Microexplosions in the Upgrading of Biomass-Derived Pyrolysis Oils and the Effects of Simple Fuel Processing

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S Supporting Information

ABSTRACT: The development of biofuels produced from biomass-derived pyrolysis oils (bio-oil) requires a deeper understanding of the bio-oil vaporization required for catalytic hydrodeoxygenation, reforming and combustion processes. Through the use of high-speed photography, bio-oil droplets on a 500 °C alumina disk in nitrogen gas were observed to undergo violent microexplosions capable of rapidly dispersing the fuel. High speed photography of the entire droplet lifetime was used to determine explosion times, frequency and evaporation rates of the bio-oil samples that have been preprocessed by filtering or addition of methanol. Filtration of the oil prior to evaporation significantly reduced the fraction of droplets that explode from 50% to below 5%. Addition of methanol to bio-oil led to uniform vaporization while also increasing the fraction of droplets that exploded. Experiments support the necessity of dissolvable solids for the formation of a volatile core and heavy shell which ruptures and rapidly expands to produce a violent bio-oil microexplosion.

KEYWORDS: Pyrolysis, Bio-oil, Biofuels, Evaporation, Combustion, Fuel additives
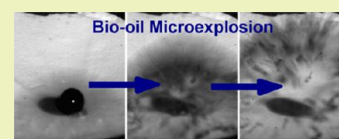
INTRODUCTION

Biomass is widely considered to be the only renewable source for the sustainable generation of liquid fuels.[1−4] Processes such as pyrolysis, liquefaction, and subsequent upgrading have led to a new class of biomass-based liquid fuels called bio-oils (pyrolysis oils).[2,5,6] Bio-oils are composed of hundreds of chemical species containing numerous functional groups including aromatics, carboxylic acids, phenols, furfurals, anhydrosugars, and alcohols.[7−9] Researchers are currently examining upgrading technologies such as hydrodeoxygenation,[10] catalytic reforming,[11,12] and cracking[1,13−15] of these highly oxidized fuels with the goal of making bio-oil a viable source for traditional fuel applications, including internal combustion, diesel, and jet engines.

Bio-oils generally perform poorly when utilized for combustion. Sandia National Laboratories performed a bio-oil study to determine the potential for using lignocellulosic derived bio-oils as combustion fuels.[16] In pilot diesel engines, bio-oils demonstrated poor combustion characteristics including high CO and particulate emissions as well as poor ignition properties. These problems were attributed to late-time gas-phase secondary pyrolysis of heavy vapors that lead to incomplete fuel combustion.[17]

An important, but not yet fully understood, phenomenon observed in numerous bio-oil combustion experiments was microexplosions, whereby droplets of bio-oil slowly combust before undergoing a violent and destructive explosion. Microexplosions are beneficial to fuel combustion because they act as a means of secondary droplet atomization, thereby increasing fuel droplet surface area and promoting evaporation. Many studies have attempted to induce microexplosions in conventional fuels by the addition of water or methanol for this purpose.[18−21] In instances where microexplosions occur, char formation significantly hinders the benefits from secondary atomization and fuel utilization.[19]

Though the mechanics of microexplosions are understood for relatively simple nonreactive binary mixtures of varying volatility, the phenomenon is greatly complicated in bio-oil by the diverse and highly reactive chemical composition. Mixtures and emulsions of binary and multicomponent fuels have demonstrated microexplosions occurring with components that include alkanes, alcohols, ethers, water, heavy fuels, and pyrolysis oils.[17,18,22] In these simple fuel mixtures, high heating rates and poor mass transfer leads to the formation of a volatile core and low volatility shell with limited mass transfer capability. The outer shell is thought to lead to superheating of the core that results in subsequent flashing to a vapor, observed as a microexplosion.[23] The bio-oil case is complicated

by the presence of reacting chemical species and wide range of species volatility. At room temperature, vapor pressures of bio-oil components are known to vary over 10 orders of magnitude.[24] Additives to pyrolysis oils have been considered to stabilize the fuel for storage and decrease the viscosity for optimal combustion properties. Light alcohols and ketones are specifically identified as cost-effective additives to bio-oils.[15,25] Methanol was identified as an ideal additive because it halves the viscosity and drastically reduces storage-related aging.[15,25,26] Little is known, however, about how methanol affects bio-oil combustion, particularly with respect to the explosion behavior.

Because of the complex chemical composition and functionality of bio-oil, droplets of traditional petroleum fuels and bio-oil evaporate differently. A conventional fuel droplet such as the diesel fraction, No. 2 fuel, evaporating in a motionless atmosphere evaporates at a rate proportional to the square of the diameter. This relationship is commonly referred to as the d^2-law,[16] which utilizes the evaporation proportionality rate constant, K_v.

$$d^2 = d_0^2 + K_v t \tag{1}$$

Several sources have claimed, based on experiments and computational modeling, that bio-oils obey the d^2-law.[17,27,28] However, others claim that a combination of the gradient in composition volatility and the complex and dynamic reactivity of bio-oil will make its evaporation behavior diverge from the d^2-law.[29−31] In general, bio-oil has been calculated to evaporate at rates substantially lower than traditional fuels ($K_{v,\text{bio-oil}}$ = 0.19−0.25 mm²/s, and $K_{v,\text{No.2}}$ = 0.56,[16]), due to the high water content of bio-oil (up to 50%[9]).

Unlike traditional fuels, pyrolysis oils are highly reactive and have the ability to undergo one of three processes upon heating: (1) evaporation of light components, (2) pyrolysis to volatile species, and (3) polymerization to heavier compounds. Experimentally, exhaust streams have been characterized as having soot, large glassy solid residuals, and hollow ceno-spheres. Cenospheres are hollow glassy spheres that are often found in solid combustion residue, resulting from the incomplete combustion of fuel droplets.[32] The soot derives from secondary pyrolysis of gas-phase species and visibly forms at late droplet residence times when the heavy volatile fraction evaporates.[17] When mass transfer limitations exist within the droplet, liquid-phase pyrolysis dominates and cenospheres are formed.[17,33] The remaining solid residuals, however, contain dense glassy solids that are still highly oxygenated and readily dissolve in methanol, indicating that they are likely the result of uncombusted fuel that has polymerized.

