‘A continuous water-in-oil emulsification process for an immediate valuation’.

Short Abstract

The development of alternative fuels and the perpetual search for improved combustion have led to the use of water as a dispersed phase in liquid biofuels. The emulsified fuel is intended to supply internal combustion engines, turbines and boilers. Dispersed water plays both a thermal and a mechanical role to optimize combustion and reduce emissions of polluting gases and particulates. The aim of this work is the design of a micro-fluidic mixer which allows continuous emulsification and can be integrated in-line in the process. The developed mixer, referred to as impact and elbow jet micro-system, is realized on the basis of a specific sizing of the microchannels, adapted to the respective flow rates and to the nature of the fluids to be emulsified.

Extended abstract of the PhD thesis of Arab Belkadi entitled "Experimental study of liquid-liquid fractionation in microchannels for the continuous production of emulsified biodiesel”.

1- Context and introduction to the work :

The objective of this study is to propose a continuous emulsification system designed and dedicated especially to water-in-oil emulsions. Targeted applications concern the field of energy conversion, such as turbines, boilers and internal combustion engines in general. This work is based on the known fact that the presence of a small fraction (less than 20%) of finely emulsified water (droplets of the order of 5 to 10 µm) in the fuel makes it possible to improve the atomization, to lower the combustion temperature and thus reduce the emissions of polluting gases and particles resulting from poor combustion. The continuous phase may be of various natures, such as conventional diesel, heavy fuel oil or lipid waste (used vegetable oils, animal fats). The constraints associated with the envisaged applications are numerous: the nature of the fluids, the fluid volume ratio in the emulsion, the need to design a compact process that allows the flows necessary for the operation of the internal combustion engines to be processed. This work has been oriented towards the proposal of a system based on the use of channels of sub-millimeter size (Dh <1 mm) and using the principle of a confined impinging flow.

Research in the field of microfluidics has been very active for two decades and shows in particular an interest in the development of emulsification processes [C.-C. Zhao (2011), H. † Schubert (2004)]. The state of the bibliographic art shows a large number of studies which deal with emulsification processes essentially applied to oil-in-water (h / e) mixtures [T. Nisisako (2009), N. Kiss (2011)]. This type of dispersion is considered to be less demanding in emulsification energy, due to the use of an aqueous phase (low viscosity) as a continuous phase. Unquestionably, the water-in-oil (e / h) emulsification processed in this work requires optimization from an energy point of view for two main reasons: the viscosity of the continuous phase is 50 to 70 times higher than that of the dispersed one (water) and secondly the range of capillary numbers investigated is about 1000 times higher than that usually explored in the scientific literature [Belkadi (2015), C.-X. Zhao (2011), T. Nisisako (2002b), T. Nisisako (2002a)].

The first work dedicated to the use of impinging jets in order to realize a liquid-liquid dispersion of immiscible fluids is carried out by Mr. Tamir [A. Tamir (1985), Kiljanski (2004)]. In this work, the emulsion is obtained from two sprays that are produced by two injectors disposed in an opposite way within the same chamber.

Later, the presence of impinging jets is demonstrated and studied in confined systems, based on the use of micro-channels with high fluid flow rates [N. Ait-Mouheb (2010), N. Ait Mouheb (2010)]. The first studies carried out on this subject concerned the mixing of miscible fluids. The efficiency of such systems as micromixers has suggested the idea of extending their use to the fractionation of immiscible fluids, such as sunflower oil and water, to form water-in-oil emulsions (e/h) [S. Nedjar (2011), A. Montillet (2013)]. However, the tested basic configuration needed to be improved as the pressure drop through the system was rather important (about 20 bars) and the granulometry of the obtained emulsion did not meet the one targeted in the present work.

Inspired by the above-mentioned research, the Ph D thesis of Arab BELKADI had as an objective to propose and test improved designs of microchannels allowing meeting the characteristics of w/o emulsions presented above. Achieving this objective implied to understand the phenomena governing the fluid splitting in the microsystems implemented with high flow-rates. Therefore the work of the Ph D thesis was developed along two axes:

- An academic one consisting of the development of methodologies allowing characterizing the flow typology and the fractionation mechanisms in microchannels based on impinging flow. Two methodologies were therefore used: the flow visualization with a high speed camera and an optical diagnostics based on a hand-made optical bench.
- A technical one which consisted of designing and testing microsystems. This axe was dependent on the first one as it was continuously fed but the results obtained by it.

