Evaporation of Biomass Pyrolysis Oil Droplets - II

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Introduction

Biomass pyrolysis oils are liquid fuels produced by the pyrolysis of wood wastes, bark or other biomass materials. They typically contain oxygenated organic compounds rather than hydrocarbons, and significant amounts of water. The evaporation and combustion behaviour of these fuels is complex: typically the initial heating period is followed by bubbling and/or "micro-explosions", after which the heavy non-volatile residue remaining pyrolyzes to a highly porous, irregularly-shaped char particle or "cenosphere". An earlier paper [1] gave the results of preliminary evaporation experiments on droplets of one example of these fuels, and developed a numerical model for droplet evaporation and pyrolysis. This paper reports on further developments in this ongoing study, addressing in particular the issues of polymerization, bubbling, the nature of the liquid phase processes and combustion.

Experiments

The suspended droplet/moving furnace technique was used to perform experiments. Droplets of 1.4 - 1.8 mm diameter were placed on the end of a quartz fibre and a preheated electric furnace moved to rapidly enclose the droplet and begin evaporation. For some experiments, a fine wire thermocouple (0.002" or 0.005" wire, type K) was used as the droplet suspension instead of the quartz fibre in order to record liquid temperatures. For experiments with pure evaporation, a nitrogen furnace atmosphere was used to suppress combustion.

A video camera and optical system recorded droplet behaviour, and droplet diameters were measured from individual images converted to computer files by a frame grabber. The very viscous and sticky nature of the fuel made precise control of the initial droplet size difficult, so that size measurements of each droplet were necessary.
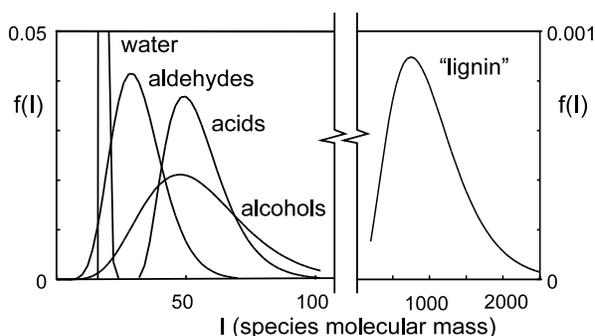
Numerical Model

Fig. 1: Distribution functions used to model the oil.

Table I: Distribution Functions for Fuel Fractions

Group	θ_{L0}	σ_{L0}	γ	w_{L0}
alcohols	55	20	0	0.20
aldehydes	32	10	0	0.10
carboxylic acids	55	12	30	0.20
"lignin"	1200	490	0	0.25
water	18	1	16	0.25

Details of the numerical model were given in the previous paper [1]. Briefly, the fuel is assumed to consist of five chemical groups (Table I), and the composition of each of these groups is described by a gamma distribution function with mean θ_{L0}, standard deviation σ_{L0} and origin γ, the component molecular mass being the distribution variable. The distributions used are graphed in Fig. 1. The distribution parameters were selected based on more detailed composition information for the fuel under test. The techniques of continuous thermodynamics were then used to derive conservation and transport equations for these distributions in the liquid and vapour phases [2]. Quasi-steady behaviour is assumed for the vapour phase, leading to a solution similar to classical droplet evaporation theory. The liquid is approximated as well-mixed, an assumption which will be discussed further later on. Vapour pressure and properties relationships, required for each chemical group as simple functions of molecular weight in continuous mixture theory [1, 2], were developed from standard correlations. Phase equilibrium was described by a continuous mixture form of Raoult's law with the Clausius-Clapeyron equation for individual component vapour pressures, a simple model, albeit somewhat crude for the polar compounds dealt with here.

The exact identity of the "lignin" component is uncertain, but detailed analyses [3] have shown that a water-insoluble fraction similar in chemical properties to lignin and its derivatives typically comprises 20-40% of the mass of a bio-oil. For modelling purposes it matters only that it is a high molecular weight component which does not vaporize significantly. It is assumed instead to pyrolyze to gas and char according to a single first-order reaction:

$$\frac{dL}{dt} = -AL\exp(-E/RT) \tag{1}$$

where L is the fraction of original lignin unconverted. Each kg of lignin produces ζ_C kg of char and $(1 - \zeta_C)$ kg of gas. The gas, a mixture of CO, CO_2, H_2O and tar vapour, was assigned the properties of CO_2, roughly representing an average product molecular weight. The literature gives a vast range of rate parameters for biomass pyrolysis: for lignin, activation energies ranging from 20 [4] to 46 [6] to 250 [5] kJ/mol have been given, while for cellulose recent studies have cited E = 120 [6] to 210 [7] kJ/mol. For this work rate parameters E = 200 kJ/mol, $A = 1.0 \cdot 10^{15}$ s^{-1} were selected based on the amount of residue remaining after experiments at different temperatures (see later). These data also gave the char yield from pyrolysis as $\zeta_C = 0.8$.

