STUDY OF THE MICRO-EXPLOSION TEMPERATURE OF WATER IN OIL EMULSION DROPLETS DURING THE LEIDENFROST EFFECT

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Abstract
To burn water in oil emulsions (W/O) is considered as an effective alternative to bring out waste oil because of a significant reduction in carbon monoxide, nitrogen oxides and particulates in the exhaust. These advantages have different origins, an important contribution is provided by the phenomenon of micro-explosion. In this work, the influence of the size of the dispersed water droplets (D_{32}), for three iso-water emulsion, in the micro explosion phenomenon is studied by the *hot plate* technique. The temperature of the emulsion droplet and the visual evolution of the samples are evaluated using a synchronized thermocouple/CCD system.
The results show that the size distribution of the dispersed water droplets plays an important role in the phenomenon of micro explosion. Moreover, some internal phenomenon as the separation process between water and oil seems to be discriminate.

Introduction
Today, stocks of fats and oily waste from animals and plants are subject to grow up because of the increasing production of food industries. These residues have a very important energy potential not too different from conventional fuels such as diesel [1]. However, these products have a fatty acid content of up to 70% by mass [2] and it is impossible to burn them because of the production of a large amount of pollutants.
To burn water in oil emulsions (W/O) is considered as an effective alternative to bring out waste oil [3,4]. Several authors have worked on the use of emulsified products in boilers or internal combustion engines. The results show a significant reduction in carbon monoxide, nitrogen oxides and particulates in the exhaust [1,5,6]. These improvements are correlated with the presence of water during the combustion process. These advantages have different origins, an important contribution is provided by the phenomenon of micro-explosion.
When a W/O emulsion droplet is heated in a flame, in function of several variables (differences in boiling point, water content, pressure) [7], its temperature could exceed the water boiling point maintaining it in liquid phase. This condition is called metastable state and not any change in phase appends until the limit of stability is reached:

$$\left(-\frac{\partial P}{\partial V}\right)_T = 0 \Rightarrow K_T \rightarrow \infty \qquad (1)$$

The isothermal compressibility diverges and the change in phase occurs. In a macroscopic system this limit is strongly affected from small perturbations as spontaneous molecular fluctuations [7]. The metastable state is broken by nucleation of small embryos of the new phase by homogeneous or heterogeneous process [8,9]. At this point, the nucleation rate strongly increasing for a minimum rise in temperature leading to a vigorous expansion of the

vapor phase. The energy so released spreads out the surrounding oil, resulting in a fragmentation into numerous and smaller droplets. In this way the combustion is more complete and effective.
A large scientific effort has been devoted to the experimental observation of the phenomenon of micro-explosion. Where the study of micro-explosion is focused on a single drop of emulsion, the experimental techniques are multiple and classified in terms of heterogeneity of the vaporization process as a measure of the intrusiveness of the measurement systems: the suspended droplets techniques [10,11,12] and the dropping tower technique [13,14] are considered respectively the most and the less intrusive ones. An alternative experimental approach is offered by the technique of the heating surface. As a matter of the fact, it is possible to observe the phenomenon of micro-explosion by placing an emulsion droplet on a hot surface. In this condition the drop levitates on its own steam by Leidenfrost effect and, due to surface forces, it retains a spherical shape [15,16].
Although the results in the literature clearly reveals the influence of some key variables (pressure, temperature, water volume, etc.,) on the delay and the rate of micro-explosion [17,18, 19], remain incomplete concerning the effects of the size of the dispersed phase on the phenomenon.
Recent new experimental results, concerning the effect of the features of dispersed water droplets in the micro-explosion effect of a W/O emulsion droplet [20], drew our attention to the interesting aspects of the temperature evolution during the micro-explosion phenomenon.
This work aims to experimentally study, by the heating surface technique, the "thermal history" and the image evolution of the W/O emulsion droplet from its setting on the hotplate until the micro-explosion.

Experimental setup

The experimental setup consists of five main elements: the hot plate, the temperature and the image acquisition system, the synchronization system and the emulsions.

Hot plate

This part consists in a little hot surface in Aluminum (*5.7mm* in diameter) electrically heated upon which the droplets are placed during the tests by a syringe. The temperature of the hot surface was checked out by a thermocouple arranged at the position of *0.25 mm* under the center of the surface and it was maintained at 636 k to obtain the Leidenfrost effect for each test.

The temperature acquisition system (thermocouple)

The used Thermocouple is a *K type*. The two conductors are placed in a protective tube made of alumina and the hot junction exceeds the protective tube of *2mm*. The cold junction is left at room temperature that is considered as the reference. The thermocouple signal, which is read by an oscilloscope, is polluted by a certain "noise" given by the interference of the system with the environment. For this reason, it is necessary to introduce a low-pass filter. The filter was built considering the resistance of the thermocouple ($R=216\ \Omega$) and a condenser ($C=10\mu F$). This results in a cutoff frequency (f_c) of 73*Hz*. The thermocouple was calibrated by comparing the measurements obtained using a digital thermocouple reader and the simultaneous signal (*V*) read by the oscilloscope. The cold junction temperature is *18.5 ° C* that it corresponds to a voltage of *0.48mV*. The calibration results in a linear law of the thermocouple as shown in Figure 1. The thermocouple can be precisely positioned by a micrometric displacement system with three degrees of freedom in the directions of axes X, Y, Z.