2- Main results obtained during the Ph D thesis of Arab BELKADI

The first investigations mainly concerned the necessity to characterize the flow phenomena that drives the formation of the emulsion in the microsystems. Inspired by the above-mentioned research [Montillet (2013)], a slightly modified version of the formerly tested micro-systems was realized. Shortened channels and an expanded cross-section (see Figure 2) were selected so as to diminish the pressure drops [A. Belkadi (2012)]. In a first step, the microchannels machined on this micro-system base, had a square cross-section of 600 µm side (see FIG 1 and 2).

In order to reduce the volume fraction of the water (ϕe) and to enhance a swirl flow favoring the fractionation of the filaments or drops of dispersed phase, the cross-section of the water inlet channel has been reduced compared to the section of the three other channels of the microsystem. The channel of the oil entrance and the two outlet channels for the emulsion had the same cross section. Four different combinations of cross sections, respectively "200µm-600µm", "300µm-600µm", "200µm-800µm" and "300µm-600µm" have been realized and tested. A 3D representation of one of these microsystems, designated as "300-600" is given in FIG. 3.

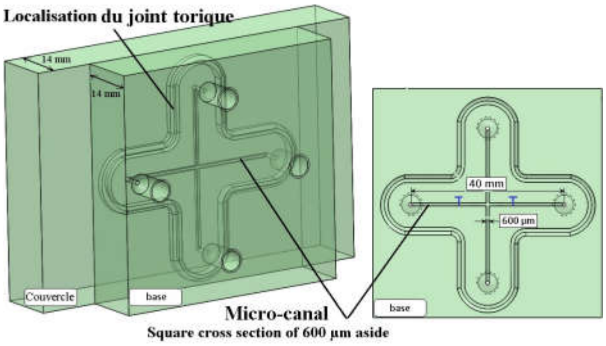


FIGURE 1 – 3D representation of the microsystem "600-600".

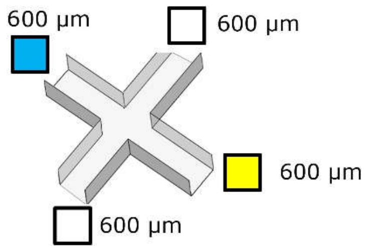


FIGURE 2 –3D view of the impingement area of the micro-system "600-600". (the blue square features the section of the water inlet channel and the yellow square features that for oil. The other channel carries the emulsion).

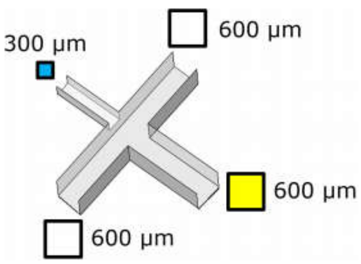


FIGURE 3 – 3D representation of the microsystem "300-600" (the blue square features the section of the water inlet channel and the yellow square features that for oil. The other channel carries the emulsion).

Their efficiency versus the production of water-in-oil emulsions (w/o) was compared. The "300-600" micro-system distinguished itself by its remarkable emulsification capabilities compared to the three other micro-systems. The flow visualization allowed observing the formation of a wounded structure in the impingement area; this one is stretched as a long filament of water along the two outlet channels.

Figure 4 provides a schematization of the typical wound structure (swirl) developed by the impact of the two fluids and Figure 5 presents an example of real flow visualization.

