Optimal Reactor Design for Ultrasonically-Enhanced Oxidative Desulfurization of Heavy Fuel Oil (HFO)

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Abstract

The combustion of hydrocarbons will continue to feed the planet's energy demand, especially for marine mobility and power generation, over the next several decades. The increasing energy demand must be coupled with the necessity to burn lower value fuels and with more stringent emissions regulations. These lower-value fuels include heavy fuel oils (HFO) and vacuum residues, which are difficult to burn cleanly due to their high viscosity, their high sulfur content, and the presence of asphaltenes (hydrocarbon aggregates and clusters with high molecular weight). To solve these problems, it is fundamental to develop advanced and innovative techniques to valorize heavy fuels and obtain more acceptable emissions. In particular, from heavy fuel oils, sulfur removal represents a fundamental objective given the most recent regulations established by the International Maritime Organization (IMO) in 2020. To achieve a very high level of sulfur removal, oxidative desulfurization (ODS) has been proposed as a valid alternative to hydro-desulfurization. The ODS process is based on a liquid-phase oxidation reaction: due to the presence of a liquid oxidant (e.g. hydrogen peroxide) and a liquid catalyst (e.g. acetic acid), it is possible to selectively oxide sulfur-containing molecules.

Ultrasonically Induced Cavitation (UIC) was proposed in the past as a technology able to improve the process selectivity and conversion. UIC is a physical process that involves the formation of vapor-filled cavities in a liquid medium irradiated by a high-frequency pressure wave source (ultrasound range, higher than 20 kHz). The high frequency pressure wave affects the formation, the dynamics, and collapse of the vapor bubbles. The vapor bubble's collapse induces a drastic increase in the mixing rate between the liquid fuel and the liquid oxidant. The high mixing rate and other peculiar phenomena, allow increasing the reaction rate of the sulfur oxidation drastically during ODS. The effectiveness of UIC applied to ODS is strongly dependent on the number and the size of vapor cavities inside the UIC reactor. Therefore, to create a process economically viable at an industrial scale, it is fundamental to design an optimized UIC reactor. This work presents a parametric study performed using a CFD code with the objective to find an optimal configuration for a reactor that uses a commercial sonotrode. The parameters of interest were the diameter of the reactor and the distance of the sonotrode from the bottom of the vessel. The CFD code was developed in-house, and based on the Volume of Fluid (VoF) approach, it was also validated with experimental results found in the literature prior to the study. In the end, an optimal reactor configuration is presented for the sonotrode under investigation.

Keywords:
Heavy Fuel Oils, Oxidative Desulfurization, Ultrasonically Induced Cavitation, Sonotrode, Reactor Optimization

