

COMBUSTION BEHAVIOUR OF PYROLYSIS OIL/DIESEL OIL EMULSIONS

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ABSTRACT The study of renewable energy sources is an important topic in the field of the combustion science. Fuels obtained from biomasses could become a valid alternative to the use of fossil fuels, also in the light of the more and more stringent environmental constraints. In the outline of alternative liquid fuels, oils obtained from the pyrolysis of wood, generated recycling wood industry scraps, appear to be very promising as concerns their use in power plants and diesel engines. However, a commercial use of such "bio-fuels" requires a systematic study of the most suitable procedures for their handling, storage, and use. Emulsions of biomass pyrolysis oil can meet some of the fuel specifications required by the present standards. In this context, it is necessary to assess the combustion property of such kind of fuels prior to their introduction in the market. Aim of this paper is to report some preliminary results concerning the combustion fundamentals of droplets composed of emulsions of biomass pyrolysis oil in commercial diesel oil.

Keywords: flash pyrolysis, emulsions, combustion.

1 INTRODUCTION

Studies concerning the combustion of 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 [1-3]. Data on fundamentals of droplets combustion are therefore necessary.

Aim of this paper is to report the combustion fundamentals of droplets composed of emulsions of biomass pyrolysis oil (PO) in commercial diesel oil. The emulsions were prepared by mixing PO and diesel oil in appropriate conditions and in the presence of a proper additive [4]. The emphasis of the work is posed on: a) size of pyrolysis oil droplets dispersed in the light fuel oil; b) addition of water. In order to evaluate the influence of droplets' dimensions on the combustion properties of the emulsions, the size of the dispersed droplets was modulated through the variation of the surfactant and co-surfactant amount and ratio. On the other hand, emulsions containing an extra amount of water (5-15% wt) were prepared, making so possible to investigate the effect of water on the combustion process. All the emulsions were characterized in terms of size distribution of the dispersed droplets by means of optical microscopy and Quasi-Elastic Light scattering.

2 PREPARATION AND CHARACTERIZATION OF EMULSIONS

Emulsions are obtained from the dispersion of two immiscible fluids, in the presence of a proper surface-active agent. The dispersion produces a continuous phase and a finely dispersed droplet phase (droplets' size is normally between 300 nm and 10 μm). The emulsification process requires a significant amount of energy, related to the consistent increase of the interface between the two phases. This energy can be provided by different methods, such as ultra-sound treatment, high-energy mixing, high-pressure filtration, etc.

The emulsions investigated during this work were prepared according to a previously described method [4,5]. Briefly, PO and diesel oil were separately heated up to 70°C. The surfactant and the eventual co-surfactant were then dissolved into the Diesel oil. Once the dissolution was complete, PO was added to the diesel/surfactant solution and, still keeping the temperature at 70°C, the mixture was homogenized with the aid of an IKA Ultra-Turrax disperser. During this step, the high shear stress imposed by the disperser results in the formation of small PO droplets, that are then stabilized by the absorption of surfactant molecules at the diesel/PO interface (see Figure 1).

In order to evaluate the influence of the droplet size distribution on the combustion properties of the emulsions, a co-surfactant was used in the preparation of selected samples. This additive was dissolved together with the surfactant into the Diesel oil, but in significantly smaller amounts. The co-surfactant action consists in modifying the interface curvature through its interaction with the surfactant, resulting in the change of the size of the droplets.

It is well known that pyrolysis oils contain a 20-30% amount of water. Moreover, it has been shown that the emulsification of diesel oil and water results in improved combustion properties, especially in terms of lowered noxious emissions [6, 7]. Therefore, emulsions containing an extra-amount of water were prepared by adding different amounts of water to the emulsions prepared according to the procedure described in the previous paragraphs. The composition of the emulsions investigated in this work is reported in Table I, together with the droplets' mean diameter as obtained by combining optical microscopy and Fiber Optic Quasi-Elastic Light Scattering (FOQELS). While optical microscopy is a very well established technique in the analysis of size distribution of emulsion droplets, FOQELS deserves some words of comment.

Table I. Composition of the investigated samples.