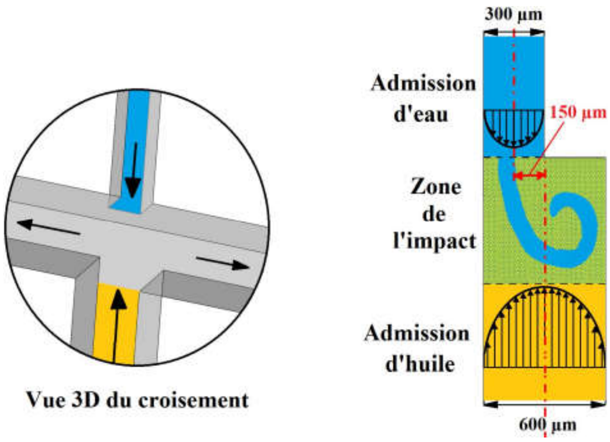
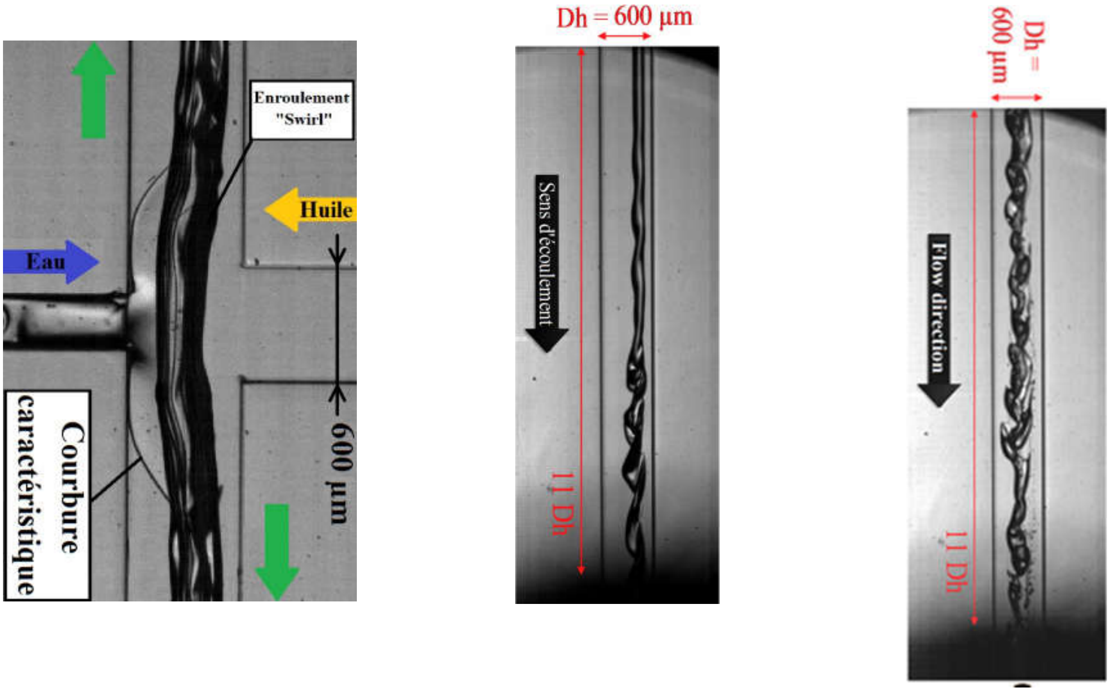


FIGURE 4 – Representation of 3D flow structures in the impingement area of the microsystem "300-600".



a) b) c)

FIGURE 5 – a) at the left: example of visualization of a typical flow structure in the impingement area of the microsystem "300-600". The water arrives from the left and the oil phase from the right of the picture (acquisition frequency of the picture: 10 kHz; water flow-rate: 9,7 mL/min and sunflower oil flow-rate : 74,0 mL/min).b) at the middle: stretching of the wounded structure (water) in the first 6 mm of a 40 mm outlet channel (same flow conditions). C) at the right: view of the wounded structure in the first 6 mm of a 40 mm outlet channel water flow-rate: 15.17 ml/min and sunflower oil flow-rate : 67.33 ml/min.

In the outlet channels, filaments and water droplets are surrounded by sunflower oil. In order to further investigate, we have focused our interest on the winding formed at the center of the cross and on its extension and fractioning in the outlet channels of emulsions. This was achieved using a hand-made optical bench as well as a high speed camera. Both techniques gave concordant results.

In particular, using the high speed camera allowed pointing out the appearance of irregular shapes on the surface of this winding (see Fig. 5-b). This is due to a rotational movement, superimposed on an advection (transport) movement in the direction of the two outputs of the micro-system simultaneously. An increase in the flow rate of the dispersed phase accelerates the rotation (accentuating centrifugal force) and advection to the outlets (Fig. 5-c). The micro-system "300-600" makes it possible to achieve an average dispersion diameter (d10) of 10 µm with a continuous phase containing 13% by volume of butanol and an average diameter (d10) of 30 µm with a continuous phase (sunflower oil) without additives (surfactant). In the range of flow-rates investigated, the present emulsification process consumes one per thousand of the lower calorific value (PCI) of the produced liquid fuel.

