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Aerosol generation by reactive boiling ejection of molten cellulose†

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The generation of primary aerosols from biomass hinders the production of biofuels by pyrolysis, intensifies the environmental impact of forest fires, and exacerbates the health implications associated with cigarette smoking. High speed photography is utilized to elucidate the ejection mechanism of aerosol particles from thermally decomposing cellulose at the timescale of milliseconds. Fluid modeling, based on first principles, and experimental measurement of the ejection phenomenon supports the proposed mechanism of interfacial gas bubble collapse forming a liquid jet which subsequently fragments to form ejected aerosol particles capable of transporting nonvolatile chemicals. Identification of the bubble-collapse/ejection mechanism of intermediate cellulose confirms the transportation of nonvolatile material to the gas phase and provides fundamental understanding for predicting the rate of aerosol generation.

1.0 Introduction

The thermal degradation of lignocellulosic biomass and cellulose-based materials is the enabling chemical process occurring during forest fires, the smoking of cigarettes, and the combustion, fast pyrolysis, and gasification of biomass for conversion to power and biofuels.^{1–3} The fuel value and environmental and health impacts of thermally degrading biomass and bio-derived

cellulose-based materials depend upon the types of vapor products produced as well as the quantity, composition, and size distribution of aerosols and particulate emitted. As much as 30% of degrading biomass can be converted to aerosols and particulate.^{4,5} Additionally, as much as 60% of the inorganic content in the condensable products of biomass pyrolysis results from the generation of aerosols.⁶ Significant technical effort has focused on understanding the degradation process to characterize and predict the distribution of pyrolysis products.⁷ However, the mechanism of aerosol generation directly from cellulose and lignocellulosic materials remains unknown.⁶

1.1 Origin of nonvolatile pyrolysis species

The dominant experimental approach to understanding lignocellulose and cellulose decomposition has focused on identifying and quantifying the product gases and hundreds of condensable vapor species.⁸ Exhaustive characterization of condensed vapors

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Broader context

The generation of aerosols from biomass occurs within numerous high temperature processes including cigarette smoking, wild fires, and the thermo-chemical conversion of biomass to biofuels. We demonstrate that primary aerosols produced directly from biomass are capable of transporting heavy nonvolatile organic polymers and inorganic compounds into the gas phase and surrounding atmosphere. In forest fires, these aerosols transport particulate into the atmosphere where they can alter high-altitude chemistry. Aerosols from cigarettes can carry heavy tars and inorganic material into the human lungs. Additionally, primary aerosols produced in pyrolysis reactors serve as nucleation sites for product organic vapors. These aerosols are entrained throughout the gas phase of condenser trains where they can deposit and reduce overall pyrolysis oil reactor performance. We elucidate the process by which primary aerosols are formed directly from molten cellulose by a vapor-bubble collapse mechanism. By understanding the mechanism of primary aerosol generation, future work can focus on minimizing the generation of aerosols and their effect on human health and industrial processes.

from lignocellulose pyrolysis reveals numerous key degradation pathways to volatile components including levoglucosan, hydroxymethyl furfural, and monolignols such as 2-ethylphenol and vanillin.^{8,9} However, the analytical identification of pyrolysis products from biomass has also observed a significant fraction of heavy, nonvolatile products including carbohydrate^{4,10} and lignin oligomers,^{11,12} as well as nonvolatile inorganic compounds including SiO₂, CaO, and MgO.²

The origin of higher molecular weight and nonvolatile species from the thermal degradation of lignocellulose and cellulose is currently unknown. One proposed explanation suggests that volatile organics produced by degradation re-condense to secondary aerosols and react to form higher molecular weight species.^{13,14} As depicted in Fig. 1, thermal degradation of lignocellulosic biomass increases volatility of organic material until it evaporates producing organic vapors. Organic vapors can thermally decompose and/or oxidize to produce permanent gases (e.g. CO or CO₂). Organic vapors can also react to form aromatics which polymerize to poly-aromatic hydrocarbons (PAHs) and form soot. Alternatively, organic vapors can condense to bio-oils or nucleate and grow secondary organic aerosols wherein re-combination reactions can occur to higher molecular weight species.

The evaporation mechanisms account for some nonvolatile pyrolysis products, but this argument does not explain the existence of intact biomass-derived oligomers, some of which are tetramers of lignin or carbohydrate polymers up to nine monomers long.^{4,11,15,16} This mystery has led to the postulation of a ‘thermo-mechanical ejection’ mechanism whereby biomass

fragment particles are entrained in the product gases and carried away as aerosols.^{4,17} This mechanism hypothesizes that the rapid increase in volume resulting from the degradation of biopolymers to gases results in ‘explosive destruction’ of the cellulose or lignocellulosic structures, thereby entraining particle fragments within the gaseous products.^{4,18}

1.2 Reactive boiling ejection of cellulose

We propose a new, alternative biomass-ejection mechanism referred to here as ‘reactive boiling ejection’ whereby primary aerosols are spontaneously generated directly from cellulose during pyrolysis. Thermal decomposition of solid, crystalline cellulose produces a short-lived (<100 ms) intermediate liquid state which exhibits violent boiling as it further degrades to vapors and gases.¹⁹ By experimentally characterizing the ejection phenomenon using high speed photography, the formation and collapse of vapour bubbles within reacting molten cellulose is identified as the driving force for ejection. The bursting of bubbles generates a liquid cavity which collapses and forms a liquid jet. Subsequent jet fragmentation produces high-velocity liquid aerosols which are entrained in the gas phase. The sequence of reaction and fluid events leading to aerosol ejection are confirmed here by high speed photography, sampling of the produced aerosols, and computational fluid dynamics (CFD) simulation of the ejection phenomenon.

The approach of combined experimental characterization and fluid modelling of reactive boiling ejection is complicated by the difficulty in describing the composition and physical properties

Fig. 1 Organic Aerosol Generation and Formation Pathways. Aerosol formation occurs through the evaporation of organic vapors. Subsequent cracking and dehydration produces aromatics that can polymerize to poly-aromatic hydrocarbons. Vapors can also thermally decompose to permanent gases. Additionally, organic vapors can nucleate small liquid particles which condense and grow to larger secondary organic aerosols. Alternatively, we propose a new mechanism whereby organic liquid particles are generated directly from solid biomass by reactive boiling ejection to primary organic aerosols.

of the intermediate cellulose liquid. While the existence of an intermediate liquid state has been proposed for over two decades,^{20,21} its existence was only recently confirmed.¹⁹ Consequently, reaction and transport characteristics of the intermediate liquid have not been previously measured. The intermediate cellulose liquid is a highly non-equilibrium, high-temperature condensed fluid that exists for only a fraction of a second. Therefore, it exhibits extreme physical properties such as low surface tension consistent with high temperature fluids near their critical point.²² These characteristics prevent utilization of conventional techniques for measurement of physical properties of stable fluids. For these reasons, we provide an estimate of the surface tension based on the ejection speeds of generated aerosols that is supported by CFD simulation. The combination of estimation of fluid properties with visual observation, chemical characterization, and simulation strongly supports the reactive boiling ejection mechanism.

2.0 Methods

Evidence for the reactive boiling ejection mechanism was obtained with several experimental and simulation methods. Observation of aerosol ejection and measurement of ejection characteristics occurred with high speed photography of molten cellulose. Aerosols ejected from molten cellulose were collected and analyzed, and their composition was compared with independent high-temperature carbohydrate experiments. The ejection events observed experimentally were compared with CFD simulations. The simulations support the estimated physical properties of intermediate liquid cellulose and provide insight into the precise details of the mechanism of the ejection phenomenon.

