The role of preferential vaporization in Fast Pyrolysis Bio Oil (FPBO) droplets evaporation

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Abstract

In this work, the evaporation process of a Fast Pyrolysis Bio Oil (FPBO) droplet is analyzed from a numerical point of view. The droplet is suspended on a thin thermocouple against gravity and evaporated in buoyancy driven convection, replicating the experimental works performed at CNR of Naples. The surrogate composition of FPBO includes nine components and it has been developed within the Residue2Heat project. The numerical modeling is performed with the DropletSMOKE++ code, a comprehensive CFD framework for the simulation of 3D evaporating droplets under gravity conditions. The diameter decay, liquid temperature and species mass fractions in the liquid phase are presented and discussed. The numerical results clearly show the presence of preferential vaporization in the mixture, following a multi-stage evaporation process due to the strong internal convection in the liquid.

Introduction

The high energy density of liquid fuels is exploited in many engineering devices such as diesel engines and industrial burners. Spray injection systems are widely used in order to disperse the liquid fuel in an oxidizing environment and the control of this process is currently an active area of research. In particular, the study of a single isolated droplet allows to neglect complex interaction phenomena among droplets and to focus on the evaporation mechanism. One-dimensional modelling of spherical fuel droplets in microgravity conditions is already well established [1-2]. Microgravity conditions can be reproduced conducting the experiments in free-falling chambers both for suspended and free droplets. However, most of experiments are conducted under the influence of a gravity field. Experimental devices are much cheaper and the operative conditions are closer to the real ones where droplets are commonly adopted. The buoyancy effects around the droplet strongly modify the evaporation mechanism across the interface, especially if the droplet is also in a relative motion to the gas as it commonly happens in spray injectors. Among the several methods available for multiphase flows, the Volume Of Fluid (VOF) methodology [3] is widely known for its simplicity, robustness and especially for the excellent mass conservation properties. In this work a full description of the boundary layer is given, allowing to evaluate the evaporation flux directly from the interfacial concentration gradient whatever the external flow field. The DropletSMOKE++ code, developed at Politecnico di Milano, is adopted in this work [4-5]. It is specifically conceived for the modeling of the evaporation of multidimensional fuel droplets in gravity conditions in convective regimes. It has been validated against a large set of experimental data, covering a wide range of operating conditions both in natural and forced convection. The droplet evaporation case analyzed in this work is based on the experimental device used at CNR of Naples. A bio oil fuel droplet (of which the surrogate mixture is available) is suspended on a thin thermocouple and evaporated under a convective flow generated by an electric coil placed below the droplet. The effect of the metallic suspension can be included in DropletSMOKE++ [5], but it has been neglected in this work (adiabatic fiber). The following paper presents the mathematical model, the numerical approach (including the mesh description) and the results for the droplet evaporation process.

Mathematical modeling

The VOF methodology is often referred to as a "one-fluid" approach, where the two phases are treated as a single fluid whose properties vary abruptly at the phase boundary [4]. A scalar marker function α represents the liquid volumetric fraction, varying from value 0 in the gas-phase to value 1 in the liquid phase. The α advection equation is:

$$\frac{\partial \alpha}{\partial t} + \nabla \cdot (\alpha \vec{v}) = -\frac{\dot{m}}{\rho_L} - \frac{1}{\rho_L} \frac{D\rho_L}{Dt} \tag{1}$$

The source terms represent evaporation and liquid density variations. The transport properties are weighted by the α function. The momentum equation describes the whole flow field:

$$\frac{\partial \rho \vec{v}}{\partial t} + \nabla \cdot (\rho \vec{v} \vec{v}) = \nabla \cdot \mu (\nabla \vec{v} + \nabla \vec{v}^{\mathrm{T}}) - \nabla p + \rho \vec{g} \tag{2}$$

while the energy equation provides the temperature field, including the interface cooling:

$$\rho C_p \left(\frac{\partial T}{\partial t} + \nabla \cdot (\vec{v} T) \right) = \nabla \cdot (k \nabla T) - \sum_{i}^{Ns} \dot{m}_i \Delta h_{ev,i} \tag{3}$$

Concerning the species transport, the equation is written only for the saturated mass fraction of each species. A major advantage of the DropletSMOKE++ code is that the evaporating flux is not obtained by semi-empirical laws, but it directly depends on the mass flux $\vec{j}_{d,i}$ at the liquid-gas interface. For a multicomponent mixture:

$$\dot{m}_i = -\frac{\sum_i^{Ns} \vec{j}_{d,i}}{1 - \sum_i^{Ns} \omega_i} \nabla \alpha \tag{4}$$

Where the term $1 - \sum_i^{Ns} \omega_i$ accounts for the global Stefan flow induced by evaporation. The α gradient describes the interface surface per unit volume and forces evaporation to happen only at the interface. The transport properties for liquid and gas phases are provided by the OpenSMOKE++ library [6].

