indicate that bubbles are likely to decrease heat transfer, thereby slowing evaporation. However, wave-breaking and bubble formation will enhance heat transfer through turbulence generation, and evaporation through increasing the surface area of the film–gas interface and also by creating submerged bubbles. Overall, the situation is too complex to speculate about the net effect for the heat transfer without further studies.

5.5. Implications of sputtering for heat transfer and evaporator efficiency

At higher flows, bubble bursting produced black liquor drops that left the falling film, a process called sputtering. Due to sputtering, the film progressively thins along the evaporator tube, leading to a decrease in the falling film velocity. Because the heat transfer coefficient is dependent on the falling film velocity, slower flow implies decreased turbulence, which further decreases the heat transfer coefficient. Sputtering also increases the risk that the film may thin to the point where it completely evaporates, leaving a dry spot. Dry spots negatively affect the heat transfer and are a significant cause of evaporator inefficiency [39].

Bubble formation and sputtering in the falling film alter the film velocity and temperature profiles [28], affecting heat transfer and thus the conditions for the heat transport equations (e.g., "the energy equation") [41,62,63] used for calculating heat transfer during falling film evaporation. Disregarding the lower circulation flow because of the sputtering, the falling film velocity probably decreases due to bubbles, thereby decreasing the heat transfer in the falling film. However, the disturbances created by the bubbles and the sputtering would locally increase turbulence in the film. It is predicted that for increasing $\dot{q}$ and convective evaporation, heat transfer should be constant, while for increasing $\dot{q}$ and nucleate boiling, heat transfer should increase. Instead $\dot{q}$ decreased in experiments where there was sputtering. Overall, this suggests that bubble and sputtering processes decrease heat transfer and evaporator efficiency.

Further planned investigations will study the effect of sputtering at high circulation flows on the heat transfer coefficient. According to standard correlations for the heat transfer coefficient in falling film evaporation, the heat transfer coefficient increases for increased circulation flow [54,64,65]. However, significant sputtering could set a limit for highest circulation flow, unless most of the sputtered drops re-enter the black liquor film.

5.6. Relevance to industrial evaporators

The most important differences between the research evaporator and industrial evaporators are size, gas flow velocity, and that industrial evaporators contain a package of heat transfer surfaces. Regarding size, the heat transfer surfaces often are comparable to the research evaporator tube diameter and are significantly longer [66]. Gas flow velocities in the research evaporator were much lower than in industrial evaporators. In an industrial evaporator, higher shear rates and flow stress should increase bubble formation, but could also decrease the surface bubble lifetime.

In the research evaporator, bubble formation and therefore bubble bursting and droplet formation (sputtering) caused black liquor drops to leave the falling film permanently. In an industrial evaporator some of the sputtered black liquor drops probably fall between the heat transfer surfaces, while others re-enter the film on the heat transfer surfaces, in part because of the narrow gaps between the heat transfer surfaces. Sputtered droplets can disturb the falling film, particularly on facing heat transfer surfaces, thereby initiating flow instabilities and providing bubble nucleation sites. The fate of sputtered black liquor needs further investigation because of the clear importance of sputtering to the development of new evaporator designs.

6. Conclusions

A large difference was observed in the behaviour of evaporating falling film for pure water and black liquor. The evaporating water film was quite similar to the non-evaporating water film; however, the evaporating black liquor film exhibited significant bubble formation, a phenomenon not observed in the non-evaporating black liquor film. This study examined potential explanations for this poorly understood bubble formation. Turbulence wave-breaking bubble formation is proposed as most likely. An alternative mechanism, nucleate boiling, is not favoured because experimental results showed that the heat transfer coefficient decreased for increased heat flux, contradicting the predicted behaviour of nucleate boiling.

The presence of bubbles has several important implications. Bubbles were observed to burst at high circulation flows, which led to a loss of black liquor from the falling film due to sputtering of bubble-burst droplets. If wave-breaking is the formation mechanism, then a broad size distribution of bubble sizes is likely to be formed. Also important to the bubble formation process and the fate of these bubbles are black liquor surfactants, which probably enhance bubble lifetime in the fluid and at the interface. If the sputtering is high, this sets a limit for the highest possible circulation flow. Bubbles also affect the heat transfer resistance and the velocity profile of the falling film, thereby affecting evaporator efficiency.

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