2.1 Materials

Microcrystalline cellulose samples (Lattice NT-200) were obtained from FMC Biopolymer and sieved to particles greater than 250 μm . Samples of cellulose exposed to the air naturally absorbed ~ 5 wt% moisture. Moisture content was determined gravimetrically by drying in a vacuum oven. Levoglucosan was purchased from Sigma-Aldrich (99%, #316555). Sucrose was purchased from Fischer Scientific (Crystalline, S5-500). $\gamma\text{-Al}_2\text{O}_3$ was purchased from Sigma-Aldrich (97%, #13-2525). Trimethylsilylimidazole was purchased from Sigma-Aldrich (#92751). All chemicals were used as received.

2.2 High speed photography

The experimental apparatus consisted of a heated surface of either $\alpha\text{-Al}_2\text{O}_3$ or Fecralloy (Fe-Cr-Al-alloy). A solid $\alpha\text{-Al}_2\text{O}_3$ disk (2 mm thick by 22 mm diameter) was held inside a stainless steel block for thermal and structural stability. The $\alpha\text{-Al}_2\text{O}_3$ disk was prepared by pressing $\gamma\text{-Al}_2\text{O}_3$ particles to 5000 psi in a hydraulic press and sintering at 1150 $^\circ\text{C}$ for 12 h. The disk was seated on a stainless steel cylinder, and it was thermally insulated and shielded from hot combustion gases. Nitrogen gas was supplied with a metering valve through a quartz tube positioned 2 cm above the disk surface to maintain an oxygen-free environment. Heat was applied directly to the stainless steel block with a MAPP torch, and the temperature of the disk was measured by direct contact with a Type K thermocouple on the

reactive surface. Particles were delivered to the disk by a controlled gravity fed addition system that entrained the particles in the nitrogen gas prior to reaction.

A similar setup was used for heating particles on the Fecralloy surface, except that a Fecralloy disk was suspended over a Bunsen burner. The Fecralloy surface was calcined beforehand at 1150 $^\circ\text{C}$ for 12 h prior to use in the experiment.

Image sequences were recorded at 1000 frames per second with a Photron Fastcam Ultima APX Imager by Photron USA, Inc. Three magnifying components were employed in series with the Infinity Long Distance Microscope by Infinity Photo-Optical Company: a TR 2x tube, a Model K2 lens, and a CF-3 Objective. Auxiliary lighting was required for use at high speeds and was provided by a Solarc LB50 lamp by Welch Allyn, Inc. The image size was calibrated by direct photographs of objects with known dimensions with identical camera configuration and focal length.

Original photographs were captured at 1024 $\times$ 1112 pixels and were cropped as needed. Electronic image adjustments were uniformly applied to entire images and image sequences. The NIH's ImageJ 1.43u²³ and GIMP 2.6.10²⁴ were used to perform uniform adjustments of contrast and brightness to grayscale images. No selective enhancements were made. Figs 3A, 3B & 6 were cropped and contrast/brightness adjusted. The image sequences can be observed in full video form in Videos S1, S2, and S3†, respectively. Additionally, original frames corresponding with Fig. 3B can be observed in Fig. S5†.

ImageJ was also used to process frame differenced image sequences (Fig. 3B). The original image sequence was contrast and brightness adjusted using ImageJ, followed by application of a mathematical differencing technique by which two consecutive frames were subtracted. The images were subtracted on a pixel level, such that the resulting value of each pixel represented the change in grayscale over 1 ms. Negligible change between frames results in a dark/black pixel, whereas significant change between frames results in a grey/white pixel. This operation was performed across the entire sequence, and both original and differenced sequences can be seen in Video S2†.

2.3 Levoglucosan polymerization

For a controlled comparison, levoglucosan reaction chemistry was examined using a custom built polymerization apparatus constructed from a glass Pasteur pipette. After purging nitrogen through the glass pasteur pipette to remove atmospheric oxygen, the narrow end was sealed with a torch. The sample of levoglucosan was then added to the open end of the pipette and tapped down to the sealed end. More nitrogen was flushed through the headspace before the open end was sealed about 5 cm from the sample. This reaction tube was then placed in a furnace at specified temperatures and time durations.

A second polymerization experiment was performed using an amber 2 mL vial that was left open to the atmosphere with the levoglucosan dispersed in the bottom of the vial based on the procedure of Radlein *et al.*⁴ This vial was kept at 240 $^\circ\text{C}$ for 20 min.

2.4 Aerosol characterization

An apparatus, depicted in Fig. S1†, similar to that used in the high speed photography was adapted to collect and rapidly

quench aerosol products. A stainless steel heating block and α -alumina disk were used in conjunction with a MAPP torch to provide heat for the pyrolysis surface. Additionally, a stainless steel gas addition halo was used to deliver nitrogen to the surface and ensure a non-oxidative environment.

Aerosols were collected using a glass slide held at a 45 degree angle about one centimeter above the reactive surface. Glass slide temperatures did not exceed 200 °C, ensuring minimal secondary reactions. Cellulose particles about 300 μm in size were slowly added to the surface in a continuous manner.

Direct measurement of the size distribution of sampled aerosols was obtained by use of visual microscopy and image processing tools. A 10x optical microscope equipped with a visual light source was used to obtain images covering an area of about 0.57 cm^2 each. This design allowed for quantitative measurement and qualitative visualization of aerosol particles in the range of 0.9 to 10 micron. The NIH program ImageJ was used to systematically count all particles with a sphericity index of 0.8–1, and the results are shown in histogram form in Fig. 5A.

For the purpose of identification, aerosols were extracted from the slides by ultrasonication in deionized water for five minutes. This procedure involved breaking the slide into small fragments and submerging the pieces in 5 mL of deionized water inside a 20 mL vial, then placing the vial into the ultrasonicator bath. This solution was then pipetted into a 3 mL syringe and filtered through a 0.2 micron PTFE filter into a 2 mL amber vial where it was left to evaporate overnight under vacuum at 70 °C. The dried aerosols were then derivatized using a 1 : 1 mixture of pyridine and trimethylsilylimidazole (TMSI) to a total volume of 1.5 mL. This mixture of methylating agent and sample was placed in a water bath at 60 °C for 30 min and immediately analyzed on an Agilent 7890 gas chromatograph with a 5975C mass spectrometer. The method used a G4513A auto injector and had a split/splitless injection port temperature of 280 °C and an injection volume of 1–2 μL . The column used was a 30 m DB-5 with a 320 μm diameter and a 1.5 μm film. Separation was obtained with the use of a temperature programmed ramp that started at 65 °C, held for 2 min, ramped to 300 °C at 6 °C per minute, and held for 30 min as suggested by Medeiros, *et al.*²⁵

2.5 CFD modeling

The hypothesized ejection mechanism was examined by comparing the measured ejection velocities (Fig. 4A) to a transient axisymmetric CFD simulation (Fig. 7). Based on first principles, specifically the conservation of mass and momentum, the incompressible Navier–Stokes equations are solved using the finite volume numerical method. This approach to cavity collapse simulation, similar to the process by Duchemin, *et al.*,²⁶ models interface transport and capillary effects with the Eulerian volume of fluids (VOF) method. However, the current approach is capable of handling topological changes in the interface, such as the formation of droplets and bubbles. Unlike previous work, the current simulation specifically considers ejection from the curved interface of a droplet, rather than an infinite pool with a flat surface.²⁶