Numerical methodology

The computational mesh describes an axisymmetric domain (Figure 1), where a 5° angle of the global cylindrical geometry is accounted for. The fluid region (blue color) and the solid region (orange color) are independently meshed. The solid region represents the metallic fiber, a long vertical thin cylinder ending with a small supporting sphere ($d_{fiber} = 125$ μm), around which the liquid droplet will be positioned. The planar heating coil in the CFD configuration (Figure 1) becomes a series of empty holes from a 2D axisymmetric point of view. The mesh is made of 60,000 cells, chosen by a sensitivity analysis on the cells size. A particularly detailed meshing is required around and inside the droplet region and around the heating coil (Figure 3). The time step is controlled by the stability constrain given by the Courant number (< 1).
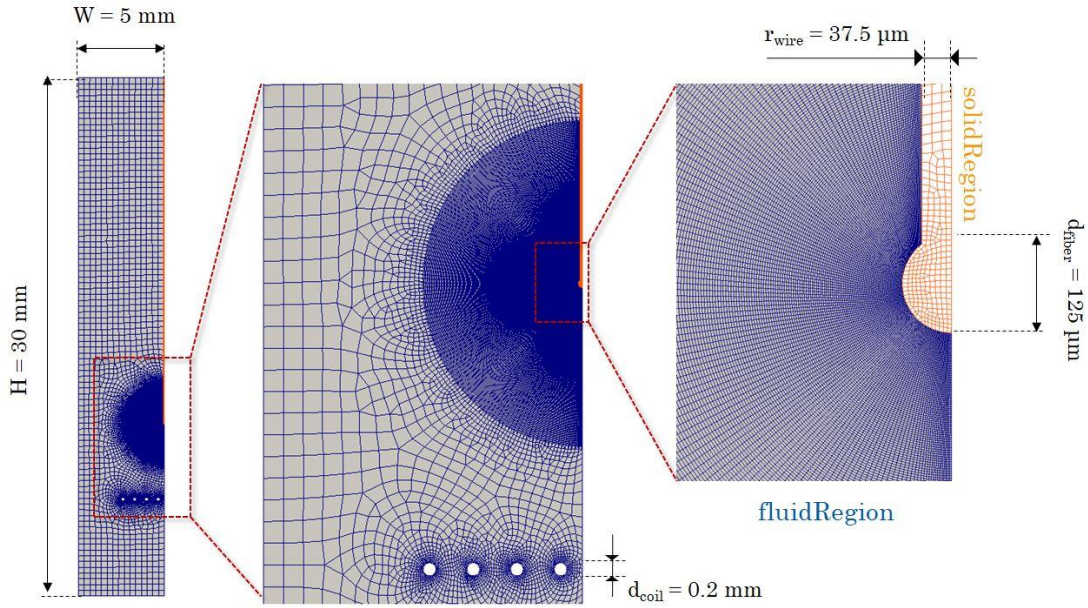
Figure 1: Computational mesh of the geometry at three levels of detail. The fluid region (blue color) and the solid region (orange color) are meshed separately. The four holes in the mesh represent the planar heating coil.

Temperature boundary condition at the heating coil

The metallic coil heats the surrounding gas, moving the fluid toward the droplet and triggering the evaporation process. However, the upward velocity of the hot gases is generally not known, since it depends on many variables such as the coil geometry, the current intensity, the coil resistivity etc. To overcome this problem, a preliminary experiment is performed:

1. The droplet is taken out of the system. The thermocouple is directly in contact with the sole gaseous phase.
2. The coil is electrically heated, providing buoyancy and an upward convective flow.
3. The temperature at the thermocouple is measured, providing the temperature profile of the gas in a fixed point.

The numerical strategy is to perform a trial and error procedure, in which the boundary condition at the heating coil surface (Figure 1) is calibrated in order to generate an upward flow which provides a temperature profile at the thermocouple equal to the experimental one. Once this is done, the droplet is suspended on the thermocouple and evaporated, maintaining the same boundary condition on the coil surface. The best boundary condition at the heating coil surface is represented by a time-varying boundary condition, imposed by this exponential function (which represents the coil heating dynamics):

$$T(t) = 1670 - (1670 - 285)e^{-0.6t} \qquad (5)$$

Fast Pyrolysis Bio Oil (FPBO) evaporation

In order to model the bio oil evaporation, a chemical and physical definition of the surrogate is necessary. The composition is reported in Table 1, including 9 components in the surrogate definition. This preliminary composition was proposed on the basis of the available information on the typical chemical composition of the FPBOs, in terms of elemental and

chemical composition, and the physical properties of the FPBOs. The work for the surrogate definition has been done within the Residue2Heat project [7].