Bio-oils are also known to contain suspended solid char particles as well as dissolved and undissolved polymers. Natural biopolymers can exist in the oil from aerosols generated during fast pyrolysis,[34] or they can form from secondary polymer-ization of the condensed oil due to aging.[26] These char particles and inorganic solids can remain in the bio-oil during utilization and are thought to affect the chemistry by providing nucleation sites that assist in evaporation or further polymerization.[31]

In this work, we directly observe the presence of micro-explosions in biomass-derived pyrolysis oils using high-speed photography and describe the sequence of events leading up to the explosion. We also examine the effects of methanol addition on the frequency and timing of microexplosions. The role of separable polymers on the microexplosion mechanism was elucidated by removal of dissolvable solids. We show that simple fuel processing can dramatically tune the evaporation

properties to promote or nearly eliminate microexplosions upon heating bio-oil.

■ MATERIALS AND METHODS

Bio-oil was obtained from the U.S. National Renewable Energy Laboratory (NREL) and was produced from the fast pyrolysis of pine in a bubbling fluidized bed reactor at 500 °C.[35] The oil was characterized before use, and its properties are summarized in Table 1.

Table 1. Characterization and Properties of Pine-Derived Bio-Oil

elemental[a], (dry), wt %	
C	37.2
H	8.0
O	52.6
N	<0.5%
water, wt %[b]	38.6
ash, wt %	0.32
filterable polymers[c], wt %	1.6
insoluble solids[c], wt %	0.6
pH	2.6

[a]Analysis performed by Galbraith Laboratories. [b]Karl Fischer water analysis, Galbraith Laboratories. [c]Solid analysis was done by 0.45 μm filtration followed by fractionation with THF.

Filtered samples were passed through a 0.45 μm syringe filter, removing a fraction of solids (2.2 wt %). The solid fraction was then fractionated into polymer (dissolves in THF,[36] 1.6 wt %) and insoluble solids (does not dissolve in THF, 0.6 wt %) fractions. Gel permeation chromatography (GPC) suggests that the soluble solids fraction has an average molecular weight of 1000 Da, nearly an order of magnitude larger than observed in the filtered bio-oil (Figure S1.1, Supporting Information). Dilutions were made on a mass basis in 25% increments ranging from pure bio-oil (0%) to filtered bio-oil (100%) by micropipetting exact volumes of the two constituents and vigorously shaking.

Charcoal addition samples were prepared by blending activated charcoal into bio-oil in known mass fractions. The activated charcoal (Sigma Aldrich #05120 Fluka), has a known particle size distribution with 75% of the particles less than 40 μm in diameter. Samples were blended in concentrations of 0.5, 1, 2, and 4 wt % charcoal.

Methanol/bio-oil dilutions were also prepared on a mass basis. Methanol and bio-oil were pipetted and mixed in ratios ranging from pure bio-oil (0%) to pure methanol (100%) in increments of 25 wt %.

Experimental methods were developed to assess the explosion frequency, droplet lifetime, and evaporation rate. The sequence of droplet evaporation events was qualitatively assessed directly from photographs. All methods examined the evaporation of a bio-oil droplet on a 2 cm pressed γ-alumina disc calcined at 1100 °C. The experimental system consisted of a pressed disk seated on a copper surface and heated by three cartridge heaters vertically mounted in a copper heating block of 2.4 cm diameter. Temperature was monitored with a thermocouple resting directly on the alumina surface prior to use and controlled by a variable voltage power supply to maintain constant temperature. Nitrogen was continuously purging parallel to the surface to maintain an oxygen-free environment. Experimental flow rates were maintained between
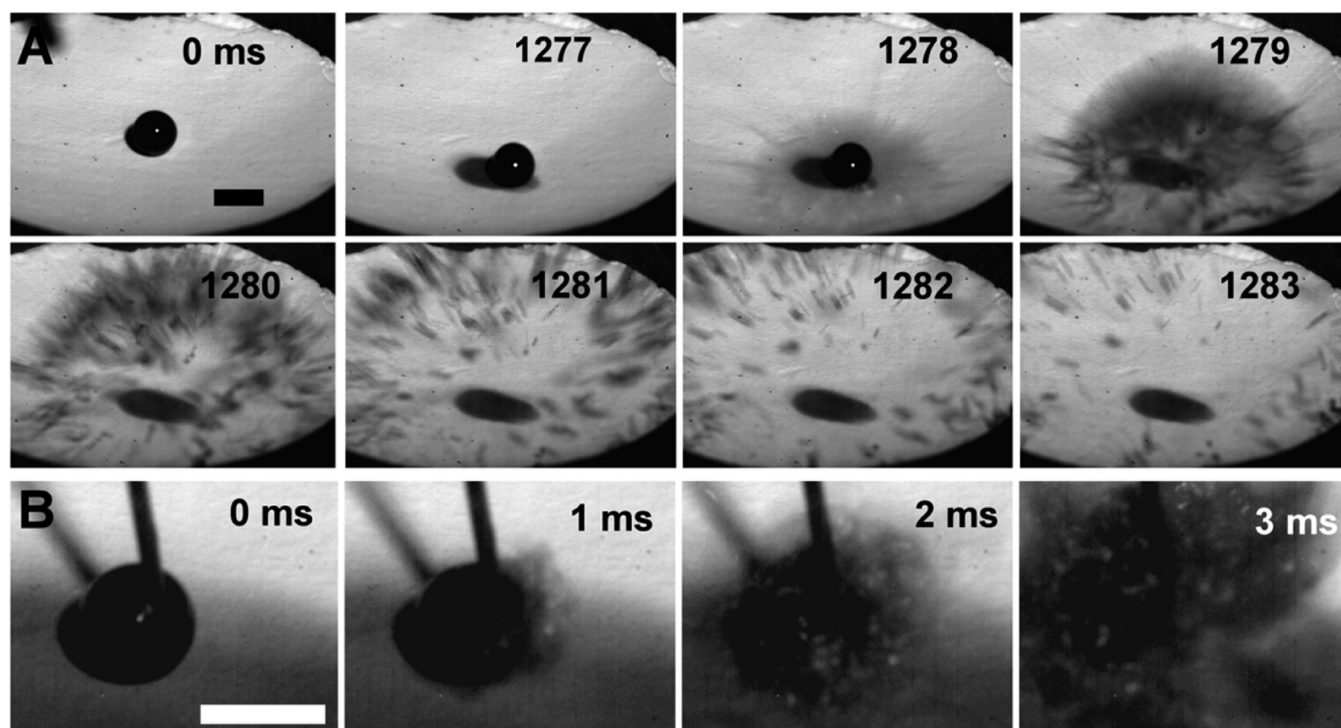
Figure 1. High speed photography of bio-oil microexplosions. (A) Droplet of bio-oil evaporates on a 500 °C alumina surface. Microexplosion (1278−1279 ms) violently disperses the bio-oil over several milliseconds. (B) Late time (1273 ms) of a droplet is probed with a rod resulting in an instantaneous microexplosion. Scale bars = 1000 μm.