Droplet Evaporation Behaviour - Experiments and Predictions

Figs. 2-4 show selected results from the model compared to the history of events recorded in the experiments at three different furnace temperatures. The model can be used to interpret some of the observations. The predicted temperature histories show that after an initial transient heating period the droplet reaches an equilibrium temperature which remains nearly constant while the light components evaporate. This behaviour was confirmed by temperature records from droplets evaporating on a thermocouple (Fig. 5). The alcohol and acid groups evaporate at the same time as the water; by themselves they would be expected to show a temperature rising with time as lighter fractions are distilled out, but the mixture is thermally dominated by water with its order of magnitude larger enthalpy of vaporization, and this keeps the temperature nearly constant. The aldehyde group, being very volatile, mostly evaporates during the initial heating. After the lighter components have disappeared the droplet temperature rises sharply and pyrolysis begins. Visual

observations showed that at a time roughly corresponding to the end of the transient heating period the droplet began to show bubbling and disruption, swelling to about twice its original diameter and collapsing again several times per second. As time progressed the liquid appeared more and more viscous and the bubbling became less intense, evidently impeded by viscosity, until it degenerated into an erratic motion of the droplet on the fibre. The model is seen to give reasonable predictions of the time at which the solid residue appears, while the time at which bubbling begins roughly corresponds to the end of the transient heating period. The bubbling therefore appears to be the evolution of water vapour, alcohols, and acids together.
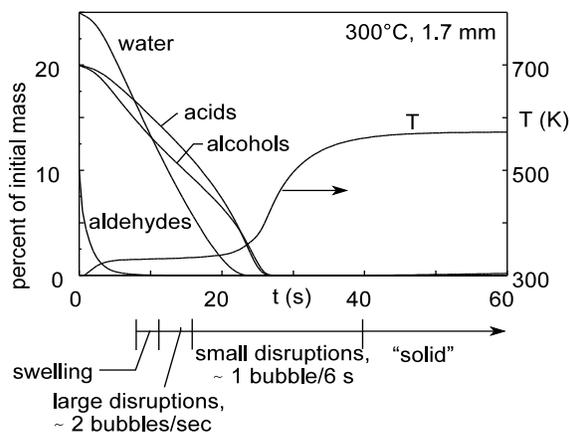

Fig. 2: Predicted masses of components and droplet temperature for a 1.7 mm droplet evaporating at 300°C. Observed droplet behaviour plotted below time scale.
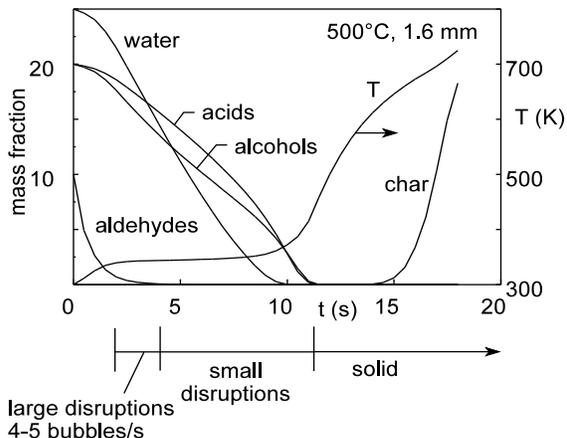

Fig. 3: Predicted masses of components and droplet temperature for a 1.6 mm droplet evaporating at 500°C. Observed behaviour plotted below time scale.
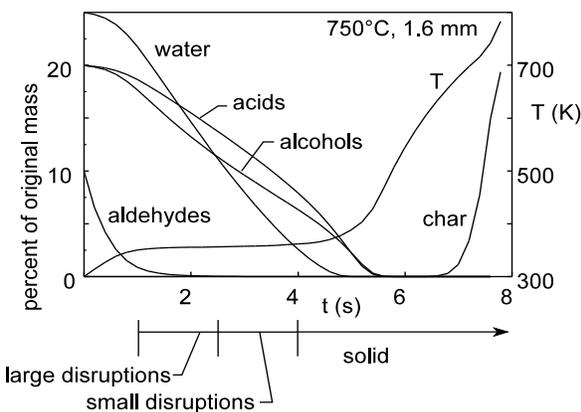