Flow simulations were performed within the OpenFOAM CFD framework described by Weller.²⁷ The code solves the discretized unsteady Navier–Stokes equation with nominally

second-order accurate spatial discretization. An incompressible, laminar flow is assumed. Pressure-velocity field coupling is accomplished with the pressure-implicit split-operator (PISO) method.²⁸ The VOF method identifies fluid phases with a dimensionless scalar color function α which is advected conservatively with the flow. The piecewise expression for α from Rusche²⁹ is defined in eqn ([1]).

$$f(x) = \begin{cases} 1 & \text{for a point inside fluid a} \\ 0 < \alpha < 1 & \text{for a point in the transitional region} \\ 0 & \text{for a point inside fluid b} \end{cases} \quad (1)$$

The unsteady evolution of the α field follows the transport equation shown in eqn ([2]) with $\mathbf{u}$ being the underlying velocity field. Due to smearing of the interface, density and viscosity values in mixed cells are weighted by α using a harmonic mean weighting scheme^{30,31} as shown in (eqn ([3])).

$$\frac{\partial \alpha}{\partial t} + \mathbf{u} \cdot \nabla \alpha = 0 \quad (2)$$

$$\mu_{HM} = \frac{\mu_1 \mu_2}{\alpha \mu_2 + (1 - \alpha) \mu_1} \quad (3)$$

Interface sharpness is maintained with the counter-gradient compression method described in Berberović *et al.*³² Capillary forces are incorporated into the cell-centered pressure field by means of the continuum surface force (CSF) model by Brackbill.³³

The computational domain is comprised of an axisymmetric, uniform, structured mesh of one million 2D cells with a bubble resolution of 100 cells across the radius R_{bubble} as shown in Fig. 2. The ratio of the bubble radius to droplet radius $R_{\text{bubble}}/R_{\text{droplet}}$ is approximately equal to 0.13.

Boundary conditions for the pressure (p) and velocity ($\mathbf{u}$) fields are described in Table 1 and applied in the manner shown in Fig. 2. Boundary condition “A” represents a no-penetration, no-slip wall with the liquid-solid interface contact angle pinned at 90°. Boundary condition “B” represents approximate far-field ambient conditions (*i.e.* a constant pressure and a uniform flow field). The variable $\mathbf{n}$ represents the outward pointing unit vector orthogonal to the boundary face. The absolute value of p_0 is inconsequential as the incompressible Navier–Stokes equation uses only the gradient of the pressure.

3.0 Results

The presented experiments include the observation of the ejection phenomenon from cellulose, the characterization of ejected aerosol particles, the observation of the mechanism within a carbohydrate surrogate, and the simulation of the proposed mechanism by computational fluid dynamics.

3.1 Cellulose aerosol ejection

We show, using high speed photography, that primary aerosols are produced from molten cellulose by the collapse of bubbles which subsequently form a liquid jet. As depicted in Fig. 3A and observed in Video S1†, solid particles of microcrystalline cellulose initially (0 ms) impact a 700 °C alumina surface before coming to rest. After one-tenth of a second, the particle is fully

Fig. 2 Bubble Collapse Simulation Design. **A.) Initial Conditions.** Computational domain and α field initial conditions (red: $\alpha = 1$, blue: $\alpha = 0$). For all simulations the bubble radius, $R_B = 15 \mu\text{m}$, and droplet radius, $R_{\text{drop}} = 113 \mu\text{m}$, with the bubble cavity initially resolved with 100 grid cells. **B.) Boundary Conditions.** Illustration of domain boundary conditions for all ejection computations. **C.) Mesh Resolution Test.** Simulated cavity collapse sequences using identical material properties with two different mesh resolutions. All but the smallest scale phenomena are fully resolved and mesh independent. $R_B = 15 \mu\text{m}$, $R_{\text{drop}} = 113 \mu\text{m}$, $\gamma = 5\text{e-}6 \text{ N/m}$, $\mu = 1\text{e-}5 \text{ kg/m}\cdot\text{s}$. Left Panel: 1 million cells. Right Panel: 1.25 million cells. The time duration between interface profiles is $750 \mu\text{s}$. Scale bar = $15 \mu\text{m}$.

Table 1 Simulation Boundary Conditions

Field	Condition A	Condition B
p	$\frac{\partial p}{\partial n} = 0$	$p = p_0$
$\mathbf{U}$	$\mathbf{u} = (0 \ 0 \ 0)$	$\frac{\partial \mathbf{u}}{\partial n} = 0$

molten as previously reported by the investigators and appears to 'wet' the surface forming a hemispherical droplet.¹⁹

Spontaneous ejection of an aerosol particle occurs at 107 ms and is visible as the trace of an ejected particle (108 ms) moving in a one millisecond increment of time. One millisecond later (109 ms), the ejected particle appears to slow considerably as

determined by the length of the particle trace. While the sizes of particles cannot be precisely determined directly from photography, the range of observed particle diameters must be greater than 0.3 microns, as limited by conventional light microscopy.³⁴ Also, the observed particles must be less than the width of particle streaks in the photographs ($<10 \mu\text{m}$). Finally, the molten droplet fully converts to gases, vapors, and aerosols leaving a clean surface (138 ms).

Molten cellulose continuously ejects aerosols. As depicted in Fig. 3B and Video S2†, a single droplet of cellulose degrading on a 700°C α -alumina surface ejects six independent particles, highlighted by arrows, over a period of seven milliseconds. Frames collected at 0 ms and 4 ms are presented in two formats to highlight the shape of the molten droplet and the path of the

Fig. 3 Aerosol Ejection from Molten Intermediate Cellulose. **(A)** A particle of microcrystalline cellulose (0 ms) thermally decomposes to molten intermediate cellulose on 700°C α -alumina (107 ms) and ejects liquid visible as a white streak (108–109 ms) travelling initially at 0.32 m/s. Subsequent evaporation completely vaporizes the molten droplet resulting in a clean surface (138 ms). **(B)** A droplet of molten intermediate cellulose on 700°C α -alumina exhibits multiple aerosol ejections highlighted with white arrows (first and third panel). Subtraction of serial frames in the second, fourth, and fifth frames indicates moving objects (white) relative to stationary background (black) and reveals movement of the droplet edge and ejected particles. Scale bars = $300 \mu\text{m}$.

ejected particles. The first and third panels are presented in greyscale, high-contrast format which reveals the highly reflective, white cellulose droplet. From these images, the lens depth of field is visible as the region 'in focus' extending from the back to the front of the particle. Particles are only visible with the photographic system and lighting scheme if their path traverses through the lens depth of field. Particles ejected towards and away from the camera are not detected.

The remaining three panels (0, 4, and 7 ms) of Fig. 3B are presented by differentiating between frames in series. By this technique, differences between sequential frames resulting from motion are indicated as white, while motionless objects which appear in repeated frames appear as black. Within these frames, multiple ejected aerosols are visible as white streaks. Additionally, the movement of the molten droplet resulting from aerosol ejection and evaporation of volatile organics is visible as a white line encircling the entire droplet. From this analysis, all of the ejected aerosols appear to exhibit initial velocities within the same order of magnitude. Also, many of the particles appear to exhibit curved trajectories.