0.3 and 0.5 SLPM, which typically convectively cooled the surface by approximately 30 °C. Further information and an experimental schematic are available in the Supporting Information.

Bio-oil droplets were formed by dispensing 5 μL from a 50 μL Acura 825 micropipet approximately 1 cm above the surface. Stopwatch trials measured either the time required for the droplet to completely evaporate or the time until a microexplosion event occurred. Additionally, explosion frequency was assessed by comparing the ratio of exploding droplets to those that evaporate without exploding. In timed and frequency trials, all data sets were collected with at least 50 runs to ensure statistical relevance, and 95% confidence intervals are reported. Statistical data are represented in Figure S1.3 of the Supporting Information.

High speed photography was used to assess evaporation rates and qualitatively describe the microexplosion phenomenon. Images were captured using a Photron Fastcam Ultima APX Imager. Auxiliary lighting was supplied by a Solarc LB150 lamp. Images were recorded at 1000 fps, and image brightness and contrast adjustments were applied uniformly across all frames using the NIH program, ImageJ.[37] For the d^2-law analysis, droplet size was assessed in consecutive frames (15 fps) by manually fitting ellipses to the droplet periphery using ImageJ.

RESULTS

Droplets of pure bio-oil were directly observed by high speed photography as they pyrolyzed and vaporized on a heated alumina surface (Figure 1A, and videos V1, V3, and V4 of the Supporting Information). After an initial heating stage, the droplets underwent a motionless evaporation phase where the square of the diameter decreased linearly in accordance with the d^2-law, followed by a brief period of vibration directly preceding an explosion event. Figure 1A shows the final frames of a microexplosion where the droplet had no visible expansion and spontaneously ruptured, creating an explosion lasting about 10 ms.

The explosion phenomenon was examined further in Figure 1B where the late stages of the droplet lifetime ($t \sim 3000$ ms) were probed with a 30 mm rod. The probe punctured the outer shell of the droplet, resulting in a violent explosion. When probed at earlier times ($t \sim 500$ ms), the droplet behaved as a viscous oil and did not explode. The shell of the droplet had viscoelastic properties in both the probed and unprobed experiments, with less jetting and deformation in times leading up to the final microexplosion (Figure S1.4, Supporting Information).

The evaporation rate was examined by performing a d^2-law analysis. For homogeneous fuels with a uniform or narrow range of chemical species volatilities, droplet evaporation in a stagnant atmosphere is known to evaporate at a rate proportional to the square of the diameter.[16] Figure 2 shows the d^2-law relationship of bio-oil as it evaporates on an alumina surface. Because of early $((d/d_0)^2 > 0.5)$ microexplosions, d^2 data could only be obtained for approximately half of the droplet lifetime. However, after an initial heat-up period ($\sim$1 s), droplet vaporization conformed to the d^2-law relationship.

Filtered samples exhibited a reduction in the frequency of microexplosions. Filtration of bio-oils through a 0.45 μm filter decreased the explosion frequency from above 50% to below 5% (Figure 3A). Interestingly, the respective average lifetimes of droplets in both explosion and explosion-free cases remained unaffected within error by the extent of filtration.

The evaporation rates of 50 samples for each of the five filtration dilutions were measured by performing a d^2-law analysis. After an initial heating period, a nearly identical
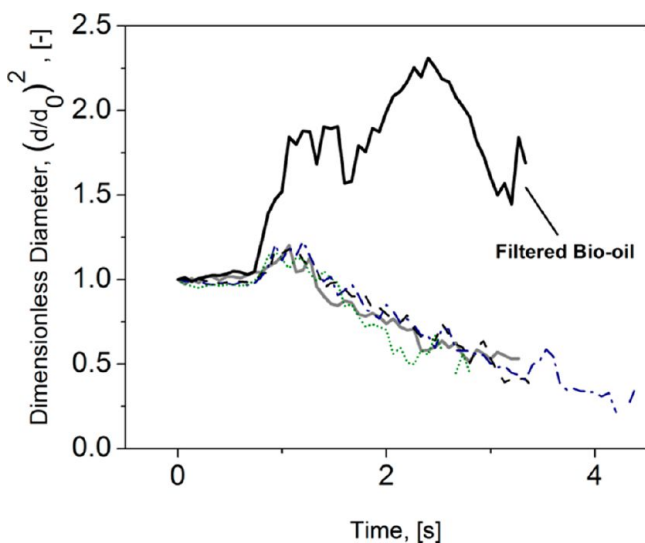
Figure 2. Evaporation of filtered bio-oils. After an initially flat heat-up period, pure bio-oil (gray solid line) evaporating on a 500 °C alumina surface is observed decreasing linearly in accordance with the d^2-law. Filtered dilutions of 25% (black dashed line), 50% (blue dashed and dotted line), and 75% (green dotted line) demonstrate nearly identical evaporation profiles and rates. In the case of the 100% filtered bio-oil (black solid line), significant char formation occurs and evaporation does not conform to the d^2-law relationship.

