Micro-explosion of liquid intermediates during the fast pyrolysis of sucrose and organosolv lignin

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ABSTRACT

A new methodology has been proposed to describe of the dynamics of bubble formation during pyrolysis of Organosolv lignin and sucrose (surrogates for biomass) using fast speed visualization (125fps) with mathematical modeling. The model uses a population balance to predict overall rates of bubble birth and death, bubble bursting, and aerosol ejection. The experimental studies were performed on a uniquely modified CDS Analytical Pyroprobe 5000 to visualize the formation of bubbles within the liquid intermediate phase at heating rates close 100 °C/s. Experimentally, we observed that bubbles follow a log-normal distribution versus bubble size within the liquid intermediate phase for both materials. This distribution function changes over time due to increased viscosity from solidification reactions that generate char and the changes in the rate of bubble formation. Micro-explosion intensity was used to estimate aerosol ejection intensity. The model predicts aerosol ejection yields of 21.18% w/w from Organosolv lignin and 17.40% w/w from sucrose during pyrolysis with an average droplet size of 10 μm.

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1. Introduction

Biomass fast pyrolysis is a relatively simple process, but is very challenging to control; it is a fast reaction in which heat transfer, mass transfer, and chemical reactions all impact the final distribution of products to varying degrees [1,2]. Lignocellulosic biomass is made up of cellulose, hemicelluloses, lignin, extractives, and ash. Many studies have been done to understand biomass pyrolysis using lignocellulose pseudocomponents like cellulose or lignin. Experimental and theoretical evidence show that during neat cellulose and lignin depolymerization, a short-lived liquid phase is formed before compounds are released from the biomass particle. This liquid phase is composed of heavy depolymerization products [3–6] and is the source of high molecular weight compounds (anhydro-sugars with DP > 2, pyrolytic lignin) in bio-oil [3,7,8].

In the liquid intermediate phase, volatile products of pyrolysis reactions (vapors and gases) form bubbles. These bubbles grow, coalesce, and collapse to release aerosols that are made up of whatever is in the liquid at that time [3,8,9]. When bubbles rise to the surface the external liquid-gas interface swells, increasing the internal pressure of the bubble (see Fig. 1A). When the internal energy exceeds the surface's free energy, the bubble collapses and bursts (see Fig. 1B) [8]. As the bubble bursts and releases gas, the liquid surface deforms and "jets" are created (see Fig. 1C). The jets then collapse and release large aerosols (0.1–1 mm) [10–12].

The dynamics of bubble formation and collapse have been extensively studied in evaporative processes, droplet combustion processes, and aeration in gas/liquid interfaces on water surfaces [12–14]. For example, bubbling in rapid boiling processes have received a lot of attention [15–18]. Bubble dynamics are affected by temperature, fluid type, and the micro-structure of the surface.

Micro-emulsion droplet combustion is a relevant example of a technology where microexplosions are important. During combustion, aerosols may be released totally or partially, destroying the mother droplet [19,20]. Microexplosion of droplets suspended on a thermocouple is commonly studied using fast speed cameras (>1000 fps) to visualize morphological changes as a function of temperature and time [21–25]. Pyrolysis oil (also known as bio-oil) is known to undergo microexplosions during combustion [25]. Bio-oil microexplosion intensity depends strongly on droplet size, temperature, and heating rate [23]. Shuhn et al. [26] described the swelling,

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Nomenclature

t	Time (s)
$\bar{f}(t, D)$	Average distribution function of bubbles (#bubbles/s m^3)
D	Bubble diameter (mm)
v	Bubble velocity (m/s)
$\dot{D}$	Bubble growth rate (m/s)
σ	Standard deviation of log-Normal distribution
γ	Mean value of log-Normal distribution
H	Particle height (m)
G	Gravity constant (m/s^2)
R	Bubble size (mm)
ρ_l	Liquid density (kg/m^3)
ρ_b	Bubble density (kg/m^3)
μ_l	Liquid dynamic viscosity (Pas)
k	Growth constant (ms^{-1})
n	Order of growth law
$R_{aerosol}$	Aerosol size (mm)
$I_{aerosol}$	Aerosol ejection intensity (m^3/s)
$N_{aerosol}$	Number of aerosols
$N_{bubbles}$	Number of bubbles
$V_{control}$	Volume of control
$V_{control}$	Volume of control
V	Particle volume (m^3)
N_0	Constant of number of bubbles/s m^3 in nucleation
J	Bubbles nucleation rate (# bubbles/s m^3)
k_b	Boltzmann constant ($kJ K^{-1}$)
T	Temperature (K)
ΔE_{cri}	Minimum free energy to form a single bubble (kJ/mol)
oh	Ohnesorge number
Ω	Surface tension (N/m^2)
B_o	Bond number
$Vneto_{aerosol}$	Total aerosol volume (m^3)
$\overline{Fa}(t, V_a)$	Average distribution function of aerosol (#Aerosol/s m^3)
V_a	Aerosol volume (m^3)
$Yield_{aerosol}$	Aerosol yield (kg aerosol/kg initial sample)
L	Lignin density (kg lignin/m^3 initial sample)
IL	Intermediate liquid density (kg IL/m^3 initial sample)
A	Aerosol density (kg Aerosol/m^3 initial sample)
PL	Pyrolytic lignin density (kg PL/m^3 initial sample)
Char	Char density (kg Char/m^3 initial sample)
Gas	Gas density (kg Gas/m^3 initial sample)
LM	Lignin monomers density (kg LM/m^3 initial sample)
ρ_{lignin}	Lignin density (kg/m^3)
Cp	Heat capacity of lignin (kJ/kg K)
h_{ext}	External heat transfer coefficient ($kW/m^2 K$)
Area	Area of transversal section of the sample (m^2)
T_f	Final temperature (K)
K_i i = 1,2,3,4,5	Kinetics coefficients (s^{-1})
K_o	Kinetic frequency factor (s^{-1})
E_a	Energy of activation (kJ/mol)
γ	Gases yield (kg gases/kg PL)
Λ	Lignin monomers yield (kg LM/kg PL)

