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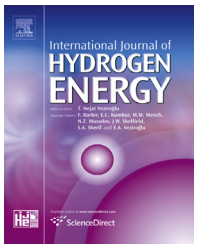

# Computational engineering study of hydrogen production via ultrasonic cavitation in water

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ABSTRACT

Ultrasonic cavitation, the formation and subsequent collapse of microbubbles, is the unique phenomenon responsible of the production of hydrogen during water sonolysis. This work presents the results of a comprehensive computational study of hydrogen production via acoustic cavitation in water. Computer simulations of chemical reactions occurring inside an ultrasonic cavitation bubble have been performed for a wide range of ultrasonic frequencies (20–1100 kHz) under different saturating gases (Ar and air), various acoustic intensities (0.5–1 W $cm^{-2}$) and diverse liquid temperatures (20–50 °C). For an Ar bubble, reactions mechanism consisting in 25 reversible chemical reactions were proposed for studying the internal bubble-chemistry whereas 73 reversible reactions were taken into account for an air bubble. The obtained results have indicated that hydrogen ($H_2$) as well as radicals, such as •OH, H•, $HO_2$• and O, are created in the bubble during the strong collapse. In all cases, $H_2$ is the main molecular product formed in the bubble at appreciable amount. The production rate of $H_2$ decreases significantly as the frequency increases. The production rate of $H_2$ is higher when water is saturated with argon than air and the beneficial effect of argon becomes more remarkable at higher ultrasonic frequencies. The numerical simulation showed the existence of an optimum liquid temperature (~30 °C) for the production of $H_2$. All the obtained results were analyzed and interpreted basing on the bubble dynamic characteristics.



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## Introduction

Hydrogen is considered to be the most viable energy carrier for the future [1]. Currently, almost 90% of the $H_2$ is produced via the reforming of natural gas or the light oil fraction with steam at high temperatures [2]. However, hydrogen production from natural gas is always associated with the emission of greenhouse gases and local pollutants. Alternative ways could be used to generate $H_2$ such as ethanol gasification [3], water electrolysis [4], biological photosynthesis [5,6] and photocatalysis [7–9]. Additionally, sonolysis of water have been successfully used for producing hydrogen [10–12]. Moreover, ultrasound assisted hydrogen production from catalysis [13], photocatalysis [14–16], digestion sludge [17–19] and anaerobic fermentation of wastewater [20] have proven their improvement potential compared to each isolated technique (without ultrasound). Sonolysis could be a promising way to produce clean hydrogen, particularly if water is used as the hydrogen source. At the moment, only some studies have been carried out at different ultrasonic conditions and the influence of operational parameters on the yield of $H_2$ was not clarified.

The passage of ultrasound irradiation of frequency in the range 20–1000 kHz through liquid water causes acoustic (ultrasonic) cavitation phenomenon, that is, the formation, growth and implosive collapse of microbubbles containing dissolved gases and water vapor [21]. Practically, all chemical and physical effects of ultrasound in aqueous solution originate from this phenomenon [22]. The rapid collapse (several nano- or microseconds) of cavitation bubbles is nearly adiabatic, rendering each individual bubble a microreactor, inside which temperatures of the order of 5000 K and pressures of hundreds of atmospheres have been shown to exist [23]. As a result, water vapor entrapped inside a bubble is dissociated into H• and •OH radicals, and with other species present, various other reactive entities such as $HO_2$• and O may form [24,25]. Parallel reaction pathways exist where volatile solutes may evaporate into the bubble and be pyrolysed by the high core temperatures [24]. The radical species produced can recombine or react with other gaseous species present in the gas phase of the cavity to yield stable species such as $H_2O_2$ and $H_2$. These two species are the most products detected and quantified during water sonolysis with a ratio ($H_2$:$H_2O_2$) of ~1.25 [11,12,26]. All chemical reactions promoted by ultrasound are known as sonochemical reactions. Under certain conditions, bubble collapse is also accompanied by the emission of light, called sonoluminescence, originating from the hot core of the bubble during the final stages of collapse [23,27].

A number of factors influence ultrasonic production of hydrogen. These include frequency of ultrasound, dissolved gas, acoustic power, bulk liquid temperature, etc. While the literature data concerning the effect of frequency and liquid temperature is scare, the effect of the other parameters are relatively known. Margulis [28] showed experimentally that during sonolysis at 1000 kHz under argon saturation the production rate of $H_2$ is 13.6 μM $min^{-1}$, which is higher than that obtained under air saturation (0.22 μM $min^{-1}$). Venault [26] showed that the production rate of $H_2$ increased linearly from 0.8 to 5 μM $min^{-1}$ when the acoustic intensity increased in the range 0.6–2.5 W $cm^{-2}$, during the sonolysis at 20 kHz of water saturated with argon. However, the very limited data available to clarify the influence of the operational parameters on the production rate of $H_2$ and the chaotic nature of acoustic cavitation renders difficult the understanding of the action mechanism of these parameters on the sonochemical production of $H_2$. In our recent paper [29], a tentative has been carried out for clarifying the mechanism of sonolysis induced-hydrogen production. A theoretical model for ultrasonic cavitation event was combined with chemical kinetics model consisting of a series of complex reactions (25 reversible reactions for argon bubble and 73 for air bubble) occurring inside the bubble has been used to estimate the production rate of $H_2$ from the gas phase of the bubbles, whereas the production from the liquid phase by radicals recombination has been estimated using material balance. The results from this study showed that, during water sonolysis, $H_2$ 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, we extended the early model to clarify, for the first time, the effect of the operational parameters on the ultrasonic production of $H_2$ in microscopic and macroscopic scale (the bubble and the solution, respectively). The computer simulations have been carried out for a wide range of operating parameters including frequency of ultrasound (20–1100 kHz), acoustic power (0.5–1 W $cm^{-2}$), saturating gas (argon and air) and liquid temperature (25–55 °C).

## Model and computational methods

The theoretical model used in the present computational study have been fully described in our previous works [29–31]. It combines the dynamic of single bubble in acoustic field with chemical kinetics consisting of a series of chemical reactions occurring in the bubble at the collapse phase. The following is a brief description of the 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 spatially uniform and the gas content of the bubble behaves as an ideal gas [32]. The radial dynamics of the bubble is described by the Keller–Miksis equation that includes first order terms in the Mach number $M = \dot{R}/c$ [33,34]:

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