3.2 Aerosol ejection velocity

Due to the extremely short time scale, small droplet size, and the opaque nature of cellulose, the mechanism resulting in the ejection of intermediate cellulose cannot be directly observed from droplets (Fig. 3). However, by measuring the distance traversed of a single ejected particle across a single frame, it is possible to determine the velocity of the ejected particle. Measurement of numerous ejection events from cellulose on high temperature surfaces leads to the distribution of velocities of observable ejected particles as shown in Fig. 4A. By this method, particles ejected from cellulose exhibit ejection velocities of 0.05–0.50 m/s.

Additionally, high speed photography of cellulose particles on high temperature (700 °C) α -alumina reveals the formation of gas bubbles within the intermediate liquid cellulose in the size range of 10–100 microns as observed in previous high speed videos.¹⁹

3.3 Ejected aerosol size distribution and composition

Aerosol particles generated directly from molten cellulose on a 700 °C alumina surface surrounded by inert nitrogen were quenched and collected on a glass slide shown in Fig. 5A. The collected particle dimensions were observed by light microscopy, and the size distribution indicates that the particle size range with the maximum number of particles is less than one micron which is consistent with existing literature.^{2–4}

The ejected aerosol particles transport nonvolatile chemical species from the pyrolyzing biopolymer. Collected, methylated aerosol particles (Fig. 5B, chromatograph i) contained levoglucosan as well as a single dominant carbohydrate dimer, cellobiosan (1,6-Anhydro- β -D-cellobiose), and almost negligible quantities of other carbohydrate dimer stereoisomers. The identity of cellobiosan within the aerosol sample was confirmed by comparison of retention times and mass spectrometry patterns with a pure cellobiosan sample that had undergone the same methylation procedure (chromatograph ii). The potential for the production of cellobiosan by dimerization of levoglucosan was examined experimentally by controlled pyrolysis of levoglucosan within an inert reaction chamber. Methylation and characterization of the levoglucosan reaction products over a temperature range of 100–500 °C indicates that levoglucosan polymerization produces carbohydrate dimers with nearly equal quantities of cellobiosan and maltosan (1 : 0.9). The observation of a single, dominant dimer exhibiting the β -glycosidic linkage existing in cellulose confirms that the observed cellobiosan

Fig. 4 Physical Properties of Molten Cellulose. **A.)** Droplets of molten intermediate cellulose exhibit ejection of aerosol particles in the range of 0.05–0.50 m/s. The relationship between ejection velocity and vapor bubble size (eqn [4]) varies with surface tension (solid lines). Comparison of observed ejection velocities with observed bubble sizes (grey box) indicates a molten cellulose surface tension of 10^{-6} to 10^{-5} N/m. **B.)** The viscosity of various oxygenated liquids including glucose, glycerol, ethylene glycol (EG), and water exhibits strong temperature dependence. Extrapolation to 750 °C using the Vogel-Fulcher-Tammann relation indicates that viscosity of oxygenated fluids approach 10^{-5} kg/m·sec.

resulted predominately from the decomposition of cellulose and was ejected as an aerosol particle. Therefore, nonvolatile cellobiosan was transported within the ejected particle and not created *via* condensation and reaction of evaporated species.

3.4 Mechanism observation

While bubble collapse and jet ejection cannot be directly observed within cellulose, a molten carbohydrate surrogate (β -D-Fructofuranosyl- α -D-glucopyranoside) was selected that exhibits a transparent molten state and produces pyrolysis products similar to cellulose (*e.g.* levoglucosan, furans, glycolaldehyde). As depicted in Fig. 6 and Video S3†, the carbohydrate surrogate melts to form a 500–800 μm diameter liquid droplet on 650 $^{\circ}\text{C}$ FeCrAlloy before decomposing to gases/vapors. FeCrAlloy was selected as the heating material for this specific experiment, because molten carbohydrates visibly de-wet thereby eliminating the role of the surface from the ejection mechanism.

Two independent ejection events are visible within 20 milliseconds which support the bubble collapse ejection mechanism. Diagrams are provided for each photographic frame highlighting the key ejection phenomena. Within the molten liquid droplet (0 ms), thermal degradation produces volatile organics and gases producing a gas bubble. One millisecond later (1 ms), the bubble bursts producing a depression on the surface of the liquid droplet and a liquid jet extending 500 μm from the liquid droplet.

A second event occurs later (16 ms, not shown) which forms a second vapor/gas bubble which grows to a diameter of 400 μm in diameter. The bubble rises and eventually rests (18 ms) beneath a thin layer of intermediate liquid near the upper right side of the droplet. Within one millisecond (19 ms), the surface tension maintaining the intermediate liquid is overcome by the vapor pressure within the bubble. The thin layer of liquid

ruptures and the gas bubble collapses forming a depression and liquid jet extending out of the molten liquid droplet. The subsequent frame (20 ms) visibly depicts the liquid droplet returned to the spherical conformation and the ejected aerosol particle moving with high velocity (0.35 m/s) as a streak through the frame.

3.5 Surface tension and viscosity estimation

The general mechanism of bubble disintegration, jet formation, and subsequent fragmentation leading to ejection permits estimation of the surface tension of molten cellulose by comparison of experimental ejection velocities with an energy balance. The initial state of a submerged bubble exhibits initial potential energy in the form of surface tension as, $E_i = \gamma A_B$, where γ is the surface tension and A_B is the surface area of the liquid/vapor-bubble interface. The final state of an ejected particle of mass, m , velocity, v , and surface area, A_{AP} , has a final energy, $E_f = \gamma A_{AP} + 0.5mv^2$. By assuming inviscid flow, these two energy states can be equated, providing an order of magnitude estimate of the surface tension, γ , as a function of the ejection velocity, the liquid density, ρ , the gas bubble size, R_B , and the size ratio, ϕ , as related by the Weber number in eqn ([4]),

$$We = \frac{\rho v^2 R_B}{\gamma} = \frac{3(1 - \phi^2)}{\phi^3} \quad (4)$$

By using a particle-to-bubble ratio of $R_{AP}/R_B = \phi = 0.20$ and a liquid density of $\rho = 1000 \text{ kg/m}^3$ †, ³⁵ (estimated by extrapolating to the predicted reaction temperature of 693–753 K^{36,37}), it is possible to relate bubble size to ejection velocity as a function of surface tension as depicted in Fig. 4A. Based on the observation that internal gas bubbles are 10–100 μm in size, and bounded by the observed domain of ejection velocities (grey

Fig. 5 Ejected Particle Characterization. **A.)** Ejected aerosols (inset photographs) exhibit a particle diameter (D_p) distribution with a maximum less than one micron. Scale bars = 10 μm . **B.)** Chemical analysis by methylation and gas-chromatography/mass-spectrometry of the collected aerosols (i) indicates that aerosols contain only one dominant carbohydrate dimer, cellobiosan, as shown in (ii). However, re-polymerization of levoglucosan (iii) is shown to produce nearly equal amounts of multiple different carbohydrate dimers. All chromatograms are scaled vertically for equal cellobiosan peak area between trials for comparison of relative dimer quantities.