The variation of the mean diameter of water droplets in the emulsions obtained with the microsystem “300-600” are plotted in Figure 6 as a function of the capillary number. The capillary number expresses the viscous to capillary forces ratio in the liquid-liquid flow. A dimensional analysis and the development of a physical model lead to two dimensionless equations that allow predicting the mean diameter of droplets [Belkadi (2015)] (Figure 7).

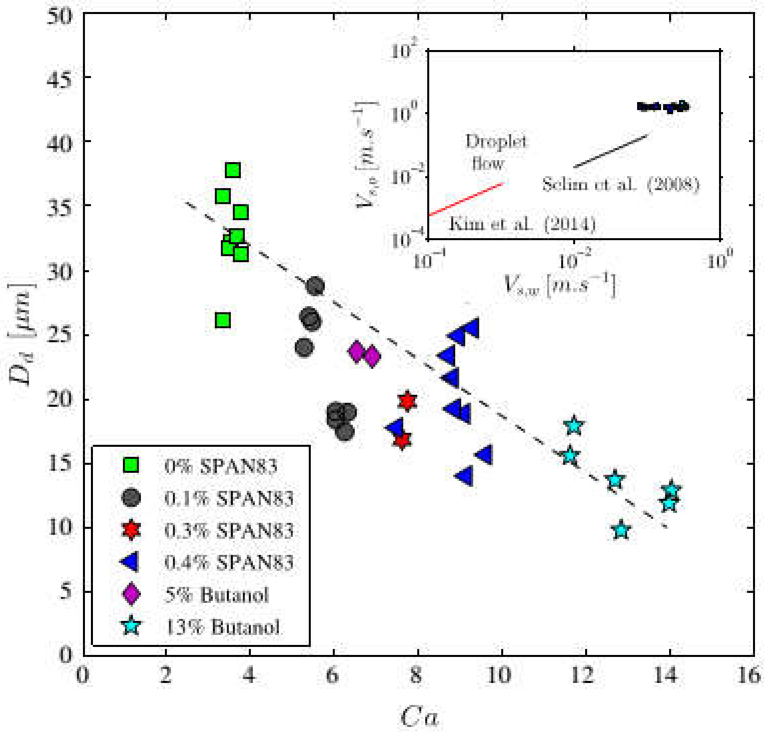
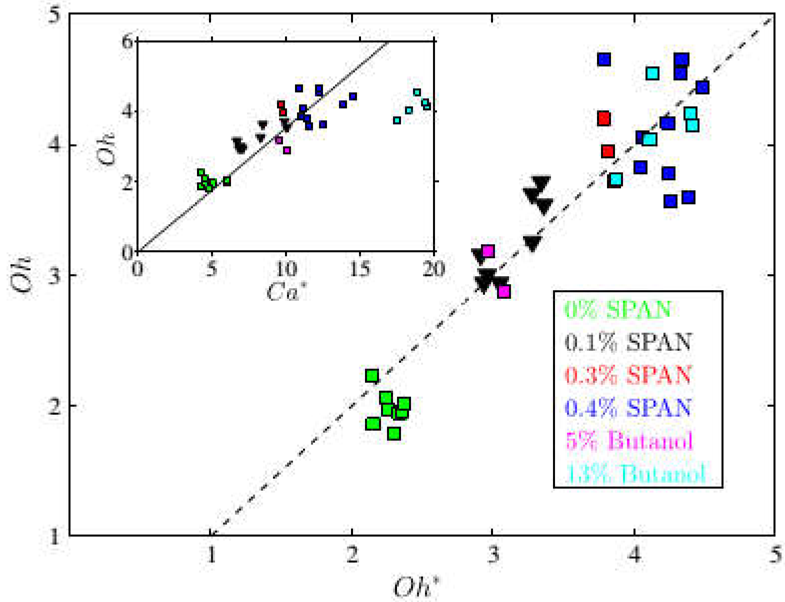


FIGURE 6: variation of the mean diameter of water droplets in the emulsions obtained with the microsystem “300-600” as a function of the capillary number. Oil phase is sun flower oil with adjunction or not of surfactant or adjunction of butanol.