Image acquisition system

The images were acquired by a High Speed Camera (CCD) Quick Star LaVision 6 using the shadowgraphy technique. The subject of the image is located between the camera and the light source, and it is placed behind a semi-transparent philter of *2 mm* thick which aims to evenly distribute the light. In this way it is possible to observe the shadows of the opaque bodies that not allow to the light to reach the sensitive part of the camera. The light source consists of a *50W* halogen spot placed at *55mm* from the focus plan. With this technique it is possible to achieve high frequency acquisition (*50kHz*) and/or very large image magnifications, according to an appropriate modulation of the halogen spot power, Figure 2.

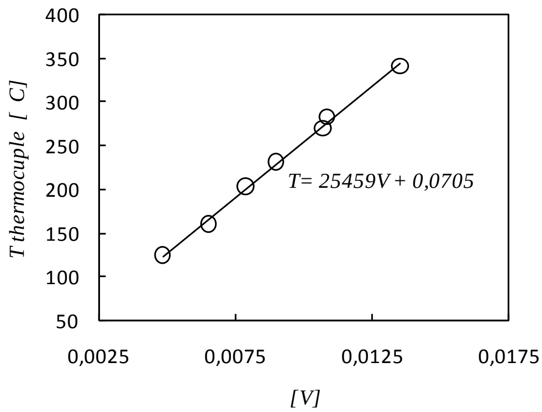


Fig. 1 Calibration of the thermocouple: linear correspondence between temperature and voltage.

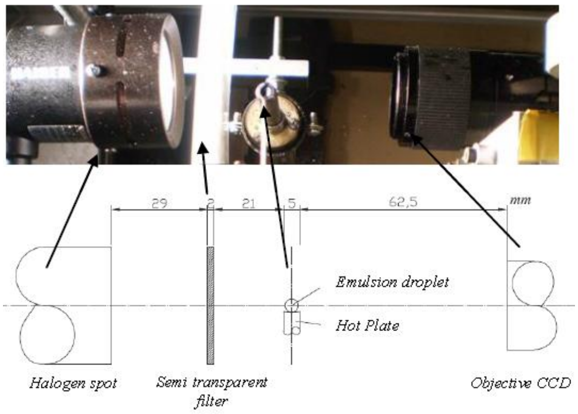


Fig. 2 Shadowgraphy disposition.

Synchronization system

The image acquisition system is synchronized with the thermocouple. The trigger of the camera records images in a continuous cycle (mode: Stop at the last frame). When the phenomenon occurs, the trigger-in signal is sent to the controller of the high speed camera. At this point the acquisition starts and the image sequence, preceding the start signal, is stored in memory. The start signal, also sent to the channel *CH2* of the oscilloscope by trigger-out, starts the acquisition of the voltage signal coming from the thermocouple by channel *CH1*. The oscilloscope is programmed to store the signal for 8 seconds: 4 seconds before and 4 seconds after the outbreak of the acquisition of the camera. The trigger system is shown in Figure 3.

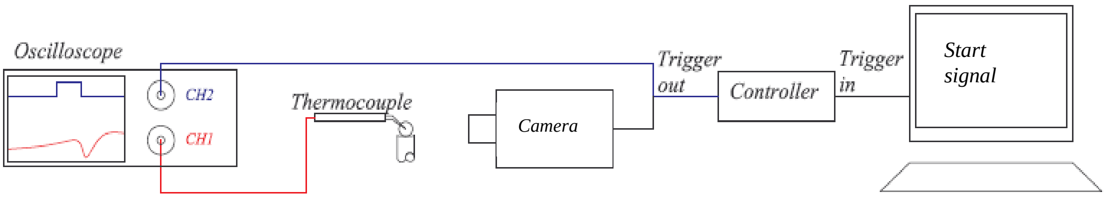


Fig.3 Trigger system.

The emulsions

All the emulsion are obtained by a stirrer working at *400rpm* for *60min* using sunflower oil, distilled water and a surfactant characterized by an HLB index of *3.7* (*Span83*). Three emulsions containing the same amount of water ($30\%_{mass}$) were selected. The emulsions are listed according to the size of the dispersed water droplets and this feature has been estimated using a microscope equipped by suitable image treatment software. The Sauter mean diameter

(D_{32}) is used to classify the size of measured droplets. Two of the three considered emulsions represent the most extreme cases of distribution (D_{32}): finely dispersed (fine emulsion) and coarsely (thick emulsion) dispersed. The third emulsion is considered as an intermediate (medium), (Tab.1).

Table 1. Features of the emulsions.

