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The size of active bubbles for the production of hydrogen in sonochemical reaction field

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ABSTRACT

The sonication of aqueous solution generates microscopic cavitation bubbles that may growth and violently collapse to produce highly reactive species (i.e. $^{\cdot}OH$, $HO_2^{\cdot}$ and H_2O_2), hydrogen and emit light, sonoluminescence. The bubble size is a key parameter that influences the chemical activity of the system. This wok aims to study theoretically the size of active bubbles for the production of hydrogen in ultrasonic cavitation field in water using a single bubble sonochemistry model. The effect of several parameters such as frequency of ultrasound, acoustic intensity and liquid temperature on the range of sonochemically active bubbles for the production of hydrogen was clarified. The numerical simulation results showed that the size of active bubbles is an interval which includes an optimum value at which the production rate of H_2 is maximal. It was shown that the range of ambient radius for an active bubble as well as the optimum bubble radius for the production of hydrogen increased with increasing acoustic intensity and decreased with increasing ultrasound frequency and bulk liquid temperature. It was found that the range of ambient bubble radius dependence of the operational conditions followed the same trend as those reported experimentally for sonoluminescing bubbles. Comparison with literature data showed a good agreement between the theoretical determined optimum bubble sizes for the production of hydrogen and the experimental reported sizes for sonoluminescing bubbles.

1. Introduction

Hydrogen has attracted increased attention as one of the most promising energy source for the future, due to the limited storage of fossil fuels and serious environmental problems [1]. Hydrogen can be produced in many ways from a broad spectrum of initial raw materials. Nowadays, hydrogen is produced predominantly from fossil fuels; roughly 96% of hydrogen is produced by steam reforming of natural gas [2]. Alternative ways could be used to generate H_2 such as ethanol gasification [3], water electrolysis [4], biological photosynthesis [5,6], photocatalysis [7–9] and sonolysis. This later could be a promising way to produce clean hydrogen, particularly if water is used as the hydrogen source.

The origin of sonochemistry is acoustic cavitation phenomenon, which is the nucleation, growth and violent collapse of microbubbles (filled with water vapor and dissolved gases) in a fluid subjected to ultrasound [10]. The quick collapse of these microbubbles is nearly adiabatic, yielding temperature of several thousands of Kelvin and pressure of several hundreds of atmospheres inside the bubble [11,12]. Under this dramatic situation, the trapped molecules in the bubble can be brought to an excited-state and dissociate. In the case of aqueous solution, various species such as $^{\cdot}OH$, $HO_2^{\cdot}$, $H^{\cdot}$, O, H_2O_2 and H_2 are created from H_2O and O_2 dissociation and their associate reactions inside the bubble [13,14]. In the case argon-saturated water, the main products of sonolysis were hydrogen peroxide and hydrogen. This later (H_2) may be formed at rate of 10–15 μM min^{-1} [15–17]. The sonolysis of acetylene in aqueous phase yielded a much higher amount of H_2, >100 μM min^{-1} [18]. Acoustic cavitation can generate simultaneously strong shear forces, microjets (near solid surfaces), microstreaming and shockwaves [19]. The extreme conditions in the interior of bubble also lead to the emission of light, called sonoluminescence (SL), which is manifested in two forms: multibubble sonoluminescence (MBSL) and single-bubble sonoluminescence (SBSL) [20,21]. The mechanism of the light emission is still under debate. Many researchers [22–24] reported that the SBSL originates from plasma emissions inside a bubble; thermal bremsstrahlung of free electrons and radiative recombination of electrons and ions. For MBSL, however, some researchers [25,26] suggested the same mechanism as SBSL and others have suggested other

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Nomenclature

c	speed of sound in the liquid medium, (m s^{-1})
f	frequency of ultrasonic wave, (Hz)
I_a	acoustic intensity of ultrasonic irradiation, (W m^{-2})
p	pressure inside a bubble, (Pa)
p_∞	ambient static pressure, (Pa)
P_A	amplitude of the acoustic pressure, (Pa)
P_v	vapor pressure of water, (Pa)
P_{g0}	initial gas pressure, (Pa)
R	radius of the bubble, (m)
R_{max}	maximum radius of the bubble, (m)
R_0	ambient bubble radius, (m)
t	time, (s)
T	temperature inside a bubble, (K)
T_∞	bulk liquid temperature, (K)

Greek letters

σ	surface tension of liquid water, (N m^{-1})
ρ_L	density of liquid water, (kg m^{-3})

mechanisms such as molecular emissions from gases [27] and chemiluminescence of ·OH radical inside bubbles [28].