$$Ca = \frac{v\,\mu_o}{\sigma_{w-o}} \qquad Oh = \frac{\mu_o}{\sqrt{\rho_w\, D_{-1}\, \sigma_{w-o}}}$$

Equation (1) proposed from dimensional analysis (-----) :

$$Oh^* = 0.1 \left(\frac{V_o\,\mu_o}{\sigma_{w-o}}\right)^{0.68} \left(\frac{\mu_o}{\mu_w}\right)^{0.53} \left(\frac{Q_w}{Q_w + Q_o}\right)^{0.1}$$

Equation (2) based on the consideration of the onservation of mechanical energy downstream the impinging zone (______):

$$\frac{\mu_o\, V_{eq}}{\sigma_{w-o}} = Ca^* = \sqrt{8}\,\frac{\mu_o}{\sqrt{D_{-1}\,\rho_w\,\sigma_{w-o}}}$$

FIGURE 7: Comparison of the Ohnesorge number Oh (Eq. (1)) with experimental Oh obtained from the "300-600" impinging flow. The equation obtained from the theoretical conservation of mechanical energy $Ca^* = 8^{1/2}$ Oh (Eq.(2)) is also compared to experimental data.

Keeping in mind that it was difficult, when using pure sun flower oil as the oil phase, to meet the ideal range of water droplets size needed to enhance a better combustion in the engines or boilers, it was necessary to improve again the design of the microsystem. The idea was then to use two microsystems in series so as to quantify the benefit brought by the treatment of the emulsion with a second impingement involving the two fluxes of emulsion from the first microsystem (Figure 8). The PhD thesis of Arab Belkadi then finished with some tests using this configuration.

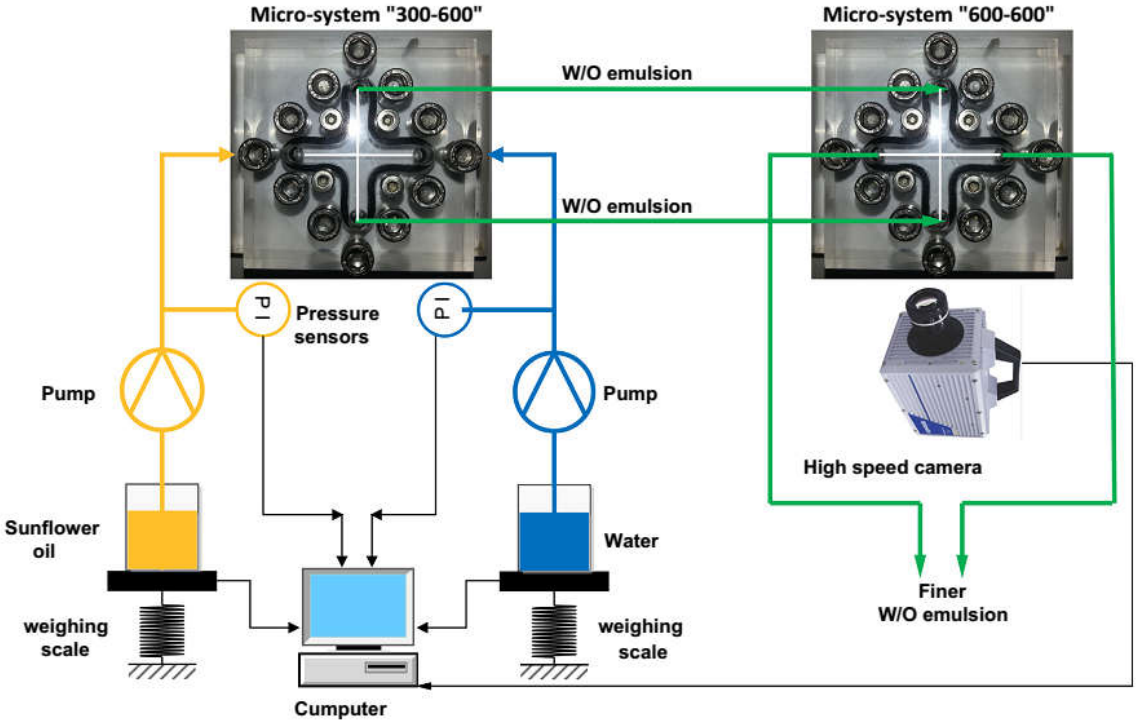


FIGURE 8: Schema of series arrangement of two micro-systems ‘‘300–600’’ and ‘‘600–600’’.