	Mass [%]			Averaged size
	Oil	*Surfactant*	*water*	D_{32} *[µm]*
Fine emulsion	*60*	*10*	*30*	*2 - 4*
Medium emulsion	*65*	*5*	*30*	*5 - 9*
Thick emulsion	*67,5*	*2,5*	*30*	*17 - 20*

Results

Once the plate reaches its set temperature ($T_{hotplate}=363°C$) and the image acquisition system is ready to record, a droplet of emulsion is placed on the test section using a syringe (needle *0.4 mm* in diameter). After a variable residence time of the droplet on the hot surface, the micro-explosion occurs. The noise generated by micro-explosions is the input that makes start recording the signal coming from the thermocouple by the oscilloscope. A typical signal supplied by the thermocouple is shown in Figure 4.

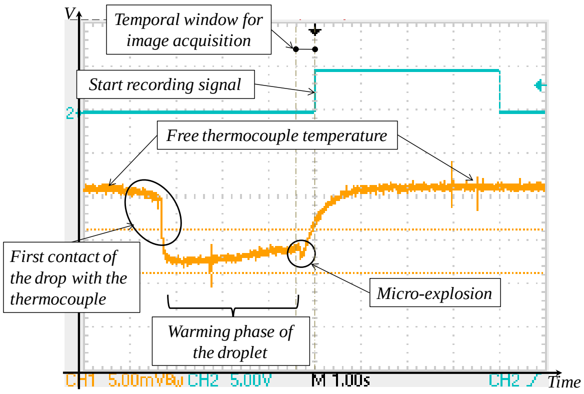


Fig.4. Signal recorded by the oscilloscope during experimental trials.

The signal is then translated into temperature using the formula given below:

$$\Delta T = a\Delta V \tag{2}$$

Where : $\Delta T = T_{mesured} - T_{reference}$ corresponds to the difference in temperature between the hot junction (measured temperature) and the cold junction (reference temperature $T_{reference}= 18.5°C$); $\Delta V = V_{mesured} - V_{reference}$ corresponds to the voltage difference between the hot junction (measured voltage) and the cold junction (voltage reference $V_{reference} = 0.4$ *mV*); $a = 25.459°C/V$ is the correlation between voltage and temperature obtained during calibration of the thermocouple. In this way we can evaluate the "thermal history" of an inner point of the emulsion droplet during the tests.

The experience begins with the thermocouple indicating a stable temperature of *296.5°C*. The droplet of emulsion is then approached to the thermocouple and placed on the hotplate. From the first contact between the droplet and the hot junction, the oscilloscope reads a significant drop in temperature: the temperature can drop to about *44 ° C* in a very short time (*0.12s*). This decrease is due to the fact that the emulsion sample is at room temperature (*18.5°C*).

From that moment, the emulsion droplet begins to heat up. This heating phase is interrupted by the violent evaporation of the dispersed water droplets. The instant of the micro-explosion is followed by a sudden drop in temperature that, depending on the emulsion feature, is between *22* and *81°C*. When the thermocouple is discovered because of the spreading of the oil, the oscilloscope shows the temperature rising until reach the initial temperature. This phase lasts about *2.5* to *3* seconds.

The images of the evolution of the drop are recorded over a period of between *0.4* and *0.8* seconds before the time of triggering, and the data obtained from the thermocouple were associated with the images.

It should be noted that, because of the phenomenon of micro-explosion is extremely fast, the image acquisition rate should be very high, (*50kHz*). However, the acquisition rate of the oscilloscope is limited to *0.25kHz*, which corresponds to an acquisition every *4ms*. This means that at each time interval, between data provided by the thermocouple, it corresponds a set of *200* images.

The results for the three emulsions tested (thick, medium, very fine) are reported and analyzed.

Thick emulsion (Figure 5):

The initial drop in temperature, resulting from contact between the sample and the thermocouple, is followed by a rising temperature time of 6 seconds. The temperature rises end tends to stabilize at about *92 ° C*. The micro-explosion appends at *95°C*.