Sample	PO	PO %wt.	Diesel %wt.	Surfactant %wt.	Co-surfactant %wt.	Water %wt.	Droplets' Mean Diameter
A	VTT	29.9	69.8	0.3			4 μm
B	VTT	29.9	69.8	0.3			10 μm
1	FORTUM	29.9	69.8	0.3	-	-	1.62 μm
2	FORTUM	28.6	66.75	0.4	-	4.25	7.34 μm
3	FORTUM	29.5	68.65	0.4		1.45	1.77 μm
4	FORTUM	29.85	69.65	0.455	0.045	-	0.70 μm
5	FORTUM	29.84	69.62	0.445	0.095	-	1.10 μm
6	FORTUM	29.86	69.67	0.45	0.02	-	0.96 μm

This technique recently introduced combines the fiber-optic (FO) detection and quasi-elastic light-scattering (QELS) to provide the particle size analysis of suspensions concentrated up to 40% by weight. Visible light from a laser diode is driven into the sample via a monomode fiber and the scattered light is collected by a second monomode fiber at an angle of 153°. The scattered light is analyzed using the established techniques of Dynamic Light Scattering (DLS) with a digital correlator. In the case of emulsions, the analysis of the resulting auto-correlation function of the scattered intensity provides the size distribution of droplets in the size range between 2 nm and 2 μm . When the droplet size approaches the upper limit, optical microscopy is the most appropriate technique.

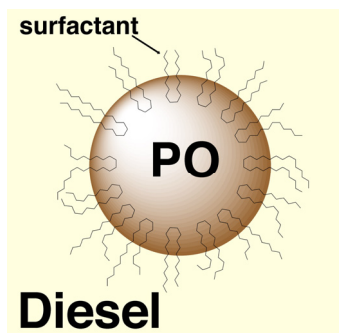


Figure 1. Sketch of a PO/diesel Oil emulsion: PO is dispersed in the form of droplets in the diesel continuous phase. Surfactant molecules are responsible for the stabilization of the interface.

3 SINGLE DROPLET COMBUSTION CHAMBER: EXPERIMENTAL SET UP AND PROCEDURES

Figure 2 shows the layout of the combustion chamber used for single droplets combustion [8]. The chamber is equipped with four quartz windows besides the gas inlet/outlet admission port. Fuel droplets are suspended at the central thermocouple. It is a bare junctions Pt/Pt-Rh $\phi=76.2 \mu\text{m}$ wire. The lateral thermocouple is an identical bare junctions Pt/Pt-Rh but $\phi=50.8 \mu\text{m}$ wire. By means of the suspension thermocouple, the temperature of fuel droplets during evaporation and combustion phases is inferred.

A variable luminosity lamp is utilised as light source to form the shadow. A high-speed digital imaging system (*Motionscope* by Redlake) is used to catch the droplet shadowgraphs. The maximum acquisition rate of the system is 8000 frames per second. However, an acquisition rate of 500 frames/sec with a shutter 1/10,000

sec was used in the tests. A microcomputer was used to control the CCD system and store the captured images sequences.

The signals from the thermocouples were acquired by means a transient recorder. The trigger of the acquisition chain (i.e., transient recorder and the CCD high speed imaging system) was given by the temperature measured by the suspension thermocouple.

Suspended droplets were ignited by a high resistive coil placed just below the droplet and electrically powered. By varying the applied voltage and the distance of the coil from droplets it is possible to vary the heating ramp in terms of temperature increase rate and maximum attained value.