vaporization period was observed for filtered samples from 0−75%, and the explosion frequency and droplet lifetimes remain nearly constant. In the 100% filtered case, however, drastic differences were observed in the droplet evaporation. Significant bubbling occurred, resulting in pulsing and droplet expansion of over 200% at early times (<2.5 s), followed by slow evaporation and steady char formation (Figure 4B,C, and video V2 of the Supporting Information). Additionally, the explosion frequency was diminished to nearly zero, resulting in the weighted average droplet lifetime of the combined explosion and explosion-free cases to be extended.

The role of suspended solids was also explored, and the lifetimes and explosion frequencies are described in Figure 3B, with additional statistical representation available in the figures of the Supporting Information. As activated charcoal is added, a slight increase in explosion frequency was observed, increasing the average frequency by 15% at 4 wt % charcoal. Similar to the filtered case, no significant decrease in the lifetime of the explosion-free case was observed. However, the addition of activated charcoal did cause the droplet explosion to occur slightly earlier. In a similar experiment, activated charcoal was added to filtered bio-oil and resulted in no statistical difference in microexplosion frequency from the base filtered case.

Lifetime analysis and droplet frequency for bio-oil samples diluted with methanol have been studied. As shown in Figure 3C, methanol addition appears to have no effect on the frequency of microexplosions; however, it does appear to delay the onset of a microexplosion. Additionally, the lifetimes of both the explosion and explosion-free cases appear to be approximately a linear combination of the pure bio-oil and methanol lifetimes.

■ DISCUSSION

Microexplosions are known to exist in rapidly heated mixtures with chemical species of varying volatility.[38] Large droplets of
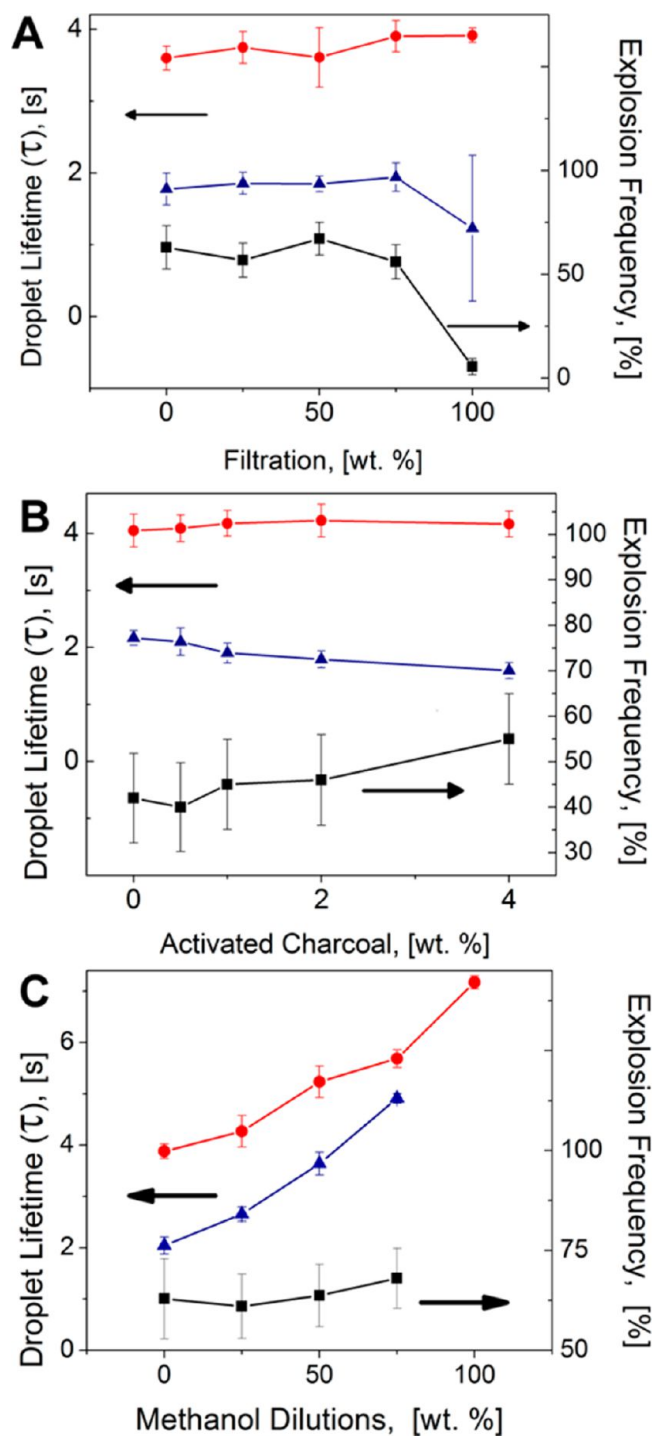

Figure 3. Lifetime analysis of bio-oil evaporation for the explosion-free case (red dot), explosion case (▲), and microexplosion frequency (■). (A) Filtration of bio-oil strongly reduces explosion frequency; however, it does not change droplet lifetimes. (B) Increasing amounts of suspended activated charcoal decreases the pre-explosion time and appears to increase explosion frequency. (C) Addition of methanol does not affect the explosion frequency; however, it strongly increases the droplet lifetimes in both the explosion and explosion-free cases.