Species	MW [g/mol]	Mass fraction [-]
Acetic acid	60.05	0.039
Glycol aldehyde	60.05	0.055
Ethylene glycol	62.07	0.055
Vanillin	152.15	0.179
Lignin Alkali	10679.16	0.078
Levoglucosan	162.14	0.296
2,5-Dimethylfuran	96.13	0.055
Oleic acid	282.46	0.023
Water	18.02	0.22

Table 1: Surrogate composition for the FPBO mixture

The DropletSMOKE++ code has been adopted to simulate a FPBO droplet evaporation. The initial conditions are reported in Table 2. The coil is heated through the boundary conditions described by Equation (5), generating an upward flow (due to buoyancy) which triggers the vaporization.

Case	Mixture	D_o [mm]	T_L [K]	T_{amb}^0 [K]	p [atm]
1	FPBO	0.940	285	285	1

Table 2: Cases for the numerical comparison with the experimental data

The results are reported qualitatively in Figure 2 and quantitatively in Figure 3. Initially the droplet is heated by the external hot flow provided by the coil, in a regime characterized by a competition between the droplet dilation (due to the decreasing density) and the slow evaporation rate. After this steady-state condition, evaporation dominates and the droplet starts shrinking. The evaporation behavior is very complex and very different to what usually happens in monocomponent droplets or simple binary mixtures. The FPBO surrogate is made of nine components with very different molecular weights, hence very different boiling points. This is favorable for the preferential vaporization of the species, as can be clearly seen in Figure 3. The diameter decay is characterized by three different slopes, indicating different global evaporation rates for the mixture. This behavior is reflected also in the liquid temperature, which reaches different temporary steady-state values (plateau). This happens because we have three main species (water, vanillin and levoglucosan) which are the main components of the surrogate in terms of mass fractions (Table 1), therefore their contribution to the evaporation process is plays a major role. Their mass fraction profile in the liquid phase is reported in Figure 3 (c): the light component (water) evaporates first due to the relatively low boiling point and continuously decreases its concentration. On the other hand vanillin exhibits an intermediate behavior, initially increasing its concentration. This is due to the evaporation of the light species, which accumulates the heavy ones. When the temperature is high enough and all the light species are evaporated, vanillin starts to vaporize and, after reaching a maximum concentration in the liquid phase, it is consumed by the process. Finally, very heavy species such as levoglucosan are continuously accumulated in the droplet due to the evaporation of the light components. At the end of the process, levoglucosan remains the only species in the droplet, which evaporates as if it was a monocomponent mixture.
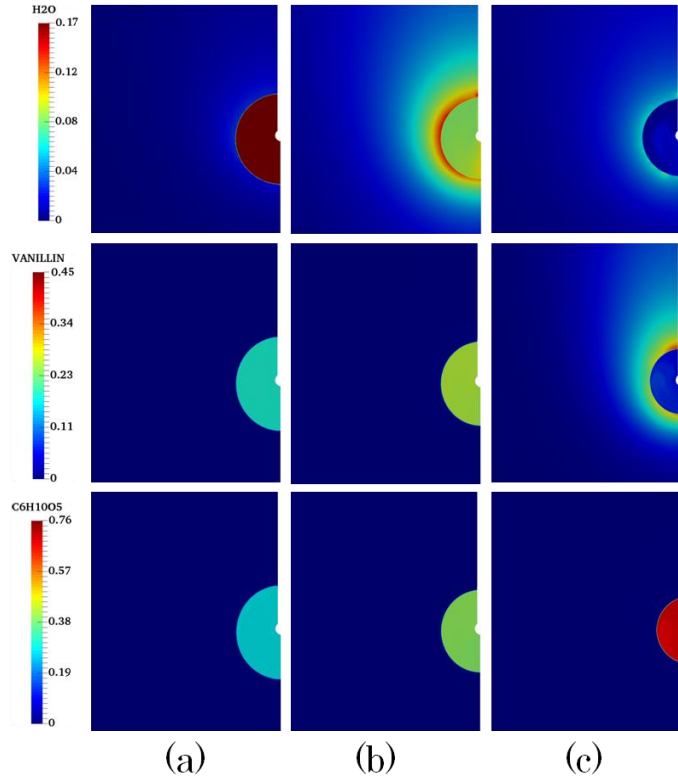
Figure 2: Numerical simulation of Case 1. Water (top), vanillin (middle) and levoglucosan (bottom) mass fractions at times t = 1 s (a), t = 2 s (b), t = 3 s (c).

