COMBUSTION FUNDAMENTALS OF PYROLYSIS OIL BASED FUELS

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Abstract

The combustion behavior of emulsions of pyrolysis oil in commercial diesel oil was studied. The emulsions were different in terms of oil concentration and size of the oil droplets in the diesel oil matrix. The study was carried out in a single droplet combustion chamber. The size of droplets varied between 400 μm and 1200 μm. They were suspended to a bare thermocouple and, hence, their temperature during combustion was measured. A high speed imaging shadowgraphy allowed following droplets evolution. Very interestingly, independently of emulsions composition, i.e., concentration of oil, surfactant and co-surfactant, as well as the size of the oil droplets in the emulsion, the homogeneous combustion rate resulted identical for emulsions and diesel oil.

Introduction

Pyrolysis oils are black-brownish liquids obtained by the condensation of vapours during the fast pyrolysis of wood and other vegetable biomasses [1]. The efficiency of the transformation process is very high, typically around 60%-70% in weight. The remaining mass is mainly reduced in char and in permanent gases whose combustible fraction may be re-utilized in the pyrolysis process to heat the pyrolyzer or for biomass drying. POs are of interest because they can represent a rationale way to use of the energy contained in biomasses. They permit also to recover energy from biomasses of low value like straw, scrapes from industry and civil wastes. The burning of POs results in a null net contribution to CO2 emissions because the carbon burned is the carbon fixed by the vegetable biomass during its life. However, pyrolysis oils are characterized by a low heating value (15-20 MJ/Kg), high density (~1.2 g/ml @ 40°C), viscosity (10-200 cSt @ 40°C) and acidity (pH ~ 3) and their quality depends on the feedstock used. The elemental composition is, in average, 50-70 %C, 0-1 %N, 4-10 % H, 25-40 %O. The sulphur is in practice absent (0-0.005%) and ash content is typically below 1 %. However, the most relevant feature in POs composition is the high water content comprising between 16% and 30%. Recently, studies and recommendations were addressed to determine pyrolysis oil composition and define the corresponding analysis procedures [2, 3].

Due to their composition, pyrolysis oils are prone to separate by an increase of temperature or storing time and work was carried out to individuate the compounds and the physical mechanisms responsible for their chemical instability [4, 5]. The tendency of POs to polymerize could prevent their storing for long periods thus rendering the oils less commercially attractive. To overcome this limitation, different strategies based on chemical and physical approaches were investigated [1,5,6]. The addition of alcohols and/or water results in a decrease of viscosity and acidity and it is effective on the droplets microexplosion and on the burning features [7, 8]. The addition of alcohols is also recommended for increasing the stability of POs [9]. However, due to the scarce autoignition properties of alcohols, their addition to POs is not recommended for the use in turbine or engines unless

cetane improvers are used [10]. On the contrary, the combustion in diesel engines is enhanced by mixing POs with oxygenated compounds characterized by high cetane numbers [11]. This choice was very effective also on the reduction of soot particulate [11].

A promising alternative to previous approaches to overcome problems of POs stability/aging is the use of POs in emulsions. In fact, the high content of polar oxygenated compounds makes the pyrolysis oils miscible with water, alcohols, etc. but immiscible with fossil fuels. Very interesting, in this framework, the emulsions of POs in distillate fuels oils. In fact, the use of limited but significant percentage of PO in light oils, 10-30% for example, can give a fuel with acceptable acidity and viscosity for the operation of many combustion systems normally utilizing fossil oils. The study of stability, corrosion, and erosion of emulsions as well as fundamental studies on their combustion properties are therefore necessary.

Combustion of emulsions is a well studied topic in the combustion field [12-14]. Of particular relevance are the emulsions of water in distillate light and heavy oil fuels due to the valuable efficacy in the reduction of pollutants generated by oil combustion [13, 15]. The lower emissions are originated from different mechanisms in the liquid and gaseous phases. Firstly, the water keeps the droplet at a lower temperature, hence reducing the liquid phase pyrolysis responsible for the formation of cenosphere [16]. Then, sudden water vaporization causes explosions of droplets. The latter phenomenon, also called secondary atomization, generates smaller liquid droplets with beneficial effects on droplets combustion and also on cenosphere consumption. Finally, OH radicals provided by water in gaseous phase will inhibit the formation of soot and will also increase its oxidation [17]. On this basis, the natural presence of water in the POs represents a real benefit in the emissions formed during combustion of POs and POs based fuels like emulsions. However emulsion introduces several additional degrees of freedom, like concentration and size of the droplets of the dispersed phase (droplets of PO dispersed in light oil in the present case), percentage and composition of the emulsifier etc. and many work is carried out to optimise the process and the product [18,19].