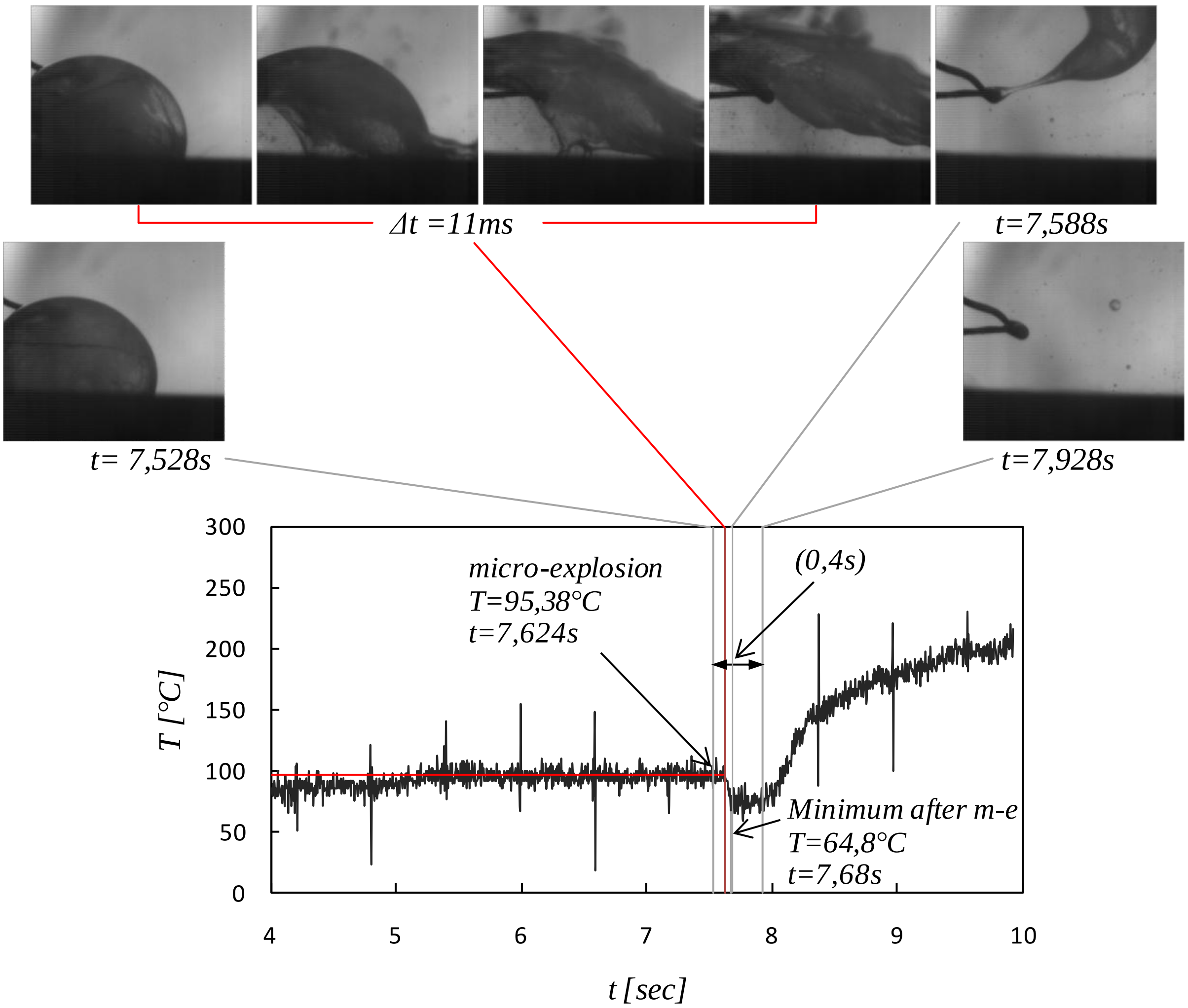


Fig. 5. Evolution of temperature and images: thick emulsion.

From the image sequences we can see that the emulsion droplet is almost entirely separated from the thermocouple after *11ms*. At this point, we observe a drop of *30 ° C* in temperature followed by a gradual increasing until the initial temperature. This increase appears to be limited by the fact that the thermocouple is in contact with the oil, even after the violent fragmentation given by vaporization of water (as shown in the image at time *t = 7.588 s*).

Medium emulsion (Figure 6):
From a qualitative point of view, the phenomenon shows the same behavior of the previous experiment. Quantitatively, however, it is evident a sharp rise in temperature which leads at *T = 199°C* the micro-explosion temperature, and then a sharp drop in temperature to about *T = 118°C* (*ΔT = 81°C*). In addition, the micro-explosion occurs in a very short time and after *1.4 ms*, the drop is completely fragmented by micro-explosion.