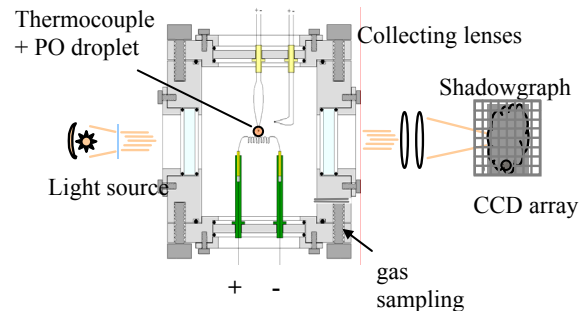


Figure 2: Experimental layout of the combustion chamber utilized in the single drop combustion tests

4 COMBUSTION TESTS

Combustion tests were carried out on emulsions and on pure pyrolysis oil (PO) and diesel oil (DO) used to form emulsions. The general thermal behavior of emulsion was intermediate between PO and DO, presenting characteristics of both the parent fuels. This is shown in Fig. 3 where the temperature of droplets of emulsion (PO 30% wt in DO), PO and DO of similar diameter (about 1 mm) is showed. All curves start to increase when the heating is switched on. After this increase the curves of PO and emulsion present a bend characterized by a flat plateau for the PO droplet. This corresponds to the vaporization of the lighter compounds, mainly water present in the PO. The evident difference of the plateau for pure PO with respect to the emulsion is due to the different content of water in the two fuels, the emulsion containing 30% of pyrolysis oil.

This heating/vaporization phase ends with the ignition of the droplets. Up to ignition, characterized for all droplets by a strong temperature increase, the temperature of DO droplets increase continuously as expected for a

multicomponent fuel with no predominance of a specific compound. It's interesting to note the large difference in the duration of the high temperature "bell shape" part of the curves that start at a droplet temperature higher than 500°C for PO and emulsion droplets. This part of the curve corresponds to the burning of cenosphere, i.e., the carbonaceous particles formed by liquid phase pyrolysis [9-11]. 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 [12]. On the contrary, heavy fuels like POs 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 a large residual. The small bump in the curve of DO does not correspond to the burning of a residual. It is due to the migration of heat from the wires of the thermocouple (heated by the flame around the droplet) toward the bare junction at the end of the homogeneous combustion (burning of the liquid fuel).

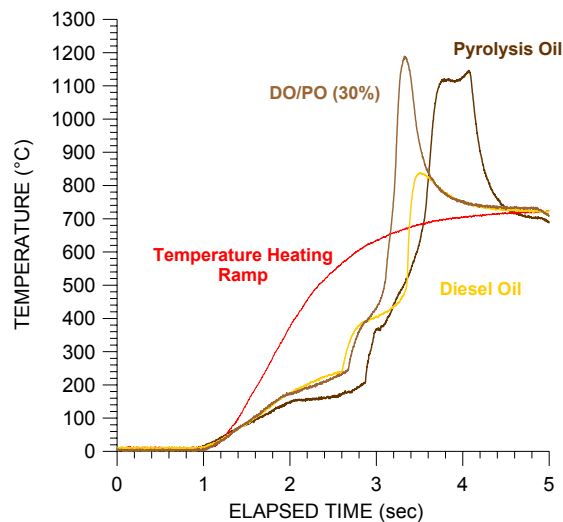


Figure 3: Measured temperature of 1 mm droplets of pyrolysis oil, diesel oil and 30% wt PO/DO emulsion.

One of the most peculiar features of PO combustion is the marked swelling due to the vaporization of light compounds inside the droplets [9-11]. This phenomenon is of strong interest because it can originate the explosion of droplets with consequent diameter reduction (secondary atomisation) and, finally, marked benefits on reduction of pollutants [6,7]. However, the effectiveness of the process is still not well studied in the case of PO emulsions.

In dedicated experiments, the micro-explosive behaviour of emulsions was therefore studied. Tests were carried out on two emulsions based on a PO provided by VTT (see Table I). Both the emulsions contained 30% wt of VTT pyrolysis oil in commercial light oil but they had different size distributions of the dispersed droplets. The emulsifier was 1% wt of oil in both the emulsions. By means optical microscopy it was qualitatively ascertained that one emulsion contained (emulsion A)

mainly oil droplets of 10 μm . In the other emulsion (emulsion B), the size distribution was peaked at lower diameters (3-5 μm) although droplets of 10 μm were also observed in the sample. Figure 4 reports the thermal behavior of droplets with similar diameter composed of the two emulsions. The curves are indistinguishable in practice. This shows that the general combustion history of the two emulsions, despite the different size distribution of the dispersed phase, does not experience marked differences. A very similar behavior was also observed in the high speed shadowgraphy where significant secondary atomization was observed for both emulsions. 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 the establishment of microexplosion regime rather than the specific size distribution.