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1. Introduction

The combustion of heavy fuels will continue to play a vital in some strategic sectors over the next few decades. One of these sectors is maritime transport. Heavy fuels will be the most used energy source for the entire two to three decades [1]. This trend is common to different types of ships for maritime transport. However, the usage of these lower-value fuels is limited by new stringent emission regulations. The International Maritime Organization has recently imposed the limit to the sulfur content in fuels at 0.5 percent by weight (IMO 2020 regulation) [1]. The new regulation imposes a drastic reduction of sulfur oxide emissions, due to maritime transportation. Heavy Fuel Oils (HFO) generally have a content of sulfur that ranges from 2.5 to 3.5 percent by weight, which justifies the need to find new sustainable processes aimed at sulfur removal from HFOs. To achieve high level of sulfur removal from HFOs, oxidative desulfurization (ODS) was proposed, in the past, as an alternative to hydro-desulfurization (HDS). Indeed, ODS presents several advantages compared to HDS regarding operating pressure and temperature and propensity in in refractory sulfur (thiophene derivatives) removal. The ODS process is based on a liquid-phase oxidation reaction. Due to the presence of a liquid oxidant (e.g hydrogen peroxide) and a liquid catalyst (e.g acetic acid), it is possible to oxidize sulfur selectively. The sulfur oxidation reaction leads to the formation of sulfones. Sulfones have a highly localized charge that makes a liquid-liquid separation possible using a polar solvent. Ultrasonically induced cavitation was proposed in the past as a way to enhance the selectivity and conversion of the ODS process. UIC is a physical process involving the formation of cavitation vapor bubbles in a liquid medium, processed with an ultrasonic source, leading to the propagation of high-frequency pressure waves. These pressure waves are generated through the vibration of a metallic probe. The sharp pressure gradients generated in the liquid medium affect the nucleation, the dynamics, and the collapse of vapor bubbles. Ultrasonic cavitation is able to enhance the ODS process, increasing the reaction rate of the sulfur oxidation reaction through three main effects. The first one is the sonochemical effect: as a consequence of the bubbles' collapse, hot spots, characterized by high temperature and pressure, are generated in the liquid medium [2–5]. The presence of hot spots leads to the formation of radicals, like H* or OH*. These unstable species increase the reactivity of the system, promoting sulfur oxidation. The second relevant effect is mixing. The vapor bubbles collapse induces the formation of micro-jets. These jets allow increasing the fluid dynamics mixing in the micro-scale. As a consequence of the mixing, the surface area, between the liquid oxidant phase and the liquid fuel phase, increases drastically [6]. These result in a global improvement of the oxidation which is dependent on the contact surface area. The third effect is asphaltenes breakage. Indeed, HFOs are characterized by a high concentration of asphaltenes, hydrocarbon aggregates with high molecular weight. During UIC, the bubble collapse induces a breaking of the most significant asphaltene clusters. As a result, the stochastic probability of oxidizing the atoms of sulfur increases. Also, the physical properties of the fuel improve because of clusters disruption. From these considerations, the sulfur oxidation rate and the effectiveness of UIC applied to ODS are strongly dependent on the size and the number of vapor cavities inside the UIC reactor. Indeed, a more significant number of bubbles and a smaller size increases the efficiency of the process drastically. Consequently, it is fundamental to design an optimized UIC reactor, when all the geometric parameters are conformed to maximize the number of vapor cavities and minimize the size of the bubbles. The optimized reactor could improve the efficiency of the ODS process, allowing to decrease the concentrations of hydrogen peroxide and acetic acid employed during the process. This last aspect is crucial to make the entire process economically convenient. To solve the optimization problem previously mentioned, an innovative CFD code has been developed, based on the Volume of Fluid (VoF) method [7]. This code can predict, with high fidelity, the formation, the dynamic, and the collapse of the vapor cavities inside the UIC reactor. An extensive parametric study has been conducted modifying different geometrical parameters of the chamber. The optimal reactor design has been identified, considering the geometrical parameters that allow obtaining a higher contact surface between the vapor cavities and the liquid phase.

2. Model description

The bubbles collapse, during the UIC process, induces peculiar phenomena that can affect the global reaction rate of the sulfur oxidation reaction in Heavy Fuels. The optimization of rectors is a fundamental task to scale up the entire process on an industrial scale. The optimization process will reduce the amount of liquid catalyst (hydrogen peroxide)and liquid catalyst (acetic acid), as well as the amount of solvent employed in the sulfones separation stage. The reduction of these solvents and their associated costs will allow obtaining a feasible, valuable and efficient process