Fig. 6 Molten Carbohydrate Ejection Mechanism. A non-wetting droplet of molten carbohydrate (β -D-fructofuranosyl- α -D-glucopyranoside) thermally decomposes on a 650 °C FeCrAlloy (Fe-Cr-Al-alloy) surface. Thermal decomposition nucleates a bubble of vapor products (0 ms) which subsequently collapses forming a liquid jet extending from the liquid droplet (1 ms). A second ejection event occurs through vapor bubble formation (18 ms), bubble collapse and jet formation (19 ms), and subsequent ejection (20 ms). Each panel is accompanied with a diagram indicating the key topological features. Scale bar = 800 μ m.

box), it is possible to estimate the surface tension of the liquid-cellulose/vapor interface as 10^{-6} to 10^{-5} N/m. This low range of surface tension is consistent with high temperature, boiling liquids near the critical point.²²

Viscosity of the high temperature, highly non-equilibrium intermediate cellulose liquid is unknown. To proceed, we estimated the liquid viscosity by extrapolation of known oxygenates and supported the resulting viscosity estimate with subsequent fluid simulations. As depicted in Fig. 4B, the viscosity of water, ethylene glycol (EG), glycerol, and sub-cooled glucose have been measured as a function of temperature.^{38,39} These molecules contain multiple hydroxyl groups consistent with anhydrosugars and anhydro-oligomers thought to comprise the intermediate cellulose liquid. Extrapolation of the measured viscosities to the considered reaction temperature of 750 °C indicates a dynamic viscosity of 10^{-5} kg/m $\cdot$ sec. Extrapolation was conducted using the Vogel-Fulcher-Tammann equation relating viscosity to temperature.^{40,41}

3.6 Ejection simulation

In this work, CFD simulations are used to corroborate the estimated surface tension, as well as the hypothesized droplet ejection mechanism. Simulation results, depicted in Fig. 7, support the proposed molten cellulose ejection mechanism and predicted fluid properties. A 3D revolved surface showing particle ejection ($\gamma = 5 \times 10^{-6}$ N/m) in Fig. 7A–B indicates that the bubble cavity collapses forming a liquid jet which is observed to fragment to liquid aerosol particles. Additionally, the jet is observed to extend from a liquid depression consistent with observations in Fig. 6 with the surrogate carbohydrate.

Simulated jet and particle velocities are in the range of 0.1–0.5 m/s in agreement with the experimentally observed ejection speeds (Fig. 4A). Surface tension values used in simulations ($5 \times 10^{-6} < \gamma < 1 \times 10^{-5}$ N/m) are within the range bound by the experimental observations and analytical deduction. The variation of material property values between simulations is outlined in Table 2. Without *a priori* adjustments, the simulation

accurately matched observed ejection velocities, giving strong support to the surface tension approximation.

The minor importance of viscosity is verified through the comparison of the results of simulation runs “2” and “3” as depicted in Fig. 7D. Here, an order of magnitude change in viscosity within the predicted viscosity range yields only a modest change in jet morphology and ejected droplet velocities after 375 μ s. Negligible loss of kinetic energy to viscous dissipation during bubble collapse and ejection affirms the secondary role of viscous forces.

To ensure adequate mesh resolution, an identical case is run on the standard grid (one million cells) and a second more resolved grid (1.25 million cells). As illustrated in Fig. 2, the one million cell mesh satisfactorily produces grid-independent results for all the large-scale features.

Table 2 Physical Properties of Simulation Runs

Case	μ (kg $\cdot$ m $^{-1}$ $\cdot$ s $^{-1}$)	γ (N $\cdot$ m $^{-1}$)	Figure	Video
1	1×10^{-5}	1×10^{-5}	Figure S13	S4
2	1×10^{-6}	5×10^{-6}	Fig. 8	S5
3	1×10^{-5}	5×10^{-6}	Figure S12	S6

3.7 Simulation mechanism

The simulated fluid collapse sequence illustrated in Fig. 7C depicts liquid film retraction and bubble collapse occurring within 375 μ s, leading to the formation of a fragmenting jet. The initial state, depicted earlier in Fig. 2, initializes the process just after the liquid film between the gas bubble and the external gas phase has ruptured. In the 75 μ s following perforation of the film (interface 1), the liquid begins to retract but retains very sharp features with extremely high curvature. Subsequent outlines depicting interface 2 (150 μ s) and interface 3 (225 μ s) indicate that the liquid rapidly retracts under the influence of surface tension.

After 300 μ s (interface 4) the bubble cavity begins to significantly collapse as fluid halfway between the top and bottom of

Fig. 7 Molten Carbohydrate Ejection Mechanism. **A.) Case 3:** Simulated bubble collapse and liquid jet formation depicting a revolved $\alpha = 0.5$ iso-surface at $t = 0.38$ ms colored by velocity magnitude ($R_B = 15 \mu\text{m}$, $R_{\text{drop}} = 113 \mu\text{m}$, $\gamma = 5 \times 10^{-6} \text{ N/m}$, $\mu = 10^{-5} \text{ kg/m}\cdot\text{s}$). **B.) Case 2:** Simulated bubble collapse and liquid jet formation depicting a revolved $\alpha = 0.5$ iso-surface at $t = 0.38$ ms colored by velocity magnitude ($R_B = 15 \mu\text{m}$, $R_{\text{drop}} = 113 \mu\text{m}$, $\gamma = 5 \times 10^{-6} \text{ N/m}$, $\mu = 10^{-6} \text{ kg/m}\cdot\text{s}$). **C.)** Simulated bubble collapse sequence. Liquid ejection occurs through the disintegration and collapse of a gas bubble and subsequent formation of a liquid jet protruding from a molten liquid depression. The duration between images is $75 \mu\text{s}$. Scale bar = $15 \mu\text{m}$. **D.)** Variation of viscosity by an order of magnitude ($\mu_1 = 10^{-6} \text{ kg/m}\cdot\text{s}$ and $\mu_2 = 10^{-5} \text{ kg/m}\cdot\text{s}$) with identical initial conditions and $\gamma = 5 \times 10^{-6} \text{ N/m}$ produces only modest changes in ejection morphology and ejecta velocity. Time = $375 \mu\text{s}$. Scale bar = $15 \mu\text{m}$.

the bubble gains radial momentum. Within the next $75 \mu\text{s}$, the bubble completely collapses focusing liquid momentum to a smaller quantity of fluid. During this span of $75 \mu\text{s}$, liquid coalescence occurs at a position above the bottom of the vapor cavity, thereby trapping small vapor bubbles within the liquid. Subsequent momentum focusing results in the formation of a liquid jet (interface 5, $375 \mu\text{s}$) which extends from the liquid depression and has fragmented to three liquid particles.

Continued extension of the liquid jet (interface 6, $450 \mu\text{s}$) slightly reduces the depth of the liquid depression. Additionally, the liquid jet has fragmented into a fourth liquid particle.

The effects of bubble-collapse on the entire liquid droplet are visible in Fig. 8, a simulation output depicting jet formation within a 270° revolved iso-surface colored by velocity magnitude. After $75 \mu\text{s}$, the potential energy within the highly curved liquid interface has translated to an increase in surface velocity

Fig. 8 Cellulose Ejection CFD Simulation. Simulated bubble collapse and liquid jet formation depicting a 270° revolved $\alpha = 0.5$ iso-surface colored by velocity magnitude ($R_B = 15 \mu\text{m}$, $R_{\text{drop}} = 113 \mu\text{m}$, $\gamma = 5 \cdot 10^{-6} \text{ N/m}$, $\mu = 10^{-6} \text{ kg/m}^2\text{s}$).

primarily at the top of the liquid droplet. As time progresses the velocity of the liquid/gas interface increases at deeper positions within the bubble cavity. After 264 μs , the cavity coalesces and the interfacial velocity achieves almost 0.5 m/s depicted as an aqua-blue surface. At this time, the liquid jet forms and a new gas bubble is entrained within the large liquid droplet. After

coalescence, the liquid jet continues to increase in length and fragment to produce aerosol particles (279 μs). Subsequent jet growth includes the fragmentation of several new aerosol particles. However, aerosol particles observed from initial fragmentation of the jet are observed to slow and recombine to form larger aerosol particles (35 μs).