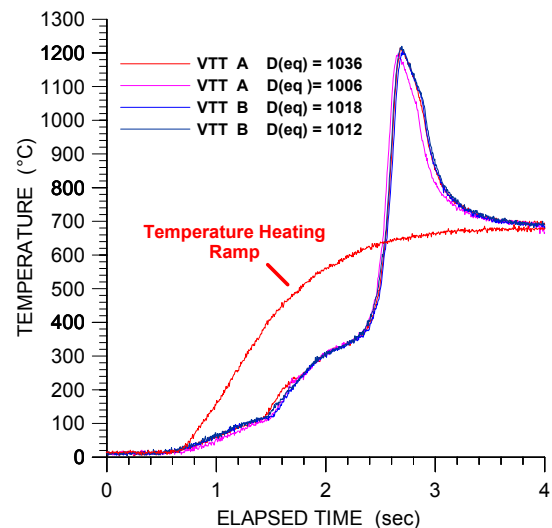


Figure 4: Thermal behavior of droplets composed of emulsions A and B of almost identical diameter.

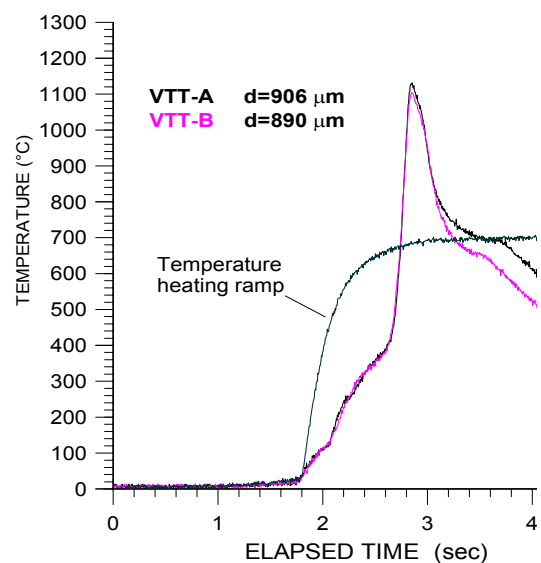


Figure 5: As in Fig. 4 but with higher heating rate.

Additional tests were carried out to study the effect of a fast heating rate on the burning behavior of emulsions A and B. When a higher heating rate is used, the processes are accelerated but the behavior of emulsions A and B remains identical (Fig. 5).

Fuels obtained from biomasses could become a real alternative to fossil fuels if they can meet some of fuel specifications required by the present standards. Besides the economics, a real penetration of such kind of fuels requires chemical and physical characteristics comparable with the corresponding fossil fuels. The fuel burning rate is one of the specifications to meet in order to use a PO based fuel in commercial combustors designed for fossil fuel. This aspect was studied by performing combustion experiments on the matrix of emulsions detailed in Table I. In particular, it was analysed the homogeneous combustion time that represents the time between droplet ignition and flame extinction. Figure 6 reports the homogeneous combustion time vs. the initial droplet diameter for the different emulsions.

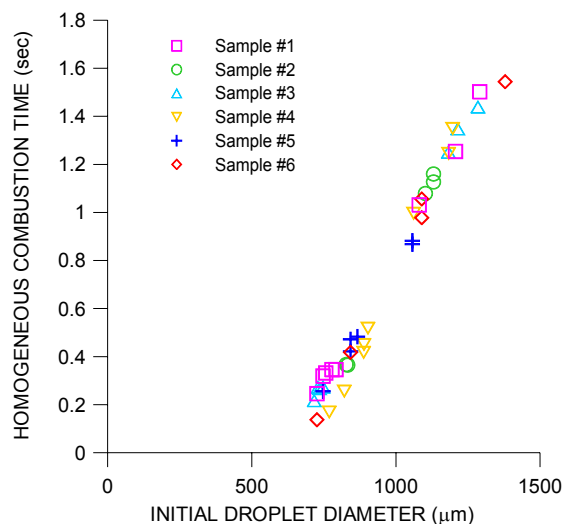


Figure 6: Homogenous droplet combustion time vs. initial droplet diameter for the different emulsions in Table I.