bio-oil ($d > 300$ μm) have been qualitatively examined and characterized experimentally as undergoing several predictable events prior to microexplosion. In a combustive environment, droplets have previously been observed to undergo an initial evaporation stage, where the light compounds evaporate
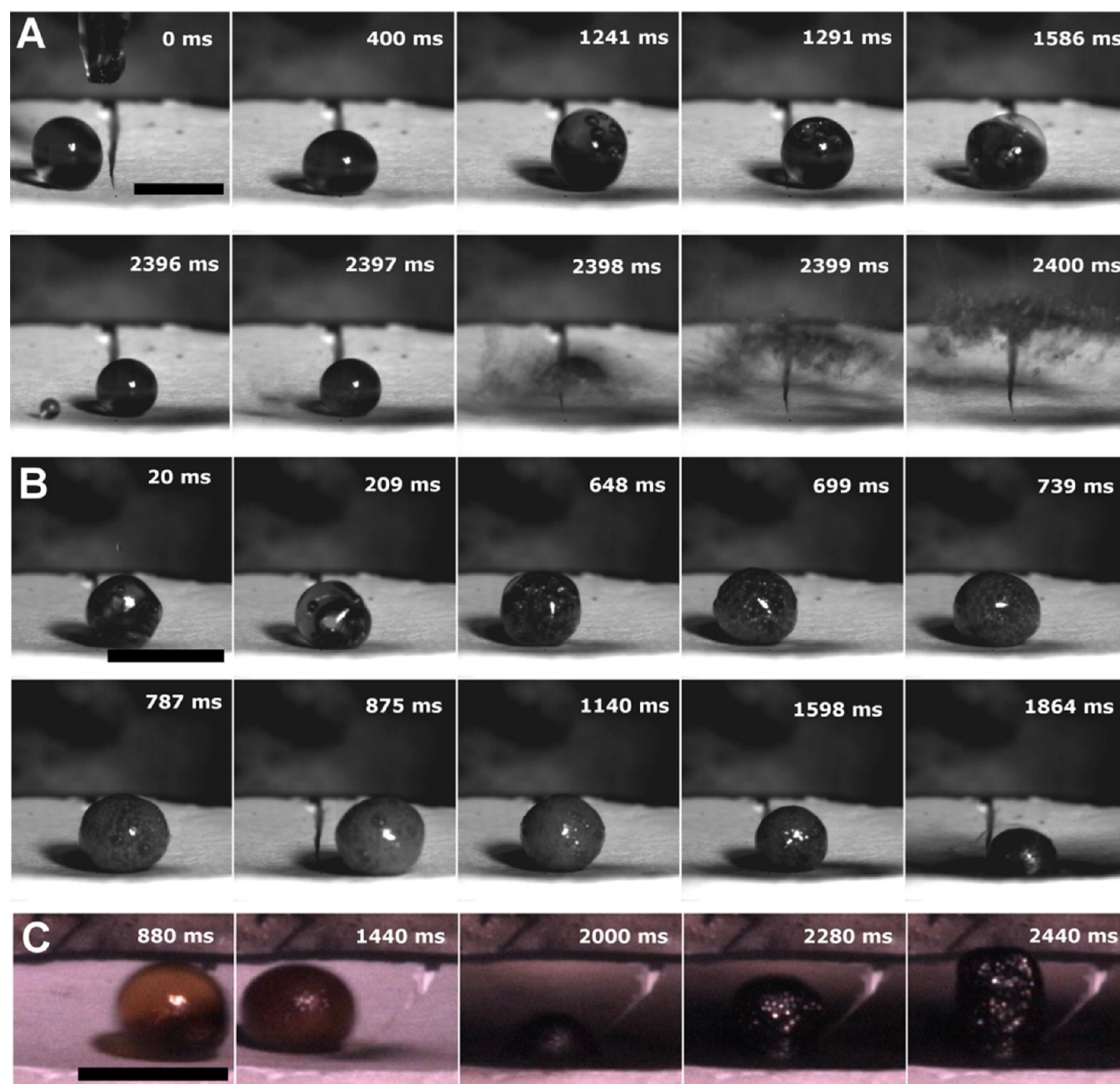
Figure 4. High speed photography of evaporating bio-oils (A) Bio-oil is heated on a 500 °C alumina surface for about 1 s. Large bubbles are observed throughout the droplet before bubbling ceases (~2 s) and ends in a microexplosion (2398 ms). Frames from video V1 (Supporting Information). Scale bar = 1 mm. (B) 100% filtered bio-oil evaporates on a 500 °C alumina surface. Large bubbles are observed during early times. The droplet then lightens with many small droplets before retracting into a solid char particle. Frames from video V2 (Supporting Information). Scale bar = 1 mm. (C) Same conditions as B, however a slower frame rate allows for the observation of late time char formation. Evaporating filtered bio-oil does not explode but rather reacts and expands at late times to produce a porous char scaffold.

($T_{droplet} \leq 100$ °C), followed by a vaporization phase in which the droplet is heated and the volatile components diffuse to and evaporate from the surface (100−500 °C). The temperature profile then stabilizes (~600 °C), at which point the sequence culminates in rapid vibrations and ultimately a micro-explosion.[16,32,33]

In our high speed photography experiments, a similar sequence of events is observed. The droplet moves freely on the surface without demonstrating any degree of wetting. After the initial heat-up period, the droplets evaporated in approximate agreement with the d^2-law relationship until

undergoing an explosion. In the cases where nucleation occurred early ($t < 300$ ms, Figure 4A, and video V1 of the Supporting Information), the droplet underwent high frequency vibrations (>30 hz), eventually leading to large bubbles, droplet deformation, and jetting (1000 ms). Jetting occurred as internal vapor bubbles burst, leading to the formation of a liquid jet extending from the liquid droplet that can be seen extensively in video V1 of the Supporting Information ($1.2 < t < 2$ s). Similarly, in the filtered case (Figure 4B, and video V2 of the Supporting Information), bio-oil droplets were observed to bubble internally at early times. Unlike the pure case, however,

the majority of the droplet lifetime ($t > 300$ ms) was dominated by a slow even bubbling of hundreds of small bubbles until it formed a dark spherical droplet that slowly shrinks and collapses into a porous char particle. The droplet keeps its roughly spherical shape throughout its lifetime.