for the large-scale valorization of Heavy Fuels. The parametric study of the reactor could be obtained with an extensive experimental campaign. Varying different design parameters and using the "trial and error" approach, the optimum design could be reached. However, such an approach would be expensive in terms of cost and time required. For these reasons, a CDF code has been developed. The code can model the presence of the cavitating vapor bubble and predict the velocity and pressure field inside the reactor. During UIC, the most relevant fluid dynamics phenomena are the propagation of pressure waves inside the liquid mixture and the cavitation of vapor bubbles. A valuable CFD code for UIC must be able to model these two critical phenomena correctly. The life of the cavitating bubbles can be divided into three main stages: nucleation or bubbles inception, bubble dynamics and collapse. Regarding the bubble inception, in the regions of the fluid domain where the pressure goes below the saturated vapor pressure of the liquid, cavitation of vapor bubbles can statistically happen. It is essential to highlight that bubbles nucleation can occur following two different pathways, called homogeneous and hydrogenous nucleation [8]. The homogeneous nucleation describes the formation of vapor bubbles in a pure liquid medium without considering the presence of any contaminant particle. In contrast, the heterogeneous nucleation mechanism describes the bubble formation due to the presence of contaminant particles in the liquid. Indeed, solid particles act like nucleation sites, where bubbles inception and growth take place. Traditionally, nucleation is modeled using the classical nucleation theory (CNT). However, this theory, in the context of vapor bubbles nucleation, overestimates the energy required to nucleate a vapor bubble [8]. This is probably due to the presence of small contaminant particles in the liquid medium or dissolved gas which reduce the energy necessary for the vapor bubble nucleation. To take into account all these questions, in the developed model, a hybrid theory has been implemented. This theory can be considered as a combination of the models proposed by Louisnard [9, 10] and Vanhille et al. [11]. The domain of existence of the cavitating bubbles is defined through the Blake threshold [12]. In a particular region of the fluid domain, cavitation can occur when the pressure amplitude must be above the Blake value (Eq. 1). Otherwise ($\mid P \mid < P_{Blake}$) cavitation cannot take place and the bubble density function N is equal to zero.

$$N = N_{max} \tanh\left(\left| \frac{P - P_{Blake}}{P_{Sat} - P_{Blake}} \right| \right) \text{if } \mid P \mid \geq P_{Blake} \tag{1}$$

P_{Sat} corresponds to the saturated vapor pressure of the liquid. The bubble density function N is described using the hyperbolic tangent function proposed by Vanhille et al. [11]. N_{max} is the maximum bubble density that can be reached within a certain region of the domain. This parameter is equal to 1×10^{12} and has been calibrated on experimental observation [13, 14]. In the CFD code, the bubbles nucleation happen instantaneously, and the equilibrium radius of the bubbles R_C is defined by the well known Young-Laplace equation (Eq. 2):

$$R_C = \frac{2\sigma}{p_G - P} \tag{2}$$

Where σ is the surface tension of the liquid phase, p_G is the pressure within the bubble, and P is the liquid pressure outside the bubble. After their nucleation, the vapor bubbles oscillate due to the propagation of pressure waves within the liquid medium. It is possible to describe the dynamics of a single bubble using the Rayleigh–Plesset (RP) equation (Eq. 4) [8].

$$\frac{3}{2}\left(\frac{dR}{dt}\right)^2 + R\frac{d^2R}{dt^2} = \frac{p_G(t) - P_\infty(t)}{\rho_L} - \frac{4\nu_L}{R}\frac{dR}{dt} - \frac{2\sigma}{\rho_L R} \tag{3}$$

In this differential equation, the bubble radius is a function of time ($R(t)$), when the vapour bubble is subject to an external pressure field, $P_\infty(t)$. Following the model proposed by Louisnard [9, 10], the collapse of the bubbles takes place when the pressure amplitude falls below the Blake pressure (Eq. 1) [12]. The collapse is modeled to happen instantaneously and the volume fraction of the vapor phase is imposed equal to 1. During the bubbles collapse, the energy stored, in the oscillating bubbles, is released in a small portion of space, producing high temperature and pressure. The energy associated with a single bubble can be expressed using the Rayleigh-Plesset equation multiplied by the time derivative of the bubble volume, $\frac{dV}{dt}$ [10]:

$$\frac{3}{2}\rho_L\left(\frac{dR}{dt}\right)^2\frac{dV}{dt} + \rho_L R\frac{d^2R}{dt^2}\frac{dV}{dt} = (p_G(t) - P_\infty(t))\frac{dV}{dt} - \rho_L\frac{4\nu_L}{R}\frac{dR}{dt}\frac{dV}{dt} - \frac{2\sigma}{R}\frac{dV}{dt} \tag{4}$$

The Volume of Fluid (VoF) method is used to model UIC [7]. The two-phase flow is modeled as a homogeneous mixture and only one set of equations is adopted for the entire computational domain.