Studies concerning the combustion of pyrolysis oil and pyrolysis oil based fuels are relatively scarce. However, the improvement of oil quality and emulsion technology is opening the way for a successful use of PO based fuels in furnaces, in turbines, as well as, in diesel engines [11,20,21]. Data on fundamentals of droplets combustion are therefore necessary. Previous studies were mainly devoted to infer the major features exhibited by pure pyrolysis oil droplets during combustion [9,22-26]. Aim of this paper is to report the experimental study on combustion of single droplets composed of emulsions of pyrolysis oil in diesel oil. The combustion of pure PO and light diesel oil are also discussed for comparison. The study was carried out at normal pressure in a single-droplet combustion chamber. The combustion behavior of droplets was followed by means of high-speed digital imaging based on a shadowgraph scheme. The droplets size ranged between 400 μm and 1200 μm. In this paper we concentrated our attention on the influence of the physical properties of emulsions, mainly the size of droplets of PO dispersed in the diesel fuel and on the percentage of PO used in the emulsion, on droplet combustion fundamentals.

Experimental results and procedures

Figure 1 shows the layout of the single droplet combustion chamber built up in order to study fuel droplets combustion. The chamber is equipped with four quartz windows besides

the gas inlet/outlet admission port. The four accesses allow different experimental procedures permitting the most adequate choice.

Fuel droplets were suspended to a bare thermocouple junction (type K, chromel-alumel, ϕ_{wire} = 75 μm). By means of the thermocouple, the temperature of fuel droplets during evaporation and combustion phases was inferred. Droplets were deposited on the thermocouple by using a Hamilton micro syringe for emulsions, light oil and pure compounds. Oil droplets were placed in position by using a thin (ϕ=76.5 μm) metallic wire being its viscosity too high to permit the use of a syringe. The frontal window was used as admission entrance to place the droplets on the suspension system.A high resistive coil, positioned just in front of the observation window and below the droplet hanging system, was used to ignite droplets.

The coil supply voltage triggered the high-speed imaging system and the acquisition chain. The trigger signal with the signals from thermocouple, pressure transducer and electrical coil supply were simultaneously acquired by a 4 channel transient recorder and stored on 3.5" diskettes. The synchronization lag between imaging system and signal acquired on the transient recorder was within 1 frame, i.e. ranged at maximum between 1 ms and 8 ms for imaging acquisition rates corresponding to 1000 frames/s to 125 frames/s, respectively.
Suspended droplets were typically not spherical. Especially the smaller ones assumed a marked ellipsoidal shape. This was observed during the initial phases of the tests. In fact, subsequently, the decrease of the surface tension due to the increases of temperature forced the droplets to assume a spherical shape. However, a not negligible vaporization could occur during this phase. Thus, the size of droplets was determined by assuming for them a revolution ellipsoid shape and measuring the two axes. The diameter of a droplet was then defined as the diameter of an equivalent sphere having the same volume of the ellipsoid. The droplet size expressed in pixels was then transformed in mm by a calibration based on the imaging of an object of known size like the quartz fiber or the thermocouple wires.