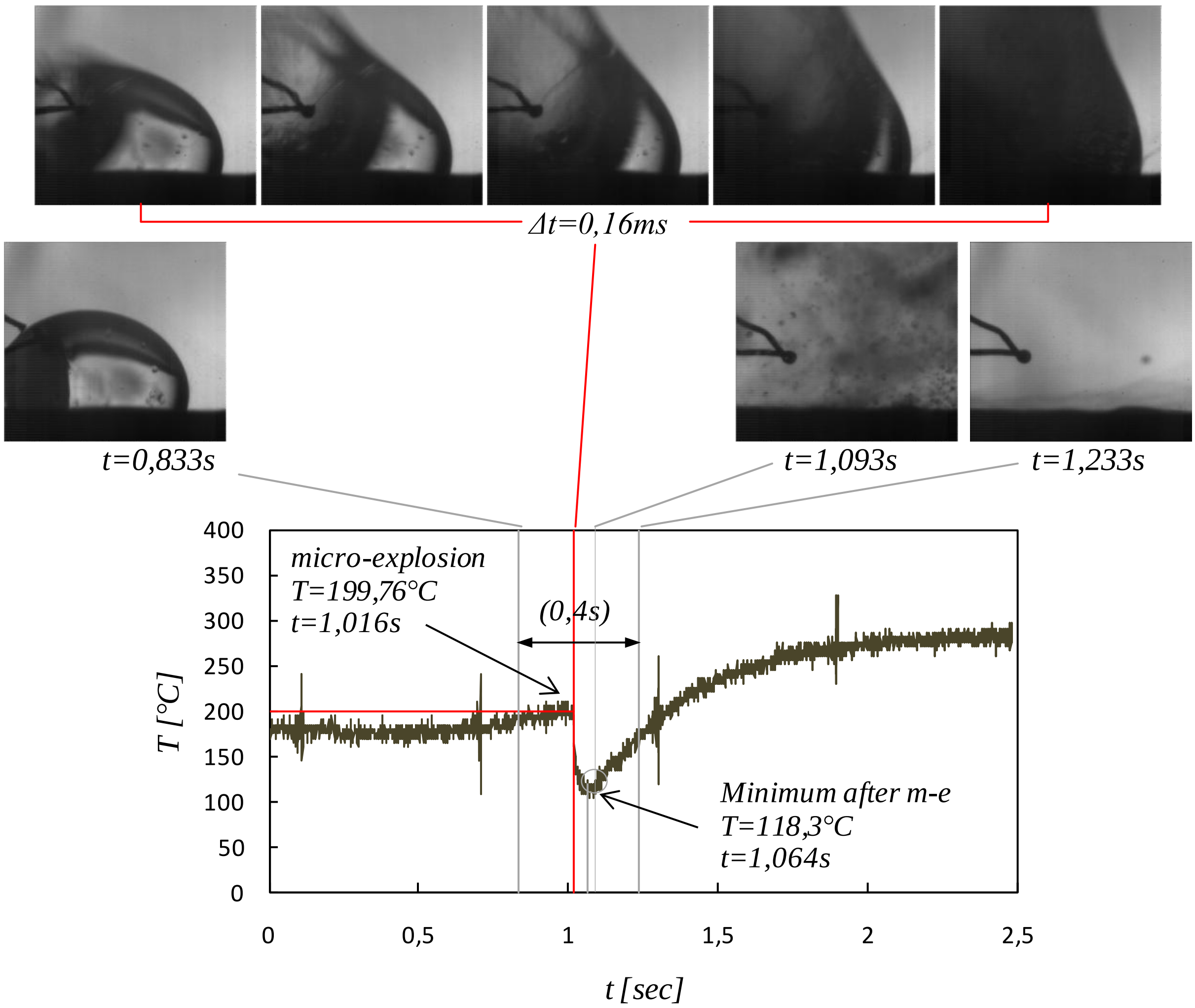


Fig.6. Evolution of temperature and images: medium emulsion.

Fine emulsion (Figure 7):
It should be noted that the micro-explosion temperature (*133°C*) is followed by a more moderate decrease in temperature compared to the previous cases (*ΔT = 20°C*).
In the sequence of images of the micro-explosion, we can see that the phenomenon is slightly slower than in the previous case. Indeed, the emulsion separates from the thermocouple in about *2 ms*.