3. CFD set up and Parametric Study

In Figure 1, it is shown a snapshot of the UIC phenomenon, captured using a high speed camera. It is clearly visible the formation of a cloud of cavitating vapor bubbles below the tip of the vibrating probe [6]. It is also possible to distinguish the cone-like structure of the bubbles cloud. The same structure has been identified in the experimental works of Žnidarčič et al. [15] and Campos-Pozuelo et al. [14].

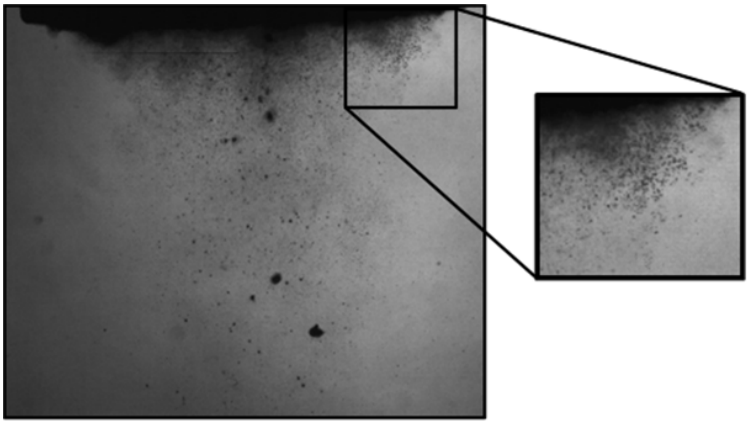

Figure 1: Vapor bubbles cloud snapshot captured using Kirana high-speed camera (Dr. Vakarelski and Professor Thoroddsen, KAUST University).

For the reasons explained above, the optimization goal of the parametric study is to maximize the surface area of the vapor bubbles available, creating, therefore, a higher number of smaller bubbles per unit volume. This objective can be reached by maximizing the total surface between the two phases, namely between the cavitating vapor bubbles and the liquid medium. In Figure 2 the total surface area of the i-th bubble is expressed as S_i.

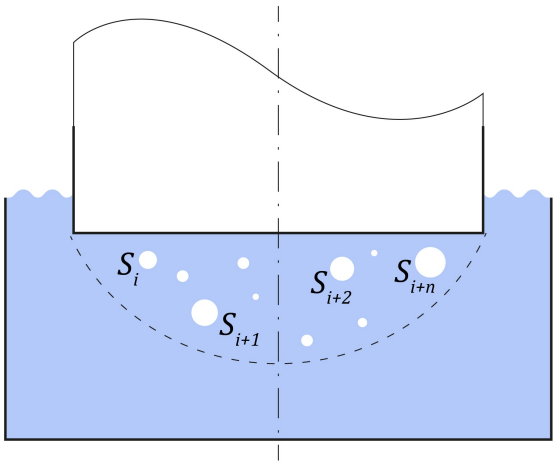

Figure 2: Surface area of the vapor bubbles.

Considering the nomenclature expressed in Fig. 2, the optimization goal of the parametric study can be expressed by the maximization of the total surface area S_{total}, where S_{total} is equal to:

$$S_{total} = \sum_{i=1}^{N} S_i \tag{5}$$

Where, i is the index of the i-th bubble and N is the total number of bubbles. The parametric study was performed running CFD simulations on a 2D (two-dimensional) computational domain which represents an actual UIC reactor. This choice is related to the necessity of reducing the computational cost of every CFD simulation. The simulations allow obtaining a parametric study able to provide an optimum configuration in a reasonable amount of time. For the present study, an ultrasonic probe composed of three cavitating modules is considered (Figure 3).