It was verified that the series of two micro-systems allowed reaching higher levels of interface surface area per emulsion volume unit (Figure 9).

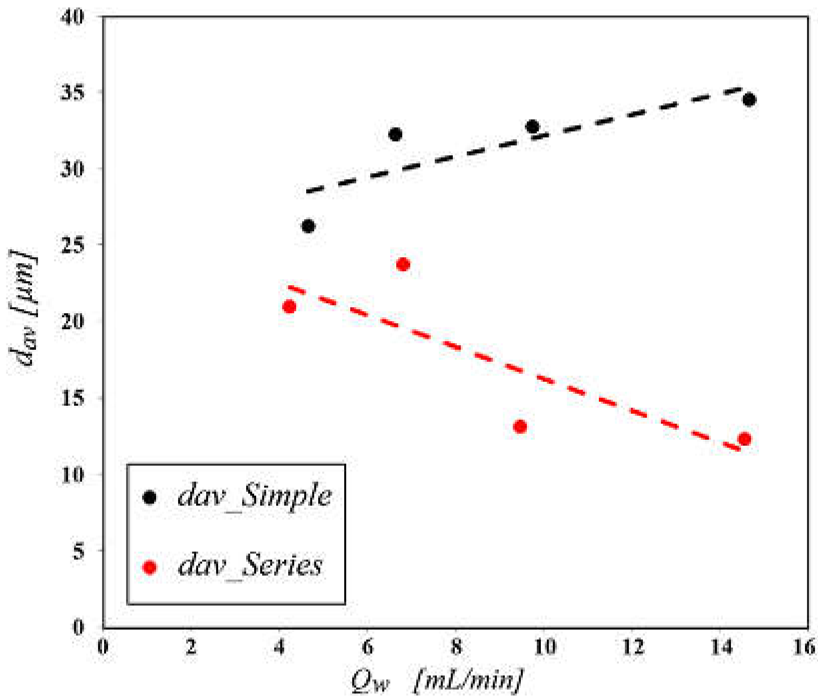


FIGURE 9: Comparison of the average diameter, d_{av}, of water in sunflower oil emulsions obtained in a single microsystem "300-600" and a series of 2 microsystems ("300-600" + "600-600") as a function of water flow rate.

These results were really promising, but in order to keep the compactness of the process an immediate perspective of this work was to think about integrating different flow perturbations in a single microsystem. The question was: 'how many perturbations is it necessary to integrate in the microsystem to obtain the ideally expected emulsion?'

3- Post PhD achievements:

In spring 2015, at the end of the PhD work, the knowledges on the flow typology in the microsystems as well as other technical information accumulated during the successive tests allowed to design a series of new generations of microsystems. The number of perturbations to be included in the microsystem as well as their geometrical characteristics were determined as a function of the oil phase (diesel, vegetal oil, animal fat…). At this stage, the characteristics of the emulsions expected for a better combustion were fully met [Belkadi, 2017 *accepted under the condition of revision*]. It was then decided to propose these new microsystems for a patent (the form was submitted at the end of 2015 and the patent should be published in June of this year) [Patent (12-2015)]. Meanwhile, the project of implementing and testing the process of emulsification for better combustion and less pollution at a pre-industrial scale was submitted to the 'Pre-maturation national program' supported by the French CNRS. Our project was retained among 195 proposals. Through this program, successful trials were made such as at the 'Istituto Motori' of Napoli in Italy (respectively in May 2016 and February 2017). An engine was fed with an emulsion of water in diesel emulsion produced at a flow-rate of 350 mL/min with a microsystem. Thanks to a fully instrumented and transparent engine, the benefit of using the water in diesel emulsion obtained from a microsystem was clearly demonstrated.

4- Perspectives:

Considering the technical aspects, the next and immediate step is to collaborate with a firm in the aim of developing commercial systems using in line the microsystems to feed less polluting boilers.

Other aspects have to be developed on an academic point of view. The particular flow observed in the microsystems need to be more thoroughly described and characterized: in particular the Rayleigh instabilities, their frequency, the size of the filaments versus the flow conditions…

Références

[N. Ait-Mouheb (2010)] Ait-Mouheb, N. “Caractérisations expérimentale et numérique de l’écoulement et du transfert de matière dans des micromélangeurs.” Ph.D. thesis, University of Nantes, France, 2010.