The microexplosion phenomenon is thought to occur by one of two mechanisms that trap volatile components within the droplet. The first mechanism considers the formation of a viscous shell/volatile core model. The second mechanism proposes that the reactivity of the bio-oil forms a polymer shell around the volatile core.

The "viscous shell microexplosion mechanism" has been examined using nonreactive multicomponent systems both experimentally and with liquid-phase diffusion-controlled transport modeling. Several groups have studied the micro-explosion phenomenon during the vaporization of nonreactive binary and multicomponent mixtures, and they have outlined the key steps that the mixture undergoes leading up to the explosion event.[21,23,31,38,39] The initial phase is a quiescent transient regime where the light volatiles diffuse to the surface and evaporate. The droplet then undergoes a strongly diffusion-limited phase where slow liquid–liquid diffusion dominates, leading to the formation of a viscous outer liquid layer (shell) around the lighter volatile components remaining in the core. This shell acts as a barrier to the transfer of lighter components, which allows the droplet temperature to increase beyond the vaporization temperatures of the volatile core. The core is then superheated and rapidly flashes, causing a nearly instantaneous expansion and subsequent microexplosion. In this mechanism, the char particles are believed to act as vapor nucleation sites, thus lowering the transition temperature and allowing the core to more readily flash to vapor.[31]

In the alternative "polymer shell mechanism", it has been postulated that during the rapid liquid heating period, polymerization of the bio-oil occurs, leading to heavy components that form a solid shell.[32] In this scenario, pressure increases in the volatile core until the polymer shell ruptures, resulting in a rapid expansion over a short period of time, causing the observed microexplosion.

In the high speed photography sequences, drastic deformation, expansion, and collapse of the bio-oil droplet without rupturing seems to indicate strong viscoelastic surface forces but not formation of a solid shell at early times. This is further confirmed by probing the droplet at early times ($t = 500$ ms) with a rod before the core superheats. At these early times, a viscous liquid is observed, and no microexplosions occur.

At late lifetimes ($(d/d_o)^2 < 0.7$, $t > 1800$ ms); however, a more viscous shell formed that did not deform or rupture easily. Droplet collisions observed in videos did not result in droplet coalescence, suggesting the formation of a polymer shell, not simply the nonvolatile liquid fraction of the bio-oil. This shell potentially formed from the polymerization of the residual nonvolatile fraction of bio-oil. As shown in Figure 1B, when a bio-oil droplet was probed at late times ($t = 1300$ ms), a violent microexplosion occurred immediately upon puncturing the outer shell of the droplet. These qualitative findings support the conclusion that a polymer shell forms during the late droplet lifetimes resulting in microexplosions in pyrolysis oils.

The role of a heavy polymer fraction in bio-oil was further explored by examining the effect of filtration on micro-explosions. Filtration through a 0.45 μm syringe filter removed 1.6 wt % polymeric solids, resulting in substantial differences in the evaporation sequences of the filtered and unfiltered bio-oils.

In the case of filtered bio-oil, gradual char formation was observed, and the microexplosion frequency was reduced from 60% to 5%. This indicates that the removed solids played a key role in formation of the viscous liquid or polymer shell and the microexplosion phenomenon within bio-oil.

It has been suggested that heterogeneous nucleation sites in bio-oil lower the transition temperature limit for flashing the volatile core, leading to microexplosions.[31,40] However, the addition of 2 wt % activated charcoal to the filtered bio-oil had no impact on the frequency of microexplosions, suggesting that the removed solids do not simply act as nucleation sites. This is consistent with experiments that have shown the presence of a suspension wire does not induce microexplosions[40] and other research that concludes that particle nucleation only plays a marginal role in the microexplosion phenomenon.[21] These results support the importance of the heavy fraction of bio-oil in the mechanism of microexplosions, which is needed in the formation of a polymer shell that entraps the volatile core.

Qualitative analysis of the evaporation phenomenon in both the filtered and unfiltered experiments also provides insight into the mechanism for microexplosions in bio-oil. In the pure bio-oil case, a cloudy quivering droplet was observed with several medium-sized (10–50 μm) vapor bubbles for the first 1000 ms (Figure 4A, and video V1 of the Supporting Information). More frequent vapor bubble formation, growth, and jetting were observed in the next 1000 ms. The last 500 ms of the droplet lifetime was characterized by a period of no observed bubbling or jetting and culminates in a microexplosion.

Filtered bio-oil did not undergo microexplosions. Instead, bubbling was observed early (200 ms) and continued with increasing intensity for the next 500 ms. Unlike the pure bio-oil, no jetting or physical distortions were observed. The droplet remained approximately spherical during its entire lifetime. However, at later times the entire droplet became more rigid as it solidified without the formation of a well-defined liquid surface. Hundreds of small bubbles accumulated within the bio-oil droplet and resulted in slow char formation for the next 1000 ms (Figure 4B,C).

This significant difference in the two evaporation phenomena (filtered versus unfiltered bio-oil) is consistent with the observed reduction of microexplosion frequency when samples are filtered. Additionally, it supports the conclusion that the heavy polymer fraction of bio-oil is needed for microexplosions to occur. Furthermore, internal droplet concentration gradients in the filtered bio-oil alone are not sufficient to form the shell/core system that results in a microexplosion, as supported by the lack of observed explosions (<3%, Figure 3A) in the filtered bio-oil experiments.