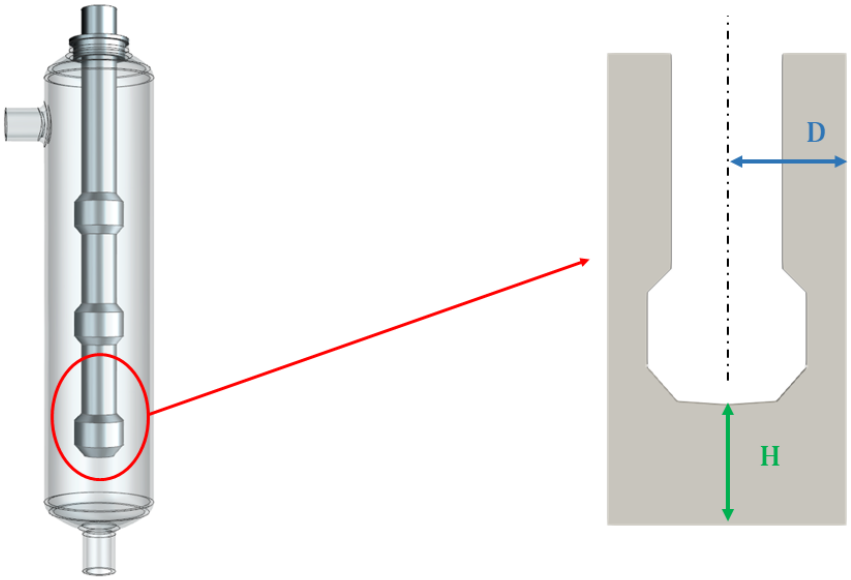

Figure 3: 2D domain with one cavitating module and geometric parameters, H and D.

However, the problem has been reduced to a module and two geometric parameters to save further computational cost. Figure 3 shows, schematically, the extraction of the 2D domain from the actual UIC reactor and the geometric parameters considered. The first parameter H is the distance between the tip of the probe and the bottom of the chamber, while the second parameter D is the distance between the wall of the chamber and the axis of the probe (Fig.3). All the geometric parameters, related to the design of the vibrating probe, were kept fixed during the parametric study. Ultrasonic cavitation is a fluid dynamics phenomenon dominated by the propagation of pressure waves inside the liquid medium. For this reason, the choice of the boundary conditions for the CFD simulation is fundamental to model the phenomenon appropriately. Considering a batch reactor and an ultrasonic probe made of steel, the interaction between the pressure wave and the rigid walls must imply a complete reflection of the pressure waves. To model this on the OpenFOAM framework, the *calculated* boundary condition has been used (Fig. 4). Moreover, at the free surface of the liquid medium, the pressure field has to match the value of the atmospheric pressure (*uniformFixedValue* in OpenFOAM framework, Fig. 4). Regarding the velocity field, the *noSlip* boundary condition has been used to model the viscous adhesion of the liquid to the reactor walls and the *zeroGradient* boundary condition has been set to imply the velocity gradient equal to zero at the free surface of the liquid (Fig. 4).

The main parameters set to run the CFD simulations during the parametric study are listed in Table1. In the same Table are also reported the parameter related to the vibration of the ultrasonic probe: vibration frequency and amplitude. In the CFD simulations, a moving mesh is responsible for the creation of the pressure waves by simulating the vibration of the sonotrode.

The parametric study has been conducted taking into account a 2D batch reactor with a single cavitating module (Fig.3). Two geometric parameters, H and D (Fig.3) were considered. The maximum and minimum values and the

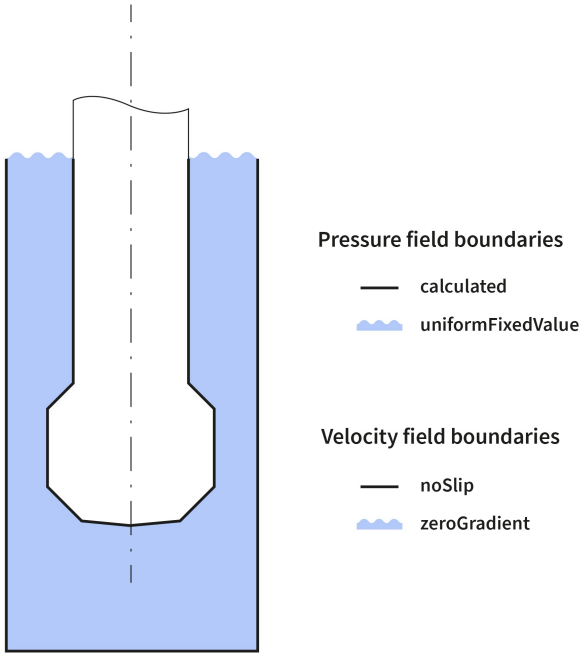

Figure 4: Boundary conditions set-up on openFoam framework.