Fig. 9 Molten Cellulose Ejection - Simulation Vorticity. Vorticity magnitude iso-lines (colored black) of simulation case #1 before (panel A: $t = 220 \mu\text{s}$) and during (panel B: $t = 250 \mu\text{s}$) ejection. Each figure shows ten iso-lines uniformly spanning $0\text{--}10,000 \text{ s}^{-1}$. The inset figures show the scope of magnification with the gas/liquid interface colored red.

Bubble collapse and jet fragmentation are observed to generate a second liquid jet extending downward into the liquid droplet. As depicted in Fig. 9, vorticity iso-lines indicate significant fluid circulation directly below the vapor cavity during (0.220 ms , frame A) and after (0.250 ms , frame B) collapse. After cavity collapse (Fig. 9B), the liquid jet extends from the surface and gas bubbles are entrained within the liquid. Relative to the size of the drop, this circulation zone is mainly localized around the cavity site. In general, even though vorticity is localized, pressure effects could potentially extend further from the jet. However, in this case, the presence of the gas-liquid interface constrains pressure. Away from the jet the surface curvature of the droplet is nearly uniform, indicating a nearly uniform pressure on the liquid side of the interface, as required by the balance of normal forces. Hence, neither vorticity nor pressure effects due to the jetting extend very far. This observation suggests that multiple jets emanating from a single droplet would not interfere with each other unless they were located close together.

The kinetic energy of the downward jet is comparable to the kinetic energy of the ejected aerosol. Integration of the kinetic energy throughout the entire liquid droplet relative to the kinetic energy of the ejected aerosols post-ejection indicates that both kinetic energies are about the same. Fluid motion throughout the droplet is distributed around the region of cavity collapse, but the liquid motion is considerably slower than the aerosol ejection velocity. This conclusion supports the adequacy of eqn ([4]), which relies on the measurement of aerosol kinetic energy, to estimate the surface tension of the intermediate liquid cellulose within an order of magnitude.

4.0 Discussion

The entire process of generating an aerosol particle from solid cellulosic biomass by reactive boiling ejection requires thermal decomposition to a liquid intermediate, nucleation and growth of vapor bubbles, and eventual bubble rupture and collapse followed by jet formation and fragmentation to aerosols. This entire sequence of events occurs extremely quickly ($<400 \mu\text{s}$), within a very high temperature system ($>400 \text{ }^\circ\text{C}$), and at very small length scales ($10^0\text{--}10^1 \mu\text{m}$).

4.1 Stage I. Intermediate cellulose liquid formation

The ejection process is enabled by the formation of an intermediate liquid from cellulose. Conclusive evidence for the existence of this intermediate liquid state has previously been identified as the key problem for understanding and predicting the thermochemical conversion of cellulose.⁴² An intermediate liquid was hypothesized to exist when pyrolyzing biomass was observed to behave like meltable solids on high temperature, moving surfaces.²⁰ Subsequent experiments reported that rapid heating and cooling produced solid cellulose products with smooth surfaces indicative of a liquid intermediate.²¹ Recently, the liquid intermediate was confirmed to exist by high speed photography¹⁹ as a short-lived intermediate that exhibits violent boiling and evaporation. This evidence is consistent with several cellulose decomposition chemical kinetic mechanisms which include an 'active cellulose' intermediate to describe pyrolysis product formation.^{43–46}

The composition of the intermediate liquid phase is unknown. A common hypothesis states that cellulose with initial chain lengths exceeding 1000 glucan monomers initially undergoes glycosidic cleavage and depolymerisation to shorter chain polymers capable of melting to a liquid.¹³ This was supported by experiments that characterized the solid residue remaining from very short residence time flash pyrolysis of pure cellulose and observed a series of anhydro-oligomers that were two-to-seven units long.⁴⁷ These results were supported by independent experiments which exposed cellulose to brief flashes of radiant heat. After characterization of the products, the authors concluded that the intermediate liquid is comprised of anhydro-oligomers,⁴ as illustrated by the first three anhydro-oligomers in Fig. 10.

4.2 Stage II. Vapor bubble nucleation and growth

The process of bubble nucleation and growth initiates a stage of potential energy generation proportional to the surface area of the vapor bubble. While the origin of vapor bubbles cannot be identified from the present experiments, at least three potential nucleation options exist: (i) homogeneous nucleation, (ii) heterogeneous nucleation, and (iii) vapor bubble entrainment.

The thermodynamic driving force for nucleation is the increased vapor pressure of evolving pyrolysis products. As pyrolysis of the nonvolatile original cellulose polymer proceeds, smaller chemical compounds are produced by reaction within the intermediate liquid which exhibit increasing volatility. The identified products of pyrolysis are primarily volatile and include a range of molecular sizes from C_1 (e.g. CO, CO_2), C_2 (e.g. glycolaldehyde), C_3 (e.g. acetone), to C_6 (levoglucosan).⁸ Anhydrosugars have been shown to exhibit vapor pressures several orders of magnitude greater than sugars, and are likely evaporated as pyrolysis products directly from the intermediate liquid.⁴⁸

Homogeneous nucleation can occur throughout the intermediate liquid.^{49,50} Alternatively, cellulose particle pyrolysis on high temperature surfaces and within fluidized reactors occurs within a thermally thick particle.⁵¹ Therefore, conversion of solid cellulose to the liquid intermediate occurs as a reacting wave through the particle.^{52,53} The presence of a solid/liquid interface introduces the potential for continuous heterogeneous nucleation of vapor bubbles within pyrolyzing biomass particles.

An alternative bubble generation process occurs through vapor entrainment during bubble collapse. As depicted in Fig. 8, the vapor cavity resulting from bursting bubbles collapses inward and can lead to several entrained gas bubbles. Coalescence near the bottom of the cavity entrains a pocket of vapor which remains within the fluid near the base of the jet. These results are consistent with the previous discovery of bubble entrainment within vapor cavities.²⁶ This observation indicates that a single ejection event can lead to the initiation of one or more subsequent ejection events, depending on the number of entrained vapor bubbles. This indicates that once the process of ejection is initiated, it can potentially continue independently of gas nucleation.

Once formed, gas bubbles grow and rise subject to buoyancy forces within the molten cellulose liquid until they reach the liquid droplet/gas interface. Bubble growth is observed within the carbohydrate surrogate (Fig. 6 and Video S3†). Additionally,

bubbles can coalesce with other bubbles or fragment to separate, smaller bubbles.