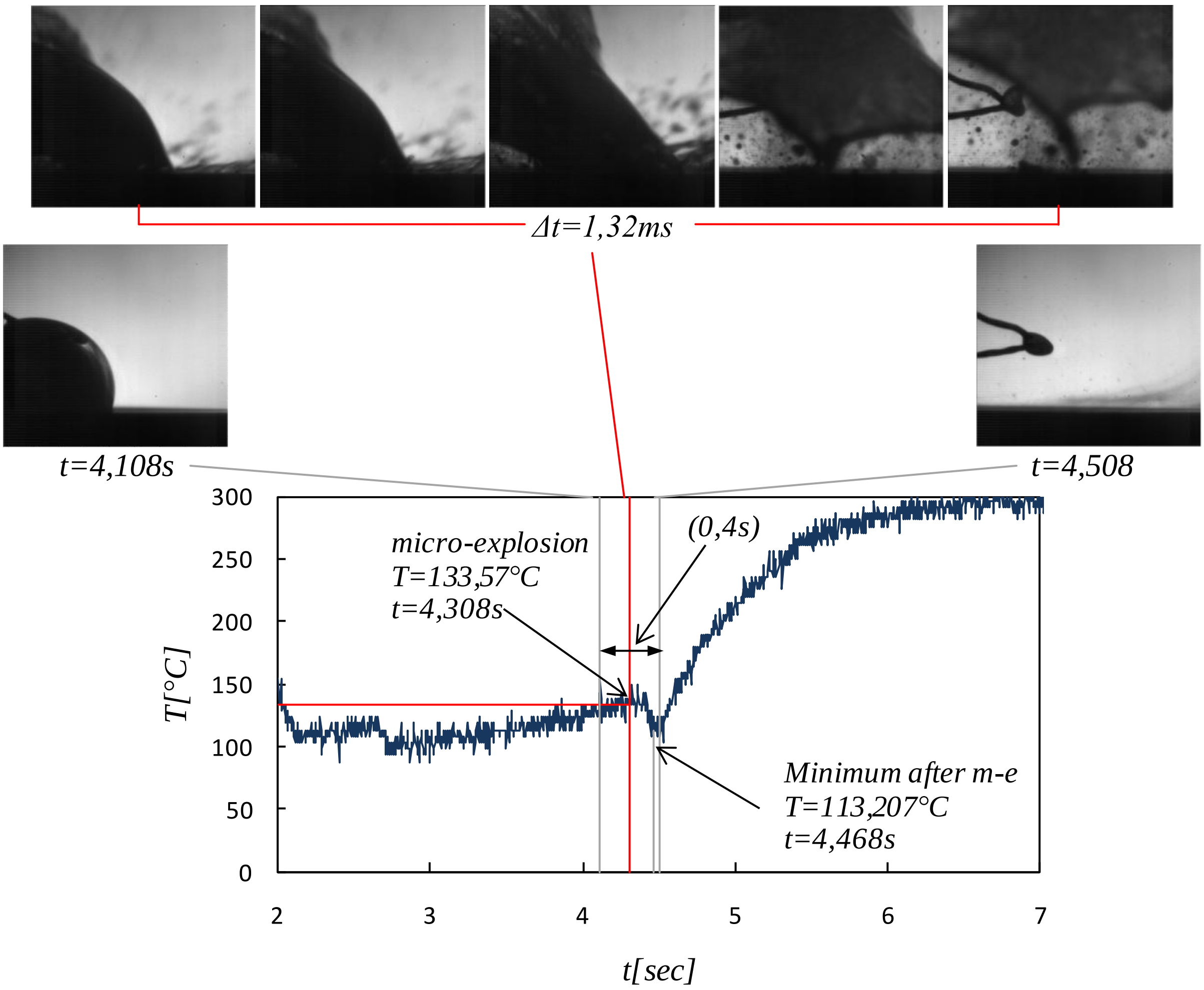


Fig. 7. Evolution of temperature and images: fine emulsion.

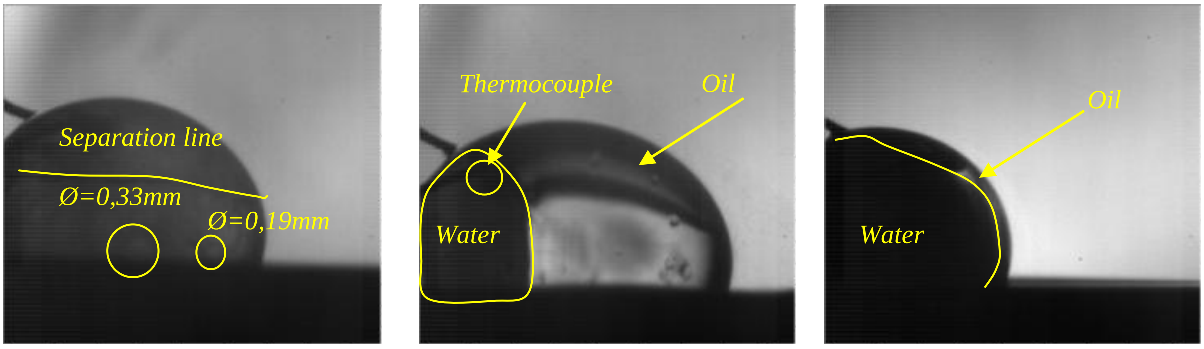
Consideration

Significant differences were noted between the three tests. The main points concern: a) temperature of micro-explosion, b) time of the phenomenon, c) oil-water separation.

Concerning the thick emulsion, the temperature of the micro-explosion is less than 100° C. We can explain this value considering that the hot tip junction of the thermocouple is placed in the upper hemisphere of the droplet. This leads us to believe that at the moment just before the micro-explosion, the difference in temperature existing between the bottom and the top of the emulsion droplet is not less than *5°C* (at atmospheric pressure, the water vaporization temperature is *100°C*). In addition, we argue that inside of the emulsion droplet it has reached a high level of coalescence (Figure 8: *thick*): dispersed water droplets between *0.33* and *0.19 mm* in diameter. There is also a clear line of separation between oil and all the coalescing water droplets. Under these conditions it is supposed to have a temperature of equilibrium liquid-vapor slightly close to *100°C*. Another important aspect is that the head of the thermocouple is immersed in the oil-water mixture. In this condition, the water can find a large external surface that can promote heterogeneous nucleation and thus to anticipate the phenomenon of vaporization.

By reducing the size of the dispersed water droplets (Figure 6), we obtain a very high temperature of micro-explosion (about *200°C*) as proof of a really state of metastability of water. In addition, the evolution of the phenomenon is very rapid and it seems to affect the fragmentation effect generated by the micro-explosion. Concerning the separation between oil and water, in this case, the coalescence appears to be partly achieved. In fact, the slight

cloudiness of the water accumulated on the left side of the drop appears as a partial separation obtained by creaming effect (Figure 8: Medium).
The last case (Figure 7) is intermediate concerning both, the micro-explosion temperature and the speed of the phenomenon (Figure 9). Regarding the effects of separation, the complete opacity reveals that there was no coalescence and probably, the separation results just from creaming effect (Figure 8: *fine*).