Mesh type	Hexa
Mesh order	Linear
Mesh size	0.2 mm
Probe vibration frequency	20 kHz
Probe vibration amplitude	164 μm
Wave period	50 μs
end Time	500 μs (10 sonotrode cycles)
delta Time	100 ns (adjustable time step)
max Courant	0.2

Table 1: Main parameter set in the CFD simulations.

intervals are reported in Table 2. It is important to note that all the length values are expressed in non-dimensional terms. For every geometric variable, ten values have been simulated (Table 2).

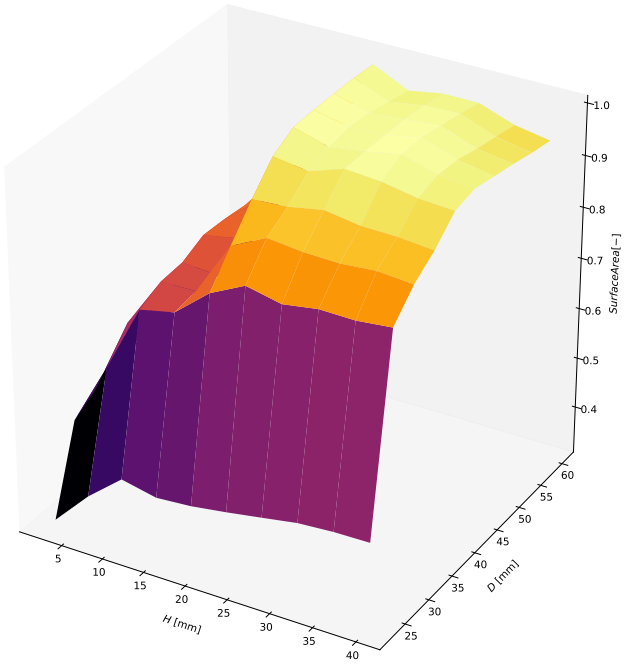

Figure 5: Surface area integral as a function of the geometric parameters, H and D.

Variable	Minimum value	Maximum value	Number of intervals
H	2.5	40	10
D	22.5	60	10

Table 2: Parameters values used for parametric study.

In Fig. 6, the results obtained with the CFD code are shown. The contour maps of velocity field (b), pressure field (a) and vapor volume fraction (c) are reported. The maps are related to the time 212.5 μs and to the geometric configuration with H and D both equal to 30. Observing the gradient in the velocity and pressure fields, the fronts of the pressure wave are clearly identifiable. As a consequence of the propagation of the pressure wave, in specific regions of the domain, there is the presence of vapour phase (Fig. 6).

For every time step of the CFD simulation, the surface area between the liquid phase and vapor phase was also calculated. The result obtained, from the simulation having D=30 and H=30, is reported in terms of evolution over time of the surface area (Figure 7). It can be noticed that after a transient with a large surface area, the evolution of the total surface of the bubble becomes periodic and presents two characteristic frequencies at 20 and 40 kHz. The occurrence of those frequencies has been found in the literature by other authors [13, 15]. The transient lasted approximately two cycles which correspond to t=1e-4 s. The values related to the first two cycles have not been considered when calculating the integral of the surface area as they are not of interest giving the characteristic time required for the process to take place which is in the order of seconds. To compare the results provided, in terms of surface area, from the different geometric configurations, the integral of the surface area with the respect to time have been considered. The integral has been evaluated starting from the 2nd cycle up to the 10th cycle of vibration of the