The size of the vapor bubble prior to rupturing is important, because it determines the quantity of interfacial surface area and potential energy of the system. Vapor bubble size is ultimately determined by the relationship between vapor generation (reaction) and the time required for the bubble to approach the droplet interface. Bubbles approaching the free surface require the draining of the film and thinning of the liquid interface.⁵⁴ Experimental measurement of film thickness during thinning has indicated that the rate of thinning increases with decreasing film viscosity.⁵⁵ Fluid modelling of film drainage using the lubrication approximation also indicates increased thinning rate as the density difference between the liquid and vapor phases increases, as the interfacial surface tension decreases, and as the vapor bubble diameter decreases.^{56,57} Additionally, the velocity of the bubble approaching the free surface has been observed to alter the time required for film thinning.⁵⁸

The resulting liquid film separating the bubble at the free surface from the external atmosphere can achieve very thin liquid film thicknesses. This thin liquid film is visible in the surrogate carbohydrate in Fig. 6 (18 ms). A critical thickness of the liquid film identifies the unstable conditions whereby perturbations within the film result in a sufficiently large hole which subsequently expands due to surface tension and ruptures the film.⁵⁹ Instability is thought to occur when the film has achieved thicknesses less than 100 nm, at which point London-van der Waals forces acting over a very short range are able to pull the two sides of the film together and initiate film rupture.^{26,54,56,60}

4.3 Stage III. Bubble rupture, collapse and jet fragmentation

Rupture of the thin liquid film initiates the collapse mechanism converting the potential surface energy within the gas bubble to liquid momentum within aerosol particles. The specific

Fig. 10 Pathways Determining the Composition of Primary and Secondary Aerosols. The intermediate chemical species within liquid (L) molten cellulose are transported to the gas phase (V) through evaporation and aerosol ejection. Primary liquid aerosols are produced by the ejection of aerosols directly from molten cellulose, and they are comprised of the thermal degradation products of cellulose including cellobiosan (1,4-beta linkage). Secondary liquid aerosols form from the evaporation of levoglucosan and volatile organics. Subsequent nucleation generates a secondary liquid aerosol wherein levoglucosan can dimerize to form both alpha and beta glucosidic linkages between the C_1, C_2, C_3 , and C_4 carbons.

mechanism for liquid jet and aerosol particle generation has been extensively studied for numerous applications.^{61–63} After the liquid film is perforated, it has been shown to retract forming an expanding toroidal rim^{63,64} similar to that observed in Fig. 8 (150 μ s). As retraction occurs, gases flow out from within the vapor cavity resulting from the difference between the vapor pressure and the environmental gas pressure.

The retracting rim of the liquid film potentially breaks up into tiny droplets referred to as ‘film droplets’.^{65,66} These small droplets are ejected in multiple directions resulting from the radial momentum of the film during retraction and the upward flow of gas escaping the vapor cavity. The mechanism of film droplet generation occurs through asynchronous breakup resulting from surface tension and film thickness variations in addition to turbulence from air escaping from the cavity.⁶³ Fragmentation is not thought to occur by capillary ripples, which propagate too slowly relative to the rate of film retraction.^{54,64}

Film droplets and their mechanism of production are not observed with the present high speed photography technique which would be incapable of observing these small particles at short timescales. Additionally, the contribution of film drops to the production of cellulose-based aerosols is unknown. However, it has been shown that the number of film drops produced increases linearly with surface area of the liquid film,^{67,68} thereby indicating that their relative importance decreases with decreasing vapor bubble size.

The cavity collapse predicted by our simulation for molten cellulose is consistent with existing literature describing collapse driven by the surface tension of the free interface. A time sequence diagram of a collapsing bubble at 6000 frames/s obtained from high speed photography of a bursting bubble reveals the transition from vapor cavity to depression and liquid jet.⁶⁹ The liquid protrusion at the top of the vapor cavity produced from the retracting film appears to grow in size and move downward into the cavity. Ahead of the protrusion, capillary waves are observed along the vapor cavity wall.^{69,70}

The resulting liquid jets observed in our work are consistent with known jet formation mechanisms. Cavity collapse has been shown repeatedly to form two liquid jets.^{71–73} One liquid jet extends downward into the bulk liquid forming a vortex ring made visible within experiment using a liquid dye.⁶⁹ This is consistent with fluid simulations which predict regions of increased vorticity within the liquid directly below the collapsed vapor cavity.^{26,54,74} For comparison, our system (Fig. 9) exhibits a similar downward flowing liquid jet observable as vorticity isolines surrounding entrained vapor bubbles.

The other more visible liquid jet extends upward from the liquid cavity and is surrounded by a distinctive vapor depression. This liquid jet is observed twice in our experiments from separate ejection events from the surrogate carbohydrate in Fig. 6 (1 ms and 19 ms).

The upward flowing jet extends from the free surface and potentially fragments to produce aerosols travelling at high velocity relative to the surrounding fluids. Extension of the jet above the original liquid level results in one of two potential outcomes. For initial vapor bubbles above a critical size, the jet is produced and subsequently retracts without releasing a jet drop.⁶² The critical bubble size for each liquid/vapor combination has been identified for numerous systems.^{62,75,76} However,

a systematic method for predicting the critical vapor bubble size remains to be developed. Alternatively, below the critical vapor bubble size, jets are observed to breakup due to surface tension producing one or more liquid aerosol particles.⁶²

Jet fragmentation is known to produce one or more aerosol particles as demonstrated in the fluid simulation of Fig. 8. Hydrodynamic instability of the liquid jet results from the reduction in surface area from the formation spherical droplets. Fragmentation is induced through the growth of sinusoidal perturbations in the jet radius which exhibit wavelengths in excess of the jet radius.⁷⁷ This is consistent with Fig. 7 and 8 and Videos S4–S6† which depict capillary waves and liquid jet fragmentation into several droplets.

The number and size of droplets produced from fragmenting jets resulting from bubble collapse is highly variable and dependent on the properties of the fluid. Numerous experimental sources report a size ratio, ϕ , of the aerosol particle radius, R_{AP} , to the bubble radius, R_B , as $0.1 < R_{AP}/R_B = \phi < 0.3$.^{62,78,79} This range of aerosol-particle-to-bubble ratios is consistent with our experimental measurements of aerosol particles in Fig. 5 which exhibit particles smaller than 10 μ m, while vapor bubbles are observed in size up to 100 μ m. The size distribution of multiple aerosol particles from a single droplet has been shown to vary minimally from the first to last ejection.⁷⁹ The range of size-ratios and variation in consecutive aerosol particle generation is consistent with the fluid simulations in Fig. 7 and 8.

4.4 Physical properties of molten cellulose

The method of surface tension estimation (Fig. 4A) based on an energy balance (eqn ([4])) between stationary bubbles and high velocity aerosols has basis in previous bubble collapse ejection simulations which develop criteria for inviscid flow. Jet velocity (measured when the jet reaches the original liquid interface level) has been shown to be predictable for large dimensionless bubble radii defined as the $(R_B/R_V) = \gamma R_B \rho / \mu^2$, where R_B is the radius of the vapor bubble, R_V is the viscous capillary length, and μ and ρ are the viscosity and density of the liquid, respectively.²⁶ Above $(R_B/R_V = 10^3)$, jet velocity is in agreement with the inviscid scaling relationship, and the dimensionless jet velocity $(V\mu/\rho)$ is predictable as: $(V\mu/\rho) = C^*(R_B/R_V)^{-0.5}$, where C is a constant. For these conditions, the energy balance assumes that viscous dissipation is negligible, and all of the potential energy of the vapor bubble is converted to the surface energy of the aerosol and the kinetic energy of the ejected aerosol and droplet. While the kinetic energy within the droplet after bubble collapse cannot be measured by experiment, simulation of the ejection phenomenon estimates that the droplet kinetic energy is about the same as the ejected aerosol kinetic energy. Therefore, this method (eqn ([4])) can sufficiently predict surface tension correctly within an order of magnitude as depicted in Fig. 4.