bubbling, aerosol ejection phenomena during micro-explosions of fast pyrolysis bio-oil blends with diesel. Teixeira et al. [19] found that the presence of high molecular weight compounds (1000 Da) in the bio-oil is important for the formation of microbursts. Filtration of these compounds (probably pyrolytic lignin) reduces the frequency of micro-explosions by 50%. The presence of solids such as char does not appear to alter the dynamics of bubble formation or the intensity of microbursts. The dynamics of bubble formation during pyrolysis has also been studied for polymers [8] and coals [12,27].

One metric to study aerosol formation is the intensity of ejection. Aerosol ejection intensity is defined as the average total number of aerosol droplets ejected per unit time [3,28–30]. Several studies report a direct relationship between the diameter of the gas bubbles within the liquid phase and the size of aerosol ejected. These relationships depend on the physical and chemical nature of the fluid and conditions (temperature and pressure) of bubbling. Many researchers have attempted to correlate the dynamic ejection aerosols with the characteristics of gas bubbles during the bursting [28,29,31]. However, given the complexity of the phenomenon, it is difficult to make a universal description of aerosol ejection. Recently, Zhang et al. [29] proposed correlations with dimensionless numbers to establish relationships between the number of aerosols ejected as a function of the physicochemical properties of the medium (liquid phase), and the diameter of the bubbles before bursting. Knowing the dynamics of bubble formation, the physico-chemical properties of the liquid intermediate and existing correlations to calculate aerosol ejection intensity [29] could enhance the predictive quality of models describing biomass pyrolysis.

Inherently connected to the outcome of the bubbling and thermal ejection phenomena is the biomass particle size. Particle size affects the internal microstructure of biomass particles and plays a determinant role in heat and mass transfer processes during biomass fast pyrolysis [32,33]. It is known that the bio-oil yield decreases as the particle diameter increases, although it does not follow a linear trend. A dramatic reduction in bio-oil and oligomeric yield occurs when the particle size increases from less than 0.1 mm to 1 mm [5,34,35]. The decrease in the lignin oligomer yield is mainly due to retention of these compounds inside the biomass particles as they are released by thermal ejection within the pores [1,5,35,36]. Two pyrolysis regimes were suggested based on particle size [5,35]. The first regime is for very small particles (mostly fragments of cell walls) which release aerosols directly off the cell walls into the reactor. In the second regime, the thermally ejected oligomers are trapped inside the cell cavities leading to the formation of secondary char and bio-oil with a lower content of oligomers [5].

Based on a thorough literature review, the authors conclude found a lack of information regarding bubble formation in fast pyrolysis of lignocellulosic materials and its contribution to aerosol ejection. In this study we aim to investigate this phenomena for Organosolv lignin and sucrose using experimental and modelling approaches. Organosolv lignin and sucrose act as surrogates for biomass components lignin and cellulose, respectively [1]. Our goal is to advance our understanding of the processes of birth, growth, coalescence and microexplosion of bubbles in the liquid intermediate phase of pyrolysis.

2. Materials and methods

2.1. Materials

In this work Organosolv lignin (371,017 Aldrich, CAS 8068-03-9) and sucrose (BioXtra, −Sigma ≥99.5%) were used. The proximate analysis of the Organosolv lignin was determined in a Mettler Toledo TGA/SDTA 851 with 20 mg of sample in an open alumina capsule using the following heating method: N_2 (25–107 °C at 100 °C/min, hold 60 min, 107–950 °C at 45 °C/min, hold 7 min, 950–600 °C, −100 °C/min) O_2 (600–750 °C at 2.5 °C/min, hold 60 min). Elemental analysis of both the Organosolv lignin