Thick *Medium* *Fine*

Fig. 8. Images acquired before the micro-explosion.

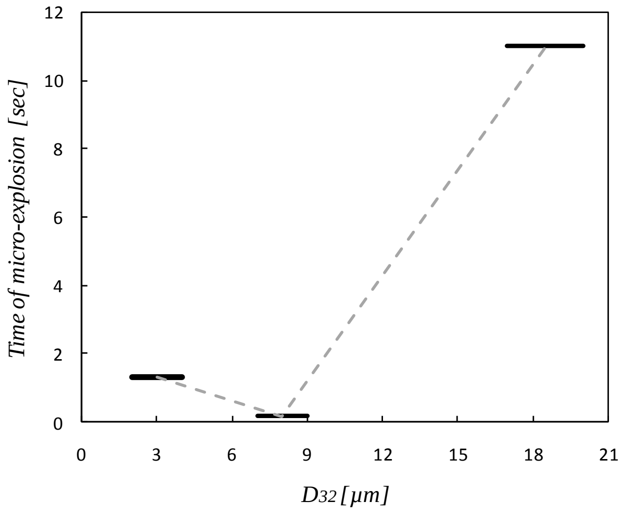


Fig. 9. Variation of the micro-explosion time (time between the onset of m-e and the moment when the thermocouple is not any more in contact with the droplet) Vs D_{32}.

The evolution of temperature for the three emulsions in the vicinity of the micro-explosion is shown in Figure 10a.

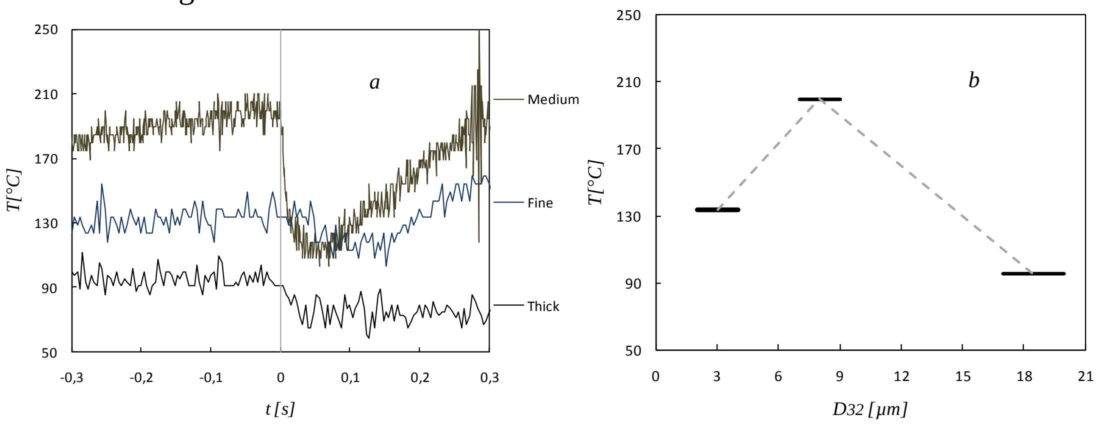


Fig. 10. : *a*) Temperature Vs time ; *b*) Micro-explosion temperature Vs D_{32}.

The results of this experiments show that the temperature of the micro-explosion depends on the size distribution of dispersed water droplets. As shown in Figure 10.b, a size reduction of dispersed droplets corresponds to a rising temperature that reached a maximum matching with the Medium emulsion. In the case of finer dispersed emulsions, the temperature of micro-explosion tends to decrease. This result seems to be in accord with the tendency reveled by Mura et al. [20].

Conclusion

The temperature evolution of three emulsions "iso-water", characterized by different distributions of dispersed water droplet size, was studied by a thermocouple inserted inside of a droplet under Leidenfrost effect. The experimental equipment was coupled and synchronized to a CCD system. The combination of both techniques allowed observing the phenomenon of micro-explosion with the temperature evolution of the sample.

The results show that the temperature of micro-explosion is related to the distribution of the dispersed water droplets. In fact, reducing the size (D_{32}), the temperature of micro explosion rises to a very high level, highlighting an important degree of metastability of the liquid water. Reducing the diameter (D_{32H2O}), it was noted that the temperature of micro-explosion tends to decrease. This behavior seems to confirm recent experimental results [20].

An important role seems to be played by the phenomena of separation within the emulsion droplet. From the images, it was found that if the D_{32} is high, the coalescence phenomenon is predominant. When the distribution becomes finer, the coalescence becomes less important and so the creaming becomes dominant. Thus in the case of the emulsion with a distribution of very fine droplets, the separation occurs only by the effect of making the micro-explosion less effective.