It is very interesting to note that emulsions show a similar behaviour. Moreover, when the homogeneous combustion time is plotted as a function of the droplet diameter at ignition, the showed trend is identical to diesel fuel also for emulsions containing different PO concentrations. This observation can bear relevant applicative fallout: in fact, the attention in the formulation of emulsions can be focused to other features of the fuel, like ignition, swelling and micro-explosions.

5 FINAL REMARKS

The combustion behavior of droplets of PO/DO (30/70 wt) emulsions was studied. The emulsions differed for the size distribution of the dispersed phase (PO droplets) and the water content. Tests were carried out in a single droplet combustion chamber. The size of droplets varied between 500 µm and 1500 µm.

Aim of the tests was to investigate the influence of the structure of emulsions on their combustion behaviour. The main results were: a) The general thermal behavior

of emulsion was intermediate between PO and DO; b) the size of the dispersed phase (PO oil droplets) in the range of few microns was of relevance for the establishment of microexplosion regime rather than the specific size distribution; c) the homogeneous combustion time of emulsion droplets was identical for all emulsions.

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REFERENCES

- [1] Jay, D. C., Sipilä, K. H., Rantanen, O. A. and Nylund, N. O., Wood pyrolysis liquid for diesel engines. In International Combustion Engines, Vol. 25-3, Fall Technical Conference, ASME, 1995.
- [2] Gust, S., Combustion experiences of flash pyrolysis fuel in intermediate size boilers, in *Developments in Thermochemical Biomass Conversion*. Bridgwater, A.V. and Boocock, D.G.B., Ed.s; Blackie Academic & Professional, London 1997, pp.481-488.
- [3] Bertoli, C., D'Alessio, J., del Giacomo, N., Lazzaro, M., Massoli, P., Moccia, V.: *Running Light-Duty DI diesel engines with wood pyrolysis oil*, SAE paper 2000-01-2975 (2000).
- [4] Baglioni, P.; Fratini, E.; Ricceri, R.; Sarti, G.; Chiamonti, D.: *Engine fuels consisting of an emulsion comprising mineral and/or natural oils, their preparation and use in internal combustion engine*, Patent WO0102516.
- [5] Chiamonti, D.; Bonini, A.; Fratini, E.; Tondi, G.; Gartner, K.; Bridgwater, A. V.; Grimm, H. P.; Soldaini, I.; Webster, A.; Baglioni, P. *Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines - Part 1: emulsion production*, Biomass & Bioenergy 2003, 25, 85-99.
- [6] Mattiello, M., Cosmai, L., Pistone, L., Beretta, F., Massoli, P., 24th Symp. (Intern.) on Combustion, Experimental evidence for microexplosions in water/fuel oil emulsions flames inferred by laser light scattering, p. 1573-1578, The Combustion Institute, 1992.
- [7] <http://www.pirelliambiente.com/>
- [8] Calabria R., Chiariello F., De Bellis V., Massoli P., Combustion fundamentals of pyrolysis oil based fuels, 4th Mediterranean Combustion Symposium, Lisbon, October 6-10 2005, paper IV.8.
- [9] Wornat, M. J., Porter, V. G., and Yang, N. Y. C., Energy & Fuels 8 (1994) 1131-1142.
- [10] Shaddix, C. R., and Huey, S. P., Combustion characteristics of fast pyrolysis oils derived from hybrid poplar in *Developments in Thermochemical Biomass Conversion*. Bridgwater, A.V. and Boocock, D.G.B., Ed.s; Blackie Academic & Professional, London 1997, pp.465-480.
- [11] D'Alessio, J., Lazzaro, M., Massoli, P., Moccia, V., Twenty-Seventh Symp. (Intern.) on Combustion, p. 1915-1922, The Combustion Institute, 1998.
- [12] Massoli, P., D'Alessio, A., Beretta F., Combust. Sci. Technol. Vol. 72, p. 271 (1990).