Confirmation of the surface tension range of approximately 10^{-6} – 10^{-5} N/m of intermediate liquid cellulose by simulation also affirms the secondary role of viscous forces by dimensional analysis. The low surface tension exhibits a viscous capillary length, defined as $R_V = \mu^2/\rho\gamma$, in the range of 10^{-2} – 10^{-1} microns with the viscosity, $\mu = 10^{-5}$ kg/m·s. Since the observed internal vapor bubbles (10^1 – 10^2 μ m) are several orders of magnitude greater than the viscous capillary length ($R_B \gg R_V$), viscous

effects are expected to be of secondary importance. This also supports the assumption of negligible viscous dissipation in the derivation in eqn ([4]), and permits simple prediction based on surface tension of ejection velocities and particle quantities from natural materials. Additionally, calculation of the Ohnesorge number of the vapor bubble collapse mechanism indicates the minimal effect of viscous forces. Defined as $Oh = \mu/(\rho\gamma L)^{0.5}$, the Ohnesorge number for vapor bubbles of radius $L = 18 \mu\text{m}$ and liquid density $\rho = 1000 \text{ kg/m}^3$, exhibits a range of $2 \times 10^{-3} < Oh < 8 \times 10^{-2}$ for the surface tension range $10^{-6} < \gamma < 10^{-5} \text{ N/m}$ and viscosity range $10^{-6} < \mu < 10^{-5} \text{ kg/m}\cdot\text{s}$.

The estimated surface tension range of approximately 10^{-6} – 10^{-5} N/m used in simulations of intermediate liquid cellulose is also consistent with existing theory and relationships between surface tension, gravitational forces and temperature. In this range, the capillary length can be calculated as $a = (\gamma/\rho g)^{1/2}$ which predicts $10 < a < 30 \mu\text{m}$. This is consistent with the liquid intermediate cellulose droplets depicted in Fig. 3A–B which exhibit significant sagging due to gravity. The radius of curvature is significantly reduced at the edges of the liquid droplet in comparison to the top. Additionally, the low surface tension is consistent with existing theory that predicts significant reduction of surface tension as the temperature of the liquids approaches the critical point.²²

4.5 Transport of nonvolatile material within aerosols

A key result of the reactive boiling ejection mechanism is its ability to transport nonvolatile material from solid biomass such as cellulose to the gas phase. As depicted in Fig. 5, aerosols ejected from the molten state contain only one dominant carbohydrate dimer (cellobiosan). As depicted in Fig. 10, this supports the hypothesis that cellulose decomposes primarily through glycosidic cleavage to anhydro-oligomers.⁴⁷ Therefore, fluid ejected from the molten state should only contain a single linkage type (β -1,4) in the form of cellobiosan. This is in agreement with Radlein *et al.*⁴ which demonstrated that anhydro-dissaccharides within bio-oils must result from primary pyrolysis, but the mechanism of transport of cellobiosan to the vapor phase was unknown.

Alternatively, anhydro-disaccharides and larger anhydro-oligomers can form within liquid products through evaporation and secondary polymerization as depicted in Fig. 10. Levoglucosan exhibits sufficiently high vapor pressure relative to glucose, carbohydrate dimers, and larger carbohydrate polymers that it significantly evaporates during pyrolysis.⁴⁸ Once evaporated, levoglucosan (and other vapors) can condense to a secondary liquid (bio-oils and secondary aerosols) wherein they can re-polymerize. Nucleophilic attack of one of three levoglucosan hydroxyl groups on C_1 of a second molecule of levoglucosan by two potential orientations produces at least six potential isomers of anhydro-dimers. Some of these dimers, including maltosan (α -1,4) and cellobiosan (β -1,4) were observed by polymerization of the pure levoglucosan sample (Fig. 5B). For a wide range of temperatures (235–400 °C), nearly a one-to-one ratio (1 : 0.9) of cellobiosan-to-maltosan was observed indicating that these two stereoisomers are formed at about the same rate. This is inconsistent with the composition of measured aerosols, and the absence of a strong maltosan peak in the aerosol chromatogram

supports the conclusion that nonvolatile cellobiosan originated from the molten liquid.

4.6 Implications and future directions

While cellulose and carbohydrates visibly exhibit particle ejections, there is interest in the ejection phenomenon in lignocellulosic materials such as trees and grasses which contain inorganic species and a significant amount of lignin. Lignocellulosic materials are predicted to exhibit an intermediate liquid phase.^{20,36} Additionally, high speed photography of hardwood lignin samples on 700 °C α -alumina (Fig. 11 and Video S7†) clearly exhibits decomposition of lignin through an intermediate liquid with bursting bubbles. However, the intermediate lignin liquid and significant char product exhibit high light absorptivity, preventing the observation of ejected particles with the current high speed photography experimental setup.

Reactive boiling ejection is a mechanism by which a distinct class of products, nonvolatile organic compounds (*e.g.* tars) or potentially entrained inorganic material (*e.g.* SiO_2), can be transported from solid biomass to the gas phase. This phenomenon explains at a more fundamental level the release of inorganic particulate into the atmosphere from forest fires, the emission of heavy tars from cigarette smoke, and the production of heavy sludge observed in bio-oils. Future experiments and fluid modeling will attempt to understand the effect of variable biomass intermediate liquid properties on the generation of film/jet particles and identify the critical bubble radius whereby particle ejection is suppressed.⁶² This knowledge will address the relative importance of the reactive boiling ejection mechanism to known aerosol formation mechanisms including gas phase nucleation shown to produce secondary aerosol particles from biomass. A more complete understanding and predictive capability of these phenomena will potentially lead to reduced aerosol generation, decreased transport of nonvolatile material, and higher quality product streams from high temperature biomass reactions.

Fig. 11 Molten Lignin Bubble Generation and Collapse. Molten lignin on 700 °C alumina decomposes through a bubbling intermediate liquid before reacting to form secondary solid char. Numerous white specular highlights indicate a smooth liquid surface surrounding each gas bubble, which are observed to burst in Video S7†. Frame width = 2.0 mm.

5.0 Conclusions

Cellulose spontaneously ejects primary liquid aerosol particles during thermal decomposition, as observed by high speed photography and confirmed by computational fluid dynamics. A single molten cellulose droplet continuously ejects multiple aerosols indicating that the ejection event is not a unique, singular phenomenon during cellulose pyrolysis. Sampling and characterization of the ejected aerosols reveals a significant quantity of the nonvolatile anhydro-dimer, cellobiosan, indicating that primary, ejected aerosols are capable of transporting nonvolatile material from cellulose to the gas phase. Measurement of the aerosol ejection velocity distribution and comparison with a simple energy balance estimates the surface tension of the intermediate cellulose liquid in the range of $10^{-6} < \gamma < 10^{-5}$ N/m.

The mechanism of reactive boiling ejection was determined to occur through three stages. During the initial stage solid cellulose thermally degrades to a molten intermediate liquid. In the second stage, vapor bubbles nucleate within the molten liquid and rise to the liquid/gas interface. Finally, the liquid film separating vapor bubble and external gas atmosphere ruptures. Subsequent film retraction and vapor cavity collapse produces a liquid jet protruding from a vapor depression. The extending liquid jet fragments producing liquid aerosol particles moving with high velocity (0.1–0.5 m/s). The bubble collapse mechanism was supported by agreement of experimental observation of ejection velocity with fluid simulation utilizing the estimated cellulose liquid properties.

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