Nomenclature

a	Coefficient of thermocouple	$[T/V]$
C	Capacity	$[F]$
D_{32}	Sauter mean diameter	$[\mu m]$
f_c	Cut off frequency	$[Hz]$
K_t	Isothermal compressibility	$[Pa^{-1}]$
P	Pressure	$[Pa]$
R	Electric resistance	$[\Omega]$
T	Temperature	$[K]$
t	Time	$[s]$
V	Volume	$[m^3]$
V	Tension	$[V]$
W/O	Water in oil emulsion	

References

[1] A.Kerihuel, M.Senthil Kumar, J.Bellettre, M.Tazerout. Mise en Evidence de la Micro-explosion dans un Moteur Alimenté par une Emulsion d'eau dans l'huile. Effect sur la Réduction de Polluants. *Congrès Français de Thermique, SFT* île de Ré, (2006).

[2] A.G. de Suoza, J.C.Oliveira Santos, M.M.Conceiçao, M.C.Dantas Silva, S.Prasad., A Thermonanalytic and Kinetic Study of Sunflower Oil. *Brazilian Journal of Chemical Ebgineering*. 21 pp.265-273, (2004).

[3] C.Ritzoulis, N.Scoutaris, K.Papademetriou, S.Stravoulias, C.Panayiotou, Milk Protein-Based Emulsion Gels for Bone Tissue Engineering. *Food Hydrocolloids*, 19, pp. 575-581, (2005).
[4] A.Kerihuel, M.S. Kumar, J.Bellettre, M.Tazerout, Use of animal fats as CI engine fuel by making stable emulsions with water and methanol. *Fuel*, 84, pp.1713-1716, (2005).
[5] A.Kerihuel, M.S. Kumar, J.Bellettre, M.Tazerout, Ethanol Animal Fat Emulsions as a Diesel Engine fuel. P.1: Formulations and influential parameters. *Fuel*, 85, 17-18, pp.2640-45, (2006).
[6] M.S. Kumar, A.Kerihuel, J.Bellettre, M.Tazerout, Effect of Water and Methanol Fractions on the Performance of a CI Engine Using Animal Emulsion as Fuel. IMECHE *J.Power and Energy*, 219, pp. 583-592, (2005).
[7] P.G. Debenedetti. Metastable Liquids, Concepts and Principles. *Princeton Univ. Press*, Princeton, NJ, (1996).
[8] Brereton, G.J. Crilly, R.J. Spears, J.R. Nucleation in Small Capillary Tubes. Chemical Physics, 230, pp.253-265, (1998).
[9] Caupin, C. and Herbert, E. Cavitation in Water: a Review. C.R. Physique, 7, pp.1000-1017, (2006).
[10] R.Calabria, F.Chiariello, V.De Bellis, P.Massoli, Combustion of Pyrolysis Oil Based Fuels. *MCS4 Lisbon*, (2005).
[11] R.Villasenor, F.Garcia, An Experimental Study of the Effects of Asphaltenes on Heavy Fuel Oil Droplet Combustion, *Fuel*, 78, pp.933-944, (1999).
[12]D.Segawa, H.Yamasaki, T.Kadota, H.Tanaka, H.Enomoto, M.Tsue. Water-Coalescence in a Oil-in-Water emulsion droplet burning under microgravity. *Proceedings of the Combustion Institute*, 28, pp.985-990, (2000).
[13]C.H.Wang and C.K.Law, Microexplosion of Fuel Droplets Under High Pressure, *Combustion and Flame*, 59, pp.53-62, (1985).
[14]C.H.Wang, W.G.Hung, S.Y.FU, W.C.Huang, C.K.Law, On the Burning and microexplosion of Collision-Generated Two-Componentdroplets: Immiscible Fuels. *Combustion and Flame*, 134 pp.289-300, (2003).
[15]T.Kadota, H.Tanaka, D.Segawa, S.Nakaya, H.Yamasaki,. Microexplosion of an Emulsion Droplet During Leidenfrost Burning. *Proceedings of the Combustion Institute*, 31, pp.2125-2131. (2007).
[16]K.Kimoto, Y.Owashi, and Y.Omae, The Vaporization Behavior of the Fuel Droplet of Water-in-Oil Emulsions on the Hot Surface. Bulletin of JSME, Vol.29 (1986), pp.4247-4255.
[17]Segawa, D. Tanaka, H. Enomoto, H. Kadota, T. Yamasaki, H. Phase-Separation Inside a Burning Droplet of Oil-in-Water Emulsion. *Proc ISME* Tokyo, 2, pp.511-516, (2000).
[18]Segawa, D. Yamasaki, H. Kadota, T. Tanaka, H. Enomoto, H. Tsue, M. Water-Coalescence in an Oil-in-Water Emulsion Droplet Burning under Microgravity. *Proceedings of the Combusti on Institute*, 28, pp.985-990, (2000).
[19]Kadota, T. Tanaka, H. Segawa, D. Nakaya, S. Yamasaki, H. Microexplosion of an Emulsion Droplet During Leidenfrost Burning. *Proceedings of the Combustion Institute*, 31, pp.2125-2131, (2007).
[20] E.Mura, C.Josset, K.Loubar, G.Huchet, J.Bellettre, Effect of Dispersed Water Droplets in Micro-Explosion Phenomenon for Water in Oil Emulsion, *Atomization and Sprays*, 20, 9, pp.791-799, (2010).