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Droplet evaporation behaviour of a liquid fuel from chicken litter

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HIGHLIGHTS

• Liquid fuel resembling petroleum fuel produced from pyrolysis of chicken litter.

• Evaporating droplets show disruption and boiling at higher temperatures.

• Polymerization of the surface layer appears to occur.

• Fuel modelled using continuous thermodynamics to represent the composition.

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ABSTRACT

Experiments on the evaporation of single droplets of a refined fraction of a liquid fuel produced by fast pyrolysis of chicken litter are presented. A computational model for the evaporation of the fuel is devised using the techniques of continuous thermodynamics, with distribution functions selected to represent the five main chemical groups in the fuel (*n*-paraffins, 1-alkenes, *n*-alkylbenzenes, *n*-alkyl fatty acids and *n*-diols) as determined through Py-FIMS and other analyses. The distribution parameters are determined directly from these analyses. This model is found to give accurate predictions of droplet temperature and diameter histories during evaporation. At ambient temperatures of 500 °C and above bubbling and disruption of the droplet surface was observed, with the bubbles exhibiting a thin skin like that of a balloon. This was attributed to polymerization of the surface layer, causing the underlying liquid to reach higher temperatures. Under most conditions a solid residue remained after evaporation, believed also to be the product of polymerization, and, at higher temperatures, of pyrolysis as well.

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Agricultural wastes are an attractive feedstock for producing alternative liquid fuels. This paper examines the evaporation characteristics of single droplets of a liquid fuel produced from chicken litter (*i.e.* chicken manure combined with waste bedding material), and presents a droplet evaporation model which uses the principles of continuous thermodynamics to represent the rather complex chemistry of this material.

1. Fuel preparation and analysis

The fuel used in this work is a refined fraction of a raw fuel produced by fast pyrolysis of chicken litter. The refined fraction has a very low oxygen content, and consequently is similar in heating value to conventional hydrocarbon fuels, although somewhat higher in distillation temperature. Details of the methods used to prepare the fuel and of its properties have been given in earlier papers by Monreal et al. [1–5]; only a summary is given here.

The raw chicken litter was first heated overnight in an oven at 100 °C, reducing the moisture content to below 10%, then crushed to pass a 1 mm sieve. It was then subjected to fast pyrolysis at atmospheric pressure in a stirred bed reactor of 5 L volume, containing 10 kg of 3 mm stainless steel shot. External heating maintained the reactor at 350 °C, a temperature which previous trials had shown to maximize the yield of liquid products. The pyrolysis gases leaving the reactor were cooled and condensed to produce raw bio-oil, and any non-condensable gases were flared off.

The raw bio-oil was allowed to sit for 24 h, causing it to separate into an aqueous upper layer and a viscous, heavy bio-oil fraction below. The aqueous fraction was decanted, and the heavy fraction (referred to as "Fraction II" in [4] and "raw viscous bio-oil" in [1]) was retained. Like many biomass pyrolysis oils, the heavy fraction was found to have some undesirable properties, among them a low heating value, a high viscosity, and a tendency to polymerize during long periods of storage [1], and was therefore





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Nomenclature

d	droplet diameter (mm or m)	
T_{BUB}	liquid bubble point (°C)	
T_D	droplet temperature (°C)	
T_{∞}	ambient temperature (°C)	
γ	distribution function origin (set to 0)	

further upgraded. The oxygen content was first reduced from 25% to 5% by mass by microwaving and solvent extraction [1,5]. To further reduce the oxygen level and produce a refined fraction enriched in hydrocarbons, the upgraded biooil fraction was then subjected to column chromatography using hexane as the eluting solvent [1,5]. The resulting product was found to have a density, heating value and ultimate analysis close to that of a petroleum fuel, although with a component molecular weight range higher than that of typical Diesel fuels. This refined fuel is the subject of the present work. Roughly 10% of Fraction II (the heavy fraction of the raw oil remaining after decanting the aqueous fraction) was recovered as refined oil [1].