It is important to point out that having very different relative volatilities of the components in the mixture is not a sufficient condition for preferential vaporization. The species vaporization occurs at the free surface and therefore internal mass transport plays a fundamental role in this sense. If the internal diffusion is slow (such as in microgravity conditions, where the internal convection is totally negligible) the species are not readily available at the surface to evaporate and they remain trapped inside the liquid phase. The only way they can reach the surface is by the interface regression due to evaporation. This means that the boiling point and the equilibrium mass fraction in the gas phase (which is ultimately the driving force for the evaporation) are relatively unimportant in this case and the droplet will evaporate most likely as a monocomponent mixture. On the other hand, if internal convection is strong enough, the internal mass transport can be much faster. This is typically the case of droplets evaporating in a convective regime, where the external fluid flow triggers internal circulation in the liquid phase. This is the case analyzed in this work, where we can clearly detect preferential vaporization of the species (Figure 3). The internal velocity field (not shown) is due to the shear stress given by the external flow on the surface and reaches and is in the order of 5-6 mm/s. The internal convection is able to transport the liquid species to the surface, making their thermodynamics (i.e. the equilibrium gaseous mass fraction) the actual driving force of the process. It is worth noticing that this phenomena cannot be modeled with a 1D code for droplet vaporization [1], since internal convection would not be predicted. This highlights the importance of adopting a CFD model for droplet vaporization, not only to account for external and internal convection, but also to correctly describe the vaporization rate of complex mixtures such as FPBOs.
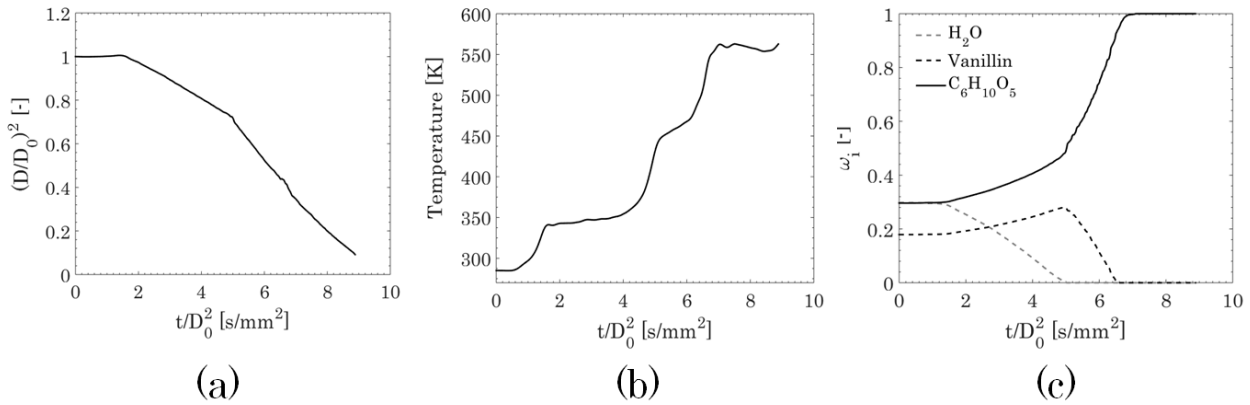
Figure 3: Squared dimensionless diameter decay (a), internal liquid temperature profile (b) and main species mass fractions at the liquid interface (c).

Conclusions

The DropletSMOKE++ code has been adopted to model the evaporation of a FPBO droplet under buoyancy driven convection. The FPBO surrogate mixture includes 9 components and has been developed within the Residue2Heat project. The VOF method has been used to track the liquid interface and it is coupled with the solution of a velocity, temperature and mass fraction field. The external gas flow causes internal recirculation in the liquid phase, because of the external applied shear stress. This triggers a strong preferential vaporization in the mixture, where components evaporate at different times and different rates. It has been pointed out that this would not be possible if internal convection was absent, because internal mass transfer would be the limiting step, enhancing the importance of using CFD models for droplet vaporization. Future developments concern the activation of gas-phase reactions, as well as the analysis on the effect of the supporting thermocouple on the evaporation process.

Acknowledgments

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