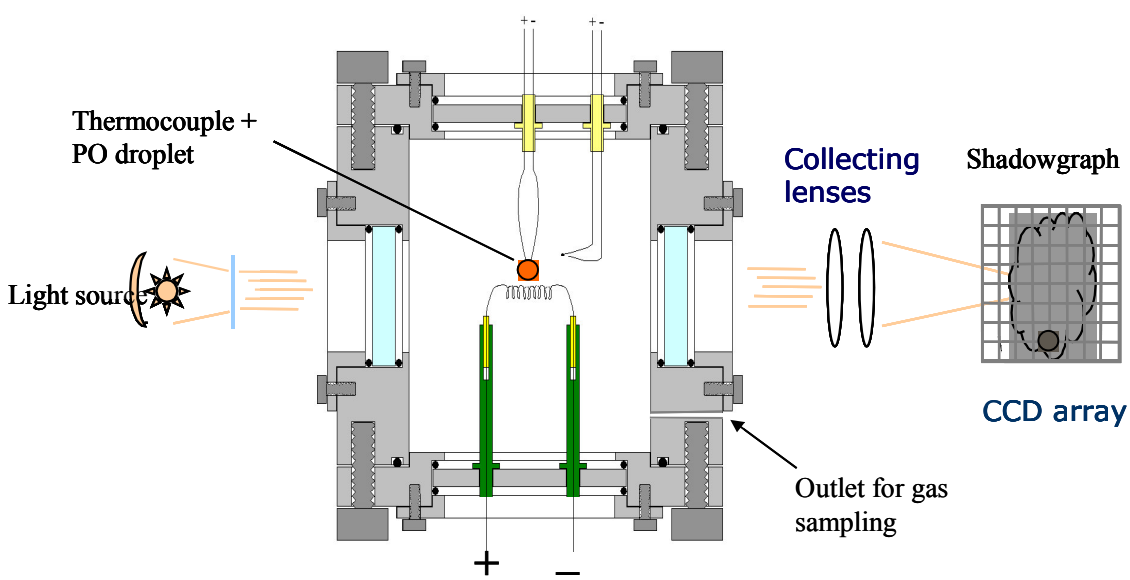

Figure 1 Single droplet combustion chamber experimental layout.

The shadowgraph technique was used to visualize the evaporation and combustion of fuel droplets. A lamp was utilized as light sources. An opaque paper was adjusted in front of the light source as a shield. A high-speed digital imaging system (*Motionscope* by Redlake) was

used to acquire the droplet shadowgraphs. The maximum acquisition rate of the system was 8000 frames per second. The digital size of the images and the total acquisition time were inversely proportional to the velocity of acquisition. Usually, a lower acquisition rate, between 500 and 1000 frames/s, was used. This choice allowed to have, simultaneously, a good resolution on the CCD's chip (in terms of pixels used to take images) and a time of acquisition long enough to follow the entire droplet heating-vaporization-combustion process. A PC was used to control the CCD system and store the captured image sequences.

Combustion of emulsions of PO in diesel oil

The combustion behavior of droplets of pure pyrolysis oil and two emulsions (A and B) were compared in the Single Droplet Combustion Chamber.

The emulsions were formed by CSGI (Florence) by using commercial diesel oil and PO provided by VTT Processes (Helsinki). Both the emulsions contain 30% wt of VTT pyrolysis oil in commercial light oil but they had different size distributions of the dispersed oil droplets. The emulsifier was 1% wt of oil in both the emulsions. Optical microscopy was used to study the oil droplet distribution in the emulsions. A qualitative analysis showed that emulsion named VTT-A contained mainly oil droplets of 10 μm. In emulsion VVT-B the size distribution was peaked at lower diameters (3-5 μm) notwithstanding droplets of 10 μm were also observed in the sample.

Figure 2 shows the temperature of droplets of pure PO and emulsion A having almost the same diameter. Both the curves start to increase when the heating is switched on and present a plateau around T=130°C. This corresponds to the vaporization of the lighter compounds, mainly water present in the PO. Thus, the different duration of the plateau for pure PO and emulsion can be ascribed to the different content of water in the two fuels being emulsion formed with 30% of oil. The plateau ends with droplets ignition.

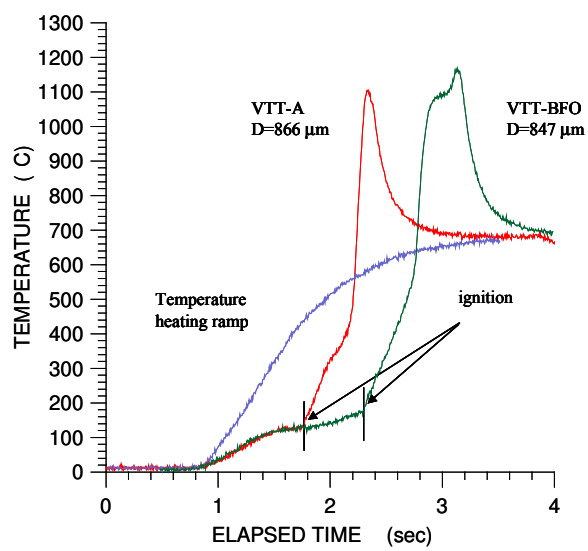

Figure 2 Temperature evolution of droplets of pure PO and emulsion 30%.

The second significant aspect is the large difference in the duration of the high temperature "bell shape" part of the curve that starts at a droplet temperature higher than 500°C. This part of the curve corresponds to the burning of cenosphere, i.e., the carbonaceous particles formed by liquid phase pyrolysis. Thus, the width of the bell curve corresponds to the quantity of solid carbonaceous residual that is formed. Light oils have a very low tendency to form carbonaceous residuals, less than 1% in wt. On the contrary, heavy fuels like PO are

prone to form carbonaceous residuals. Thus, the narrow high temperature peak, experienced by drops of emulsion, means a small formation of residual and it is in agreement with the limited content of oil in the emulsion. The large high temperature peak observed in oil drop combustion corresponds to the formation of large residual.