In cases where microexplosions did not occur, the remaining viscous liquid solidified into a char which can be burned to CO and CO_2. Figure 4C shows the late time ($t > 3$ s) of an unfiltered bio-oil droplet that did not explode charring on the 500 °C surface. The droplet was initially observed to shrink as the volatile components evaporated. As the droplet solidified from the bottom upward, it slowly bubbled and grew vertically, creating a porous char scaffold. At late times ($t > 2$ s), the only fraction remaining in the bio-oil was the heavy, nonvolatile fraction that remained after pyrolysis. A significant amount of surface blackening was also observed from the secondary pyrolysis of the vapors at late times. These charring effects are not preferred due to their slow combustion rates,[27] and inducing microexplosions would be preferable for use in the traditional combustion and refining processes.

Methanol is considered as an additive to bio-oil for its ability to prevent aging in which the oil viscosity increases with time.[25] In our experiments, methanol dilutions delay the time for microexplosions to occur in the fuel−methanol mixture. Additionally, it increases the mixture volatility, resulting in more rapid vaporization rates (Figure S1.5, Supporting Information). The rate curve is linear, suggesting that the rate was a weighted average of the individual components (bio-oil/methanol). These rates were determined only for explosion-free case, and they did not account for the beneficial effects of secondary atomization due to the presence of microexplosions.

On the basis of the measured vaporization characteristics of both pure and methanol-diluted bio-oil, it was determined that pure bio-oil (1) vaporizes at the slowest rate and (2) exhibits microexplosions earlier. The addition of methanol to the fuel contributed significantly to the rate of change of the droplet size and resulted in a more uniform evaporation sequence. Additionally, delay observed in the onset of the microexplosion was consistent with other fuel additives described in the literature, where high moisture content was shown to delay explosion times in bio-oils.[31] While methanol did not promote earlier microexplosions in bio-oil, it did increase the evaporation rate and frequency of explosions, which reveals new ways for the fuel additive to improve the end-use of bio-oils.

CONCLUSIONS

Bio-oils derived from pyrolysis of biomass exhibited violent microexplosions when rapidly heated for the purpose of vaporization or combustion. Rapid droplet heating and reaction led to internal bubbling and ultimately a violent micro-explosion. The addition of methanol did not increase microexplosion frequency and evaporation rates, while partial filtration of bio-oil increased the frequency of microexplosions. Filterable polymers present in the bio-oil were shown to be necessary for microexplosions to occur, while the presence of additional nucleation sites on solid particles within bio-oil seemed to have a minimal impact on microexplosion frequency or timing. Qualitatively, experimental results suggest the formation of a polymer shell upon heating of bio-oil droplets, leading to pressurization of the droplet core, thus resulting in a microexplosion from sudden expansion.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Videos V1 (sc300148b_si_005.avi), V2 (sc300148b_si_006.avi), V3 (sc300148b_si_007.avi), and V4 (sc300148b_si_008.avi) include a more detailed depiction of the events presented in Figures 1 and 4. (Note to Reader: Video V1 is large and may take several minutes to open.) Figures detail the experimental setup and statistical analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Czernik, S.; Bridgwater, A. V. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* **2004**, *18* (2), 590−598.

(2) Mettler, M. S.; Vlachos, D. G.; Dauenhauer, P. J. Top ten fundamental challenges of biomass pyrolysis for biofuels. *Energy Environ. Sci.* **2012**, *5* (7), 7797−7809.

(3) Ragauskas, A.; Williams, C.; Davison, B.; Britovsek, G.; Cairney, J.; Eckert, C.; Frederick, W., Jr; Hallett, J.; Leak, D.; Liotta, C. The path forward for biofuels and biomaterials. *Science* **2006**, *311* (5760), 484−489.

(4) Sanderson, K. US biofuels: A field in ferment. *Nature* **2006**, *444* (7120), 673−676.

(5) Mettler, M. S.; Paulsen, A. D.; Vlachos, D. G.; Dauenhauer, P. J. Pyrolytic conversion of cellulose to fuels: Levoglucosan deoxygenation via elimination and cyclization within molten biomass. *Energy Environ. Sci.* **2012**, *5* (7), 7864−7868.

(6) Mettler, M. S.; Paulsen, A. D.; Vlachos, D. G.; Dauenhauer, P. J. The chain length effect in pyrolysis: Bridging the gap between glucose and cellulose. *Green Chem.* **2012**, *14* (5), 1284−1288.

(7) Bridgwater, A. V. *Progress in Thermochemical Biomass Conversion*; Blackwell Science Ltd.: Oxford, U.K., 2001; Vol. 1.

(8) Piskorz, J.; Scott, D. S.; Radlein, D. Composition of Oils Obtained by Fast Pyrolysis of Different Woods. In *Pyrolysis Oils from Biomass*; Soltes, J.; Milne, T. A., Eds.; ACS Symposium Series 376; American Chemical Society: Washington, DC, 1988; pp 167−178.

(9) Mohan, D.; Pittman, C. U.; Steele, P. H. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels* **2006**, *20* (3), 848−889.

(10) Yang, J.; Dauenhauer, P. J.; Ramasubramaniam, A. The role of water in the adsorption of oxygenated aromatics on Pt and Pd. *J. Comput. Chem.* **2013**, *34* (1), 60−66.

(11) Colby, J. L.; Dauenhauer, P. J.; Michael, B. C.; Bhan, A.; Schmidt, L. D. Improved utilization of biomass-derived carbon by co-processing with hydrogen-rich feedstocks in millisecond reactors. *Green Chem.* **2010**, *12* (3), 378−380.

(12) Dreyer, B. J.; Dauenhauer, P. J.; Horn, R.; Schmidt, L. D. Enhanced olefin production from renewable aliphatic feedstocks and co-fed lignin derivatives using experimental surrogates by millisecond catalytic partial oxidation. *Ind. Eng. Chem. Res.* **2010**, *49* (4), 1611−1624.

(13) Di Blasi, C. Modeling chemical and physical processes of wood and biomass pyrolysis. *Prog. Energy Combust. Sci.* **2008**, *34* (1), 47−90.