Fig. 4: Predicted masses of components and droplet temperature for a 1.6 mm droplet evaporating at 750°C. Observed droplet behaviour plotted below time scale.
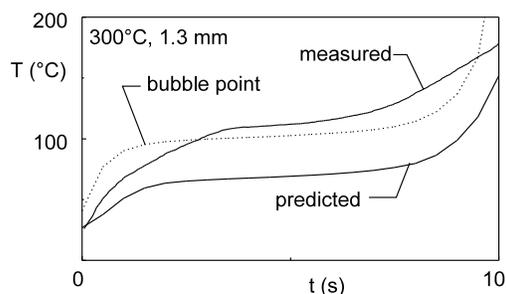

Fig. 5: Measured temperature for 1.3mm droplet suspended on 0.005" thermocouple at 300°C; average of 10 trials. Predicted temperature and bubble point, with correction made for heat transfer through the thermocouple.

The bubbling/disruptive behaviour indicates internal boiling, which is normally associated with large concentration differences between the surface and the interior of the droplet. Droplets of hydrocarbon fuels, even when stationary, normally have some degree of internal circulation induced by gas phase convection, and show behaviour intermediate between well-mixed and molecular diffusion limits. However, the high viscosity of the bio-oil makes internal circulation less likely,

although some mixing should be caused by the bubbling. Although superheating of the liquid can occur in internal boiling, it does not appear to have happened here. Fig. 5 shows temperatures recorded for a droplet on a 0.005" thermocouple as well as predicted liquid and bubble point temperatures. Radiant heating, internal mixing, and thermocouple error contribute to the measured temperatures being higher than the predicted ones, but nonetheless the measurements are close to the bubble point, which in turn is not far above the predicted liquid temperature, and significant superheating is not evident. Estimates were made of the limit of superheat for the assumed biooil composition: the thermodynamic limit of superheat was estimated at 300°C using the modified Berthelot method [8], while the kinetic limit was estimated at 225°C [9], both well beyond the temperatures recorded here. As a caveat, it should be noted that the droplet support in these experiments probably acted as a nucleation site to initiate boiling; superheat may be possible in unsupported droplets, leading to observations of more violent "microexplosions" in drop tube experiments on bio-oils [10].

The observations of the droplet becoming more viscous, and of the droplet surface "skinning over", are suggestive of polymerization, which is known to occur when biomass pyrolysis oils are moderately heated [11]: 80°C is often quoted as the temperature at which this begins. To assess the role this played in droplet processes, gel permeation chromatography (GPC) was used to estimate the molecular weights present in samples of fuel. For fresh fuel, the tests gave a number mean molecular mass $M_n = 3675$ and a mass mean $M_w = 5305$, while for droplets after evaporation at 230°C the values were $M_n = 3884$ and $M_w = 7312$, each of these being the average of 4 samples. These numbers indicate that the fuel already contained polymer components before use: lignin is of course itself a polymer, as is cellulose, but the fuel had also been in storage for about a year prior to the GPC test, so it may simply have polymerized as part of the aging to which these fuels are susceptible [11]. The numbers also show that the size of polymer chain did not change substantially with heating, although some change in structure is indicated by the difference in M_w / M_n ratio. GPC does not measure the amount of substance of a given molecular weight present, so that it is possible that some compounds polymerized to produce chains of the same length as those already present. A filtration test was performed to see if any cross-linking of existing polymer had occurred on heating, but none was found. The presence of polymer from the beginning and the lack of evidence for significant further polymerization suggests an alternative explanation for the increasingly solid nature of the droplet surface: lack of mixing leads to an augmented concentration of "lignin" polymer at the surface, which simply dries out much as paint does to form a surface film.

These remarks about drying and polymerization also explain obervations about the residue remaining after evaporation. Experiments were performed in which droplets were exposed to the furnace until the end of the bubbling and disruption period - essentially until all visible signs of change had ceased - after which they were withdrawn, and the residue weighed. Fig. 6 shows the residual mass fraction as a function of temperature, each point being the average of 4-6 droplets. A comparison set of droplets was given a long-term exposure, about five times longer than the time to the end of disruption. At high temperatures the residues were char cenospheres, irregular, porous and friable, and the residual mass did not vary significantly with temperature (Fig. 6). At lower temperatures, however, the mass was much greater, and the residue had a completely different appearance, being round, smooth and glossy, with a somewhat porous interior and a surface increasingly "sticky" to the touch as the exposure temperature dropped. These residues had clearly