The high-speed shadowgraphy permitted to infer complementary information about the combustion behaviors of pure oil and emulsion droplets. Both pure oil and emulsion droplets experienced large swelling. However, emulsion droplets show in addition an accentuated sparkling explosions behavior producing few smaller droplets that escape away (fig. 3). This, if confirmed in dedicated experiments, is a relevant aspect to be studied because the occurring of secondary atomization ("microexplosion regime") is fundamental in the reduction of emitted particulate.

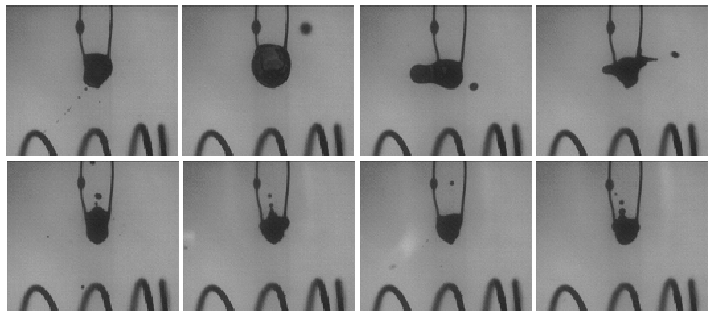

Figure 3 Images sequence of sparkling explosion of an emulsion droplet.

Figure 4 reports the thermal behavior of droplets of almost equal diameter of emulsions A and B. The curves are indistinguishable in practice. This shows that the two emulsions, despite the different size distribution of the dispersed phase, do not experience particular differences. A very similar behavior was also observed in the high speed shadowgraphy. Interesting enough, emulsion B presents a significant secondary atomization as already observed for emulsion A.

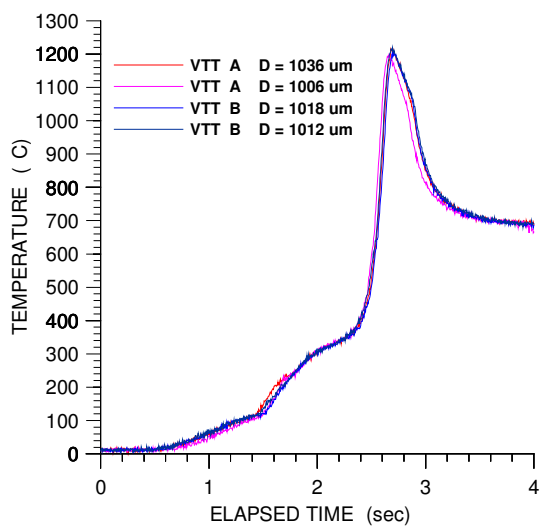

Fig. 4 Temperature evolution of droplets of emulsions A and B of similar diameter.

This series of tests suggests that the size of the dispersed phase (PO oil droplets) in the range of few microns is of relevance for occurring of the microexplosion regime rather than the specific size distribution.

In a successive series of tests, the combustion behaviour of emulsions with different PO concentration (10% and 30%, respectively) was compared with commercial diesel oil. Figure 5 shows selected images sequences relative to the combustion of pure PO (a), emulsion 30% of PO (b), and diesel oil (c), respectively. From the picture, it appears that the general combustion behaviour of emulsions is intermediate with respect to pure PO and commercial diesel oil.

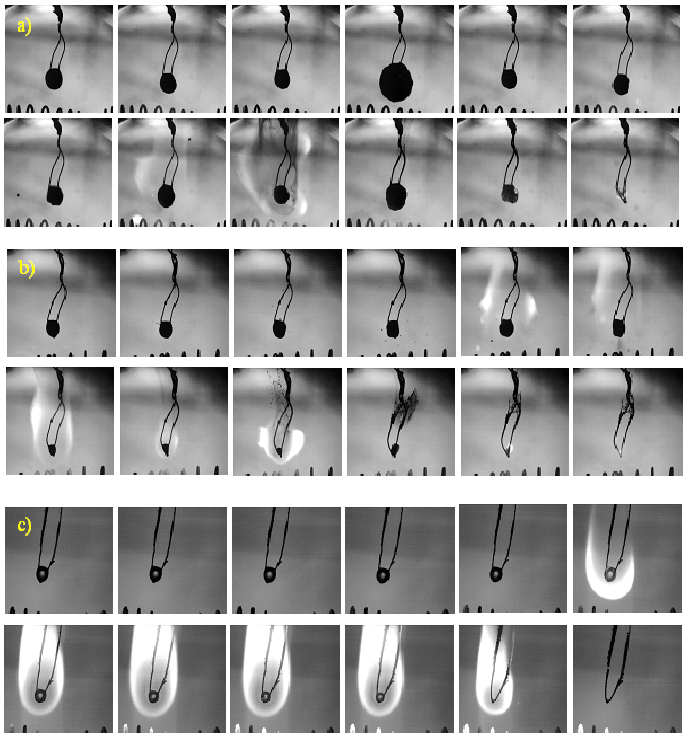

Figure 5 Images sequences relative to the combustion of pure PO (a), emulsion 30% of PO in diesel oil (b), and diesel oil (c), respectively.