[N. Ait Mouheb (2010b)] N. Ait Mouheb, C. Solliec J. Havlica P. Legentilhomme J. Comiti J. Tihon, A. Montillet. “Flow characterization in T-shaped and crossshaped micromixers.” Microfluidics and Nanofluidics 10.6 (2010) 1185–1197.

[A. Belkadi (2012)] A. Belkadi, A. Montillet J. Bellettre P. Massoli, D. Tarlet. “High-speed w/o emulsification within impinging and cross-flowing minichannels.” Proceedings of the 3rd European Conference on Microfluidics. Heidelberg, Germany, 2012.

[A. Montillet (2013)] A. Montillet, M. Tazerout, S. Nedjar. “Continuous production of water-in-oil emulsion using micromixers.” Fuel 106 : 410–416.

[A. Belkadi (2015)] Belkadi, A. Étude expérimentale du fractionnement liquide-liquide en micro-canaux pour la production en continu de biodiesels émulsionnés. Ph.D. thesis, SPIGA, University of Nantes, France, 2015.

[A. Belkadi (2016)] A. Belkadi, D. Tarlet, A. Montillet, J. Bellettre and P. Massoli, “ Study of two impinging flow microsystems arranged in series. Application to emulsified biofuel production”, Fuel (170) 185-196.

[A. Belkadi (2017)] A. Belkadi, A. Montillet, J. Bellettre. « Biofuel emulsifier using high velocity impinging flows and singularities in micro-channels”, submitted to J. Energy Resources Technology, accepted in May 2017 under the condition of a revision.

[J.M. Galindo Alvarez (2008)] Galindo Alvarez, J.-M. Etude de l’inversion de phase catastrophique lors de l’émulsification de produits visqueux. Ph.D. thesis, Nancy, 2008.

[T. Kiljanski (2004)] Kiljanski, Tomasz. “Preparation of emulsions using impinging streams.” AIChE Journal 50 : 1636–1639.

[N. Kiss (2011)] N. Kiss, H. Pucher J. Wieser S. Scheler H. Jennewein D. Suzzi J. Khinast, G. Brenn. “Formation of O / W emulsions by static mixers for pharmaceutical applications.” Chemical Engineering Science 66 : 5084–5094.

[S. Nedjar(2011)] S. Nedjar, M. Tazerout, A. Montillet. “Synthèse en continu d’émulsions de type « eau dans huile » à l’aide de micromélangeurs.” *la Société Française de Génie des Procédés*. Poster - 13e congrès de la société Française de Génie des Procedés, 2011.

[T. Nisisako (2009)] T. Nisisako, T. Hatsuzawa. “A microfluidic cross-flowing emulsion generator for producing biphasic droplets and anisotropically shaped polymer particles.” Microfluidics and Nanofluidics 9.2-3 (2009) : 427–437.

[T. Nisisako (2002a)] T. Nisisako, T. Higuchi, T. Torii. “Formation of droplets using branch channels in a microfluidic circuit.” Proceedings of the 41st SICE Annual Conference. SICE 2002.. vol. 2. 2002a, 957–959.

[T. Nisisako (2002b)] T. Nisisako, Toshiro Higuchi, Toru Torii. “Droplet formation in a microchannel network.” Lab on a chip 2.1 (2002b) : 24–6.

[Patent (12-2015)] J. Bellettre, A. Belkadi and A. Montillet « Dispositif et procédé pour réaliser une émulsion en continu de deux liquides immiscibles » Patent N° 1562682 submitted on December 17th 2015.

[H.Ã. Schubert (2004)] H.Ã. Schubert, R. Engel. “Product and formulation engineering of emulsions.” Chemical Engineering 82 : 1137–1143.

[A. Tamir (1985)] A. Tamir, S. Sobhi. “A new Two-Impinging-Streams Emulsifier.” AIChE Journal 31.12 (1985) 2089–2092.

[C.-X. Zhao (2011)] C.-X. Zhao, A.P.J. Middelberg. “Two-phase microfluidic flows.” Chemical Engineering Science 66.7 (2011) : 1394–1411.