not pyrolyzed, but had simply dried out, leaving unconverted lignin and perhaps additional polymer. These low temperature observations are probably irrelevant to practical combustion, but are of some value in selecting values for pyrolysis rate constants. The residue fraction at high temperature (750°C) is clearly char, and this value is used to set ζ_C. At 300°C and lower temperatures the residue fraction is larger than the char yield and does not change with increasing exposure, but at 400°C it is initially equal to that at 300°C and then drops to the char value with longer exposure. It appears then that pyrolysis occurs slowly at 400°C but not at 300°C, and this criterion together with the time scales recorded in the experiments was used to select the rate parameters for the pyrolysis reaction. The activation energy selected (E = 200 kJ/mol) is at the upper end of the range given by the literature, but values around 50 kJ/mol such as used by Grønli *et al.* [6] gave excessively long pyrolysis times at high temperature or too rapid pyrolysis at low temperature, depending on the value of pre-exponential A used. Model predictions of residue are also shown in Fig. 6, with the time of exposure being arbitrarily defined as the time till all the volatile liquid components disappeared plus three seconds to allow for withdrawal from the furnace. Since the model does not include drying or polymerization phenomena and assumes a well-mixed liquid, it is not successful in predicting the larger residues at low temperatures.
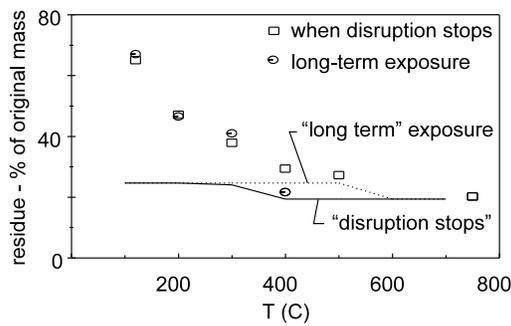

Fig. 6: Measured percent of original mass remaining as residue when disruption stops and after long-term exposure as a function of temperature. Comparison with predicted residues (lines).
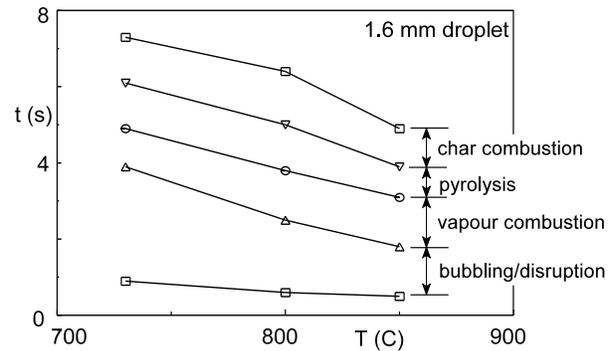

Fig. 7: Events in single-droplet combustion. Each point is the average of 10-12 trials.

Droplet Combustion

Fig. 7 summarizes observations of burning droplets made with air as the furnace atmosphere. The events are similar to those of pure evaporation, with an initial heatup period, followed by bubbling and disruption. At some point during the bubbling phase the vapour ignites and forms an envelope flame. Disruption continues during combustion, but when the volatile components of the liquid have disappeared the vapour flame extinguishes and pyrolysis begins. There is an interval after the extinction of the gas flame before the char begins to burn, presumably occasioned by the need for the products of vapour combustion to dissipate before oxygen can gain access to the char surface, and the moment of char ignition is difficult to discern exactly from the video frames. The "liquid" and "solid" phases of combustion are roughly equal in duration, somewhat different from solid fuel combustion, in which the char stage is usually much longer than the pyrolysis and volatiles combustion stage. This can be attributed to the large amount of heating required to supply the

enthalpy of vaporization of the water in this fuel. As one would expect for a fuel with such a high content of water and oxygenates, ignition times are long: hydrocarbon droplets of the same size have ignition times of around 1 s at these temperatures. The ignitable limit temperature is also high, the temperature of 730°C shown in Fig. 7 being the lowest at which consistent ignition could be achieved.

Conclusions

The model presented here reproduces reasonably well the time scales of the processes of evaporation of biomass pyrolysis oil. However, more work needs to be done on liquid phase mixing processes.

Acknowledgements

Nomenclature

A	pre-exponential, s^{-1}	γ	distribution origin	**Subscripts**	
E	activation energy, kJ/mol	ζ_C	fraction converted to char		
L	lignin fraction unconverted	θ	distribution mean (= mean	L	liquid phase
R	universal gas constant		mol mass)	0	initial value
w	mass fraction	σ	dist'n standard deviation		

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