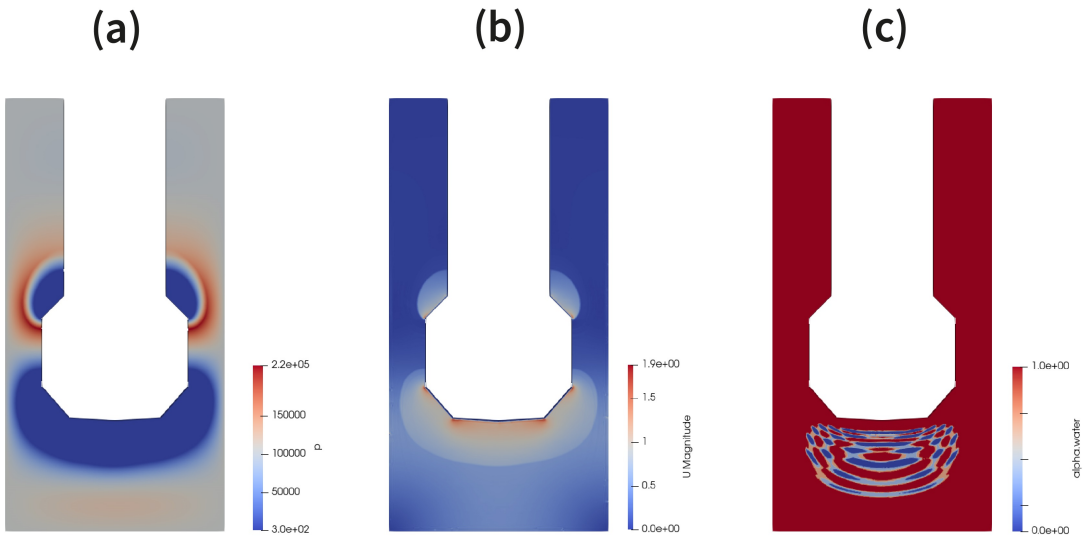

Figure 6: Pressure field (a), velocity field (b) and vapor volume fraction for the CFD simulation related to H=30, D=30.

ultrasonic probe. The integral in time provide information about the total surface area every geometric configuration is able to generate in 8 cycles (Figure 5).

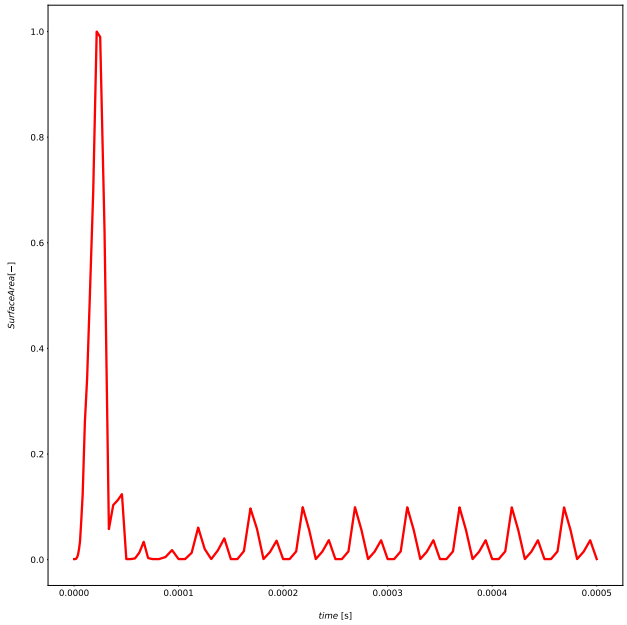

Figure 7: Surface area of the simulation having H=30 and D=30.

The results of the series of simulations are displayed in Fig. 5. It can be noticed the surface area increases progressively with the diameter (D) until an asymptote is reached at D=50. The value of H peaks at a value equal to 20 which is, therefore, the sweet spot at which place the bottom of the reactor.

4. Conclusions

This paper demonstrates a computational approach devoted to the evaluation of an ODS reactor design. The main contribution here was to establish a numerical methodology for the simulation of ultrasonically induced cavitation in a large-scale device. The optimum size for the UIC reactor was found for a given ultrasonic probe structure and frequency. This kind of analysis can be extended and automated in the future, in order to create a tool that can be used for more complex evaluations and studies.

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