The different phases suffered by droplets during their life are well shown in Fig. 6 where they are reported the temporal diameter reduction of droplets composed of diesel oil and emulsions. Initially droplets underwent a volume expansion of about 5%. After, the evaporation starts and strong and sudden variations of diameter are observed for emulsion droplets. This behaviour continues along all the burning phase even if less marked for 10% emulsion. The large diameter oscillations correspond to droplets swelling with subsequent expolsion and contraction. However, the median line of the curves for emulsions is very close to the diesel oil behaviour. This implies a similar overall burning time as well evidenced in figure 7.

Figure 7 reports the homogeneous combustion time for emulsions with PO concentration of 10% and 30%, respectively, and diesel oil droplets vs. droplet diameter at ignition. The homogeneous phase is defined as the time between the ignition of droplets and flame extinction. Interesting enough, the homogeneous combustion phase shows a similar trend for emulsions and diesel oil, despite the different structure of the flame and its time and spatial evolution as before discussed.

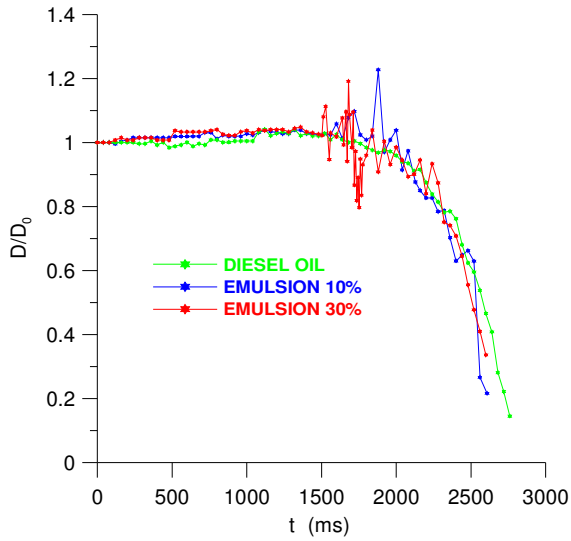

Figure 6 Temporal variation of diameter of emulsions and diesel oil droplets.

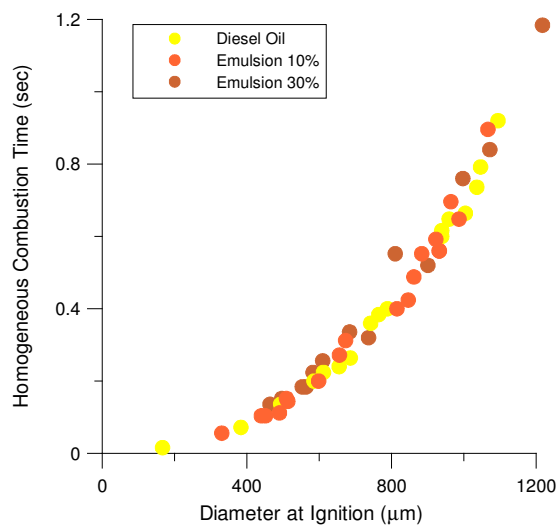

Figure 7 Homogeneous combustion time for emulsions and diesel oil droplets vs. droplet diameter at ignition.

Final Remarks

The preliminary results concerning the combustion of single droplets composed of emulsions of pyrolysis oil in diesel oil have been obtained. The combustion of pure pyrolysis oil and light diesel oil droplets are also discussed for comparison. The study was carried out at normal pressure in a single-droplet combustion chamber. Droplets size ranged between 400 µm and 1200 µm. The combustion behavior of droplets was followed by means of high-speed digital imaging based on a shadowgraph scheme. This series of tests suggests that: 1) the general combustion behavior of emulsions is intermediate with respect to pure PO and commercial diesel oil; 2) the size of PO oil droplets in the range of few microns is of relevance for occurring of the microexplosion regime rather than the specific size distribution; 3) the homogeneous combustion phase shows a similar trend for emulsions and diesel oil,

despite the different structure of the flame and also its time and spatial evolution.

Acknowledgements

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