(14) Rennard, D.; Dauenhauer, P.; Tupy, S.; Schmidt, L. Autothermal catalytic partial oxidation of bio-oil functional groups: Esters and acids. *Energy Fuels* **2008**, *22* (2), 1318−1327.

(15) Boucher, M. E.; Chaala, A.; Roy, C. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part I: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass Bioenergy* **2000**, *19* (5), 337−350.

(16) Shaddix, C. R.; Hardesty, D. R. *Combustion Properties of Biomass Flash Pyrolysis Oils: Final Project Report*; SAND99−8238; Sandia National Laboratories: Albuquerque, NM, 1999.

(17) Wornat, M. J.; Porter, B. G.; Yang, N. Y. C. Single droplet combustion of biomass pyrolysis oils. *Energy Fuels* **1994**, *8* (5), 1131−1142.

(18) Yap, L. T.; Kennedy, I. M.; Dryer, F. L. Disruptive and micro-explosive combustion of free droplets in highly convective environments. *Combust. Sci. Technol.* **1984**, *41* (5−6), 291−313.

(19) Law, C. K. A model for the combustion of oil/water emulsion droplets. *Combust. Sci. Technol.* **1977**, *17* (1−2), 29−38.

(20) Avedisian, C. T. *Fundamental Droplet Combustion Characteristics of Mixtures and Emulsions: Final Report*; DOE/ER/13092-T1; DE89002862; Sibley School of Mechanical and Aerospace Engineering: Ithaca, NY, 1988; p 11.

(21) Kadota, T.; Yamasaki, H. Recent advances in the combustion of water fuel emulsion. *Prog. Energy Combust. Sci.* **2002**, *28* (5), 385−404.

(22) Lasheras, J. C.; Fernandez-Pello, A. C.; Dryer, F. L. On the disruptive burning of free droplets of alcohol/n-paraffin solutions and emulsions. *Symp. (Int.) Combust., [Proc.]* **1981**, *18* (1), 293−305.

(23) Law, C. K. Internal boiling and superheating in vaporizing multicomponent droplets. *AIChE J.* **1978**, *24* (4), 626−632.

(24) Oja, V.; Suuberg, E. M. Vapor pressures and enthalpies of sublimation of d-glucose, d-xylose, cellobiose, and levoglucosan. *J. Chem. Eng. Data* **1998**, *44* (1), 26−29.

(25) Diebold, J. P.; Czernik, S. Additives to lower and stabilize the viscosity of pyrolysis oils during storage. *Energy Fuels* **1997**, *11* (5), 1081−1091.

(26) Boucher, M. E.; Chaala, A.; Pakdel, H.; Roy, C. Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part II: Stability and ageing of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass Bioenergy* **2000**, *19* (5), 351−361.

(27) Shaddix, C. R.; Tennison, P. J. Effects of char content and simple additives on biomass pyrolysis oil droplet combustion. *Symp. (Int.) Combust., [Proc.]* **1998**, *27* (2), 1907−1914.

(28) Landry, E. S.; Mikkilineni, S.; Paharia, M.; McGaughey, A. J. H. Droplet evaporation: A molecular dynamics investigation. *J. Appl. Phys.* **2007**, *102* (12), 124301−7.

(29) Hallett, W. L. H.; Clark, N. A. A model for the evaporation of biomass pyrolysis oil droplets. *Fuel* **2006**, *85* (4), 532−544.

(30) Brett, J.; Ooi, A.; Soria, J. The effect of internal diffusion on an evaporating bio-oil droplet − The chemistry free case. *Biomass Bioenergy* **2010**, *34* (8), 1134−1140.

(31) Stamatov, V.; Honnery, D.; Soria, J. Analysis of the pre-conditions for micro-explosions of bio-oil droplets. *Analysis* **2005**, *17*, 20.

(32) D'Alessio, J.; Lazzaro, M.; Massoli, P.; Moccia, V. Thermo-optical investigation of burning biomass pyrolysis oil droplets. *Symp. (Int.) Combust., [Proc.]* **1998**, *27* (2), 1915−1922.

(33) Garcia-Perez, M.; Lappas, P.; Hughes, P.; Dell, L.; Chaala, A.; Kretschmer, D.; Roy, C. Evaporation and combustion characteristics of biomass vacuum pyrolysis oils. *IFRF Combust. J.* **2006**, 200601.

(34) Teixeira, A. R.; Mooney, K. G.; Kruger, J. S.; Williams, C. L.; Suszynski, W. J.; Schmidt, L. D.; Schmidt, D. P.; Dauenhauer, P. J. Aerosol generation by reactive boiling ejection of molten cellulose. *Energy Environ. Sci.* **2011**, *4* (10), 4306−4321.

(35) Rennard, D.; French, R.; Czernik, S.; Josephson, T.; Schmidt, L. Production of synthesis gas by partial oxidation and steam reforming of biomass pyrolysis oils. *Int. J. Hydrogen Energy* **2010**, *35* (9), 4048−4059.

(36) Scholze, B.; Hanser, C.; Meier, D. Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin): Part II. GPC, carbonyl goups, and 13C-NMR. *J. Anal. Appl. Pyrolysis* **2001**, *58−59*, 387−400.

(37) Rasband, W. S. *ImageJ*, 1.43u; National Institutes of Health: Bethesda, MD, 1997−2011.

(38) Ryddner, D. T.; Trujillo, M. F. A Fully Resolved UWS Droplet Simulation. In *ILASS-Americas 24th Annual Conference on Liquid Atomization and Spray Systems*, San Antonio, TX, 2012.

(39) Wang, C. H.; Liu, X. Q.; Law, C. K. Combustion and microexplosion of freely falling multicomponent droplets. *Combust. Flame* **1984**, *56* (2), 175−197.

(40) Calabria, R.; Chiariello, F.; Massoli, P. Combustion fundamentals of pyrolysis oil based fuels. *Exp. Therm. Fluid Sci.* **2007**, *31* (5), 413−420.