Analyses of the refined product carried out using several different techniques are given by Monreal and Schnitzer [1]. Of these, the pyrolysis field ionization mass spectrometry (Py-FIMS) analysis was used as the starting point for re-constructing the composition of the fuel for computational modelling purposes. This mass spectrometry technique allows the separation of compounds of higher molecular mass than do ordinary GC-MS techniques, and in this case gave the relative abundance by ion count of approximately 400 different species with values of (m/z) ranging up to 500. Since z in most cases was a single charge, m/z could be directly interpreted as species molecular mass. These species were initially identified as belonging to the following groups: "lipids" (a generic long chain category including *n*-alkanes and 1-alkenes), *n*-alkanes, 1-alkenes, alkyl aromatics, free fatty acids, phenols and lignin monomers, lignin dimers, sterols, suberin, heterocyclic nitrogen compounds, peptides and carbohydrates, plus a substantial quantity of unidentified compounds. In earlier work by Monreal and Schnitzer [1], the tentative assignment of the various m/z signals in the pyrolytic biooils samples was made using a previously published database established from studies of soil humic substances and standards [6,7]. The latter assignment of each identified m/zin the refined biooil was not confirmed by MS/MS studies; therefore, the assignment of the m/z signals to specific compounds and compound class had some level of uncertainty, with potential contributions of more than one compound per m/z signal. In many cases (about 1/3 of the fuel) a given m/z could be assigned to more than one group. For example, the m/z value of 394 can be assigned to either a $C_{26:1}$ fatty acid, an n- C_{28} alkane or ethylcholestatriene, and the intensity at this value may be due to a combination of the contributions of these three species. However, we know that the content of steroids in plant biomass is, on average, low (less than 0.1% wt/wt), as was the sterols content of the raw Fraction II [4]. Thus, it was assumed that since roughly 10% of Fraction II was recovered as refined product [1], one could expect that the refined oil would contain about 10 times as much of the groups retained (i.e. the hexane soluble groups) as Fraction II did. The "unidentified" category (about 30% of the refined bio-oil fuel [1]) was then filled with the missing quantities of alkanes, alkenes, alkylbenzenes and *n*-diols, assigned to produce the proportions indicated by Fraction II. The resulting composition is given in Table 1. For later computational modelling purposes, this was simplified by neglecting the minor components, giving the composition in Table 2. As a check, the ultimate analysis (i.e. the

- θ distribution function mean (=mean molecular mass) (kg/kmol) σ
- distribution function standard deviation (kg/kmol)

elemental composition by mass) of the simplified composition was estimated using a representative compound from each group, chosen as that with a molecular mass corresponding to the mean of the distribution function used to describe that group in the computational model (see later, Section 3, and Table 4). Table 3 shows that this analysis is close to the measured ultimate analysis from [1].

2. Experiments

Droplet evaporation experiments were performed using the suspended droplet-moving furnace technique: an electric furnace preheated to the desired temperature was moved rapidly by an air cylinder to envelope a droplet suspended from a quartz fibre, the progress of evaporation was recorded using a video camera. and droplet sizes were measured from individual frames. A nitrogen atmosphere was used to prevent combustion, simulating conditions in spray combustion in which droplets evaporate in a cloud rather than burning individually. The droplet shape was approximated as a prolate spheroid, and the volume-equivalent spherical diameter was calculated from measurements of the major and minor diameters. More details are given in [8,9]. The quartz suspending fibre used was roughly 0.2-0.3 mm in diameter, with a bead of about 1.1 mm formed on the end to assist in retaining the droplet. Droplets were generated with a uniform volume of 2 µL, giving an overall droplet diameter of about 1.7 mm including the bead volume.

Information on the distillation characteristics of the fuel was required in order to fit distribution functions for the model. However, the ASTM standard distillation test requires 100 mL of fuel, which was substantially larger than the samples of fuel produced. As a substitute for this test, some experiments were carried out using a bare wire Type K thermocouple of 0.005 in. (0.13 mm) wire diameter as the droplet suspension, with a bead of refractory cement of about 1.1 mm diameter formed on the junction to aid in holding the droplet. Thermocouple alloys have thermal conductivities of the order of 200 times those of liquid hydrocarbons [10,11], and even a fine thermocouple wire appreciably increases heat conduction into the droplet. In the computational model, a simple correction is applied for this, which approximates the additional heat transfer as one-dimensional conduction along a length of wire δ representing the thermal boundary layer around the droplet:

$$\dot{Q}_{\textit{THERMOCOUPLE}} = 2\lambda_{\textit{WIRE}} \frac{\pi}{4} d^2 \frac{(T_\infty - T_D)}{\delta} ~(\textit{W})$$

where *d* is the wire diameter, the factor 2 accounts for the presence of two wires, and the wire thermal conductivity λ_{WIRE} is taken as

 $\lambda_{WIRE} = 16.16 + 0.0236T_{WIRE} (W/mK); T_{WIRE} = (T_{\infty} + T_D)/2$

The latter expression is for chromel and alumel wires in parallel, with individual conductivities from data given by Sundqvist [10]. The effective boundary layer length was set to δ = 3.5 droplet radii, based on earlier experiments with n-dodecane droplets. This correction typically reduced the calculated evaporation lifetime of the Download English Version:

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