One of the most fundamental parameters which characterize the sonochemical reaction field is the size of bubbles that can undergo inertial collapse to produce reactive species, sonoluminescence and hydrogen. The measurement of this parameter is difficult due to the chaotic nature of acoustic cavitation. There have been several studies [29–34] investigating the cavitation bubble size using different techniques, with the majority conducted at 20 kHz. Recently, Brotchie et al. [35] investigated the effects of ultrasound frequency and applied acoustic power on the size distribution of sonoluminescing bubbles in water using a pulsed ultrasound method. They found that the mean bubble size increased with increasing acoustic power and decreased with increasing ultrasound frequency. However, to the best of our knowledge, the size of active bubbles for the production of hydrogen in ultrasonic cavitating field was never addressed neither experimentally nor theoretically. In our recent paper [36], a model for single bubble sonochemistry has been combined with material balances in the aqueous phase for clarifying the mechanism of sonolysis induced-hydrogen production. The results from this study showed that H_2 is produced mainly in the gas phase of the bubbles via the recombination of the primarily radicals (H· and ·OH) formed by splitting of water vapor molecules under the high temperature developed at the collapse phase of the bubble. In the present work, the early developed model for single bubble sonochemistry have been used for predicting the size (in term of ambient bubble radius) of sonochemically active bubbles for the production of hydrogen. Computer simulations were conducted for bubbles oscillating in water saturated with argon. The effect of various experimental parameters including ultrasonic frequency (140–1100 kHz), acoustic intensity (0.75 and 1 W cm^{-2}) and liquid temperature (20–50 °C) on the size of actives bubbles for the production of H_2 were clarified.

2. Theoretical model and computational methods

The model adopted in the present numerical simulations have been fully described in Refs. [36–39]. It combines the dynamic of single bubble in acoustic field with chemical kinetics consisting of series of chemical reactions occurring in the bubble at the collapse phase. The following is a brief description of the model.

2.1. Bubble dynamics model

A gas and vapor filled spherical bubble isolated in water oscillates under the action of a sinusoidal sound wave. The temperature and pressure in the bubble are assumed to be spatially uniform and the gas content of the bubble behaves as an ideal gas [40]. The radial dynamics of the bubble is described by the Keller–Miksis equation that includes first order terms in the Mach number $M = \dot{R}/c$ [41]:

$$\left(1-\frac{\dot{R}}{c}\right)R\ddot{R}+\frac{3}{2}\left(1-\frac{\dot{R}}{3c}\right)\dot{R}^2=\frac{1}{\rho_L}\left(1+\frac{\dot{R}}{c}+\frac{R}{c}\frac{d}{dt}\right)\left[p-p_\infty-\frac{2\sigma}{R}-4\mu\frac{\dot{R}}{R}-p_s(t)\right] \quad (1)$$

in this equation dots denote time derivatives (d/dt), R is the radius of the bubble, c is the speed of sound in the liquid, ρ_L is the density of the liquid, σ is the surface tension, μ is the liquid viscosity, p is the pressure inside the bubble, p_∞ is the ambient static pressure and $p_s(t)$ is the time-dependent pressure field driving the bubble into oscillation. In the case of bath-type sonochemical reactor, actual acoustic field in the reactor is a damped standing-wave field [42]. However, when a bubble is irradiated by an acoustic wave whose wavelength is much longer than the bubble radius, the acoustic pressure can be described assuming a traveling-wave field as follows [38]: $p_s(t) = -P_A \sin(2\pi ft)$, where P_A is the acoustic amplitude of the acoustic wave and f is its frequency. The acoustic amplitude P_A is correlated with the acoustic intensity I_a, or power per unit area, as $P_A = (2I_a\rho_L c)^{1/2}$ [43].

The expansion of the bubble is assumed as isothermal and its total compression is considered as adiabatic [44]. These assumptions, which are widely accepted since the lifetime of an oscillation at high frequency is relatively short with a very rapidly occurring collapse event, were pointed out by Yasui et al. [45] using a more detailed model. We also assume that the vapor pressure in the bubble remains constant during the bubble expansion phase and there is no gas diffusion during expansion and no mass and heat transfer of any kind during collapse. Storey and Szeri [46] demonstrated that the inclusion of mass transfer on the bubble dynamics has practically no effect on the maximum bubble temperature attained in the bubble at the collapse when the compression ratio of the bubble (R_{max}/R_{min}) is less than 20 (R_{max} is the maximum radius of the bubble and R_{min} is the minimum bubble radius at the collapse). This level of R_{max}/R_{min} was never attained in the present numerical study. Therefore, in order to reduce computational parameters, the current model takes, as input, initial bubble vapor content and neglects mass and heat transfer during bubble expansion and collapse.

Based on the above assumptions, the pressure and temperature inside the bubble at any instant during the collapse phase can be calculated from the bubble size as

$$p=\left[P_v+P_{g0}\left(\frac{R_0}{R_{max}}\right)^3\right]\left(\frac{R_{max}}{R}\right)^{3\gamma} \quad (2)$$