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Modeling of sonochemistry in water in the presence of dissolved carbon dioxide

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ABSTRACT

CO_2 capture and utilization (CCU) is a process that captures CO_2 emissions from sources such as fossil fuel power plants and reuses them so that they will not enter the atmosphere. Among the various ways of recycling CO_2, reduction reactions are extensively studied at lab-scale. However, CO_2 reduction by standard methods is difficult. Sonochemistry may be used in CO_2 gas mixtures bubbled through water subjected to ultrasound waves. Indeed, the sonochemical reduction of CO_2 in water has been already investigated by some authors, showing that fuel species (CO and H_2) are obtained in the final products. The aim of this work is to model, for a single bubble, the close coupling of the mechanisms of bubble dynamics with the kinetics of gas phase reactions in the bubble that can lead to CO_2 reduction. An estimation of time-scales is used to define the controlling steps and consequently to solve a reduced model. The calculation of the concentration of free radicals and gases formed in the bubble is undertaken over many cycles to look at the effects of ultrasound frequency, pressure amplitude, initial bubble radius and bubble composition in CO_2. The strong effect of bubble composition on the CO_2 reduction rate is confirmed in accordance with experimental data from the literature. When the initial fraction of CO_2 in the bubble is low, bubble growth and collapse are slightly modified with respect to simulation without CO_2, and chemical reactions leading to CO_2 reduction are promoted. However, the peak collapse temperature depends on the thermal properties of the CO_2 and greatly decreases as the CO_2 increases in the bubble. The model shows that initial bubble radius, ultrasound frequency and pressure amplitude play a critical role in CO_2 reduction. Hence, in the case of a bubble with an initial radius of around 5 μm, CO_2 reduction appears to be more favorable at a frequency around 300 kHz than at a low frequency of around 20 kHz. Finally, the industrial application of ultrasound to CO_2 reduction in water would be largely dependent on sonochemical efficiency. Under the conditions tested, this process does not seem to be sufficiently efficient.

1. Introduction

Due to increased concern over carbon dioxide (CO_2) emissions and their effect on the environment and climate change, many methods have been devised to reduce or control them over recent decades. The most common technique currently undergoing global research and development is CO_2 capture and storage (CCS), whereby CO_2 is captured and commonly stored in deep geological formations [1]. Another method that has more recently been considered is CO_2 capture and utilization (CCU), which involves, by various means, recycling CO_2 into fuel gases, e.g. CO or CH_4 [2]. However, CO_2 reduction by standard methods (hydrogenation, electrochemical reduction, photocatalytic reduction, etc.) is difficult, since CO_2 is a very stable molecule. Sonochemistry may be able to contribute to the scientific and technical studies on this issue. The experimental approach may employ a gas mixture that contains the CO_2 to be bubbled through water and subjected to ultrasound waves. Ultrasound through water involves the use of sound waves of a high frequency ranging from 20 kHz (i.e. with a cycle of 50 μs) to several MHz (i.e. with a cycle lower than 1 μs) that consist of rarefaction and compression cycles. Low-to-medium-frequency ultrasound is typically used for sonochemistry to reach higher localized temperatures and pressures [3]. The chemical effect of ultrasound comes from acoustic cavitation phenomena, i.e. after expansion to many times their initial size, the oscillation and collapse of bubbles filled with dissolved gases and with vapor from the liquid. When ultrasound is applied to liquid water, the liquid directly in contact with the bubble interface may be displaced during stable oscillating cycles (i.e. with bubbles oscillating around a mean radius for many acoustic cycles) or transient collapsing cycles (i.e. with bubbles existing for only a short time before collapsing). Bubbles can collapse after

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Nomenclature

a	NASA coefficient
A	preexponential factor
c	speed of sound in the liquid phase, ($m\,s^{-1}$)
C	molar concentration, ($mol\,m^{-3}$)
C_p	thermal capacity, ($J\,kg^{-1}\,K^{-1}$)
D	mass diffusivity, ($m^2\,s^{-1}$)
e	internal energy, ($J\,kg^{-1}$)
$\dot{e}$	time derivative of internal energy, ($W\,kg^{-1}$)
E	energy activation, ($J\,mol^{-1}$)
f	frequency, (Hz)
h	enthalpy, ($J\,kg^{-1}$)
I	intensity, ($W\,m^{-2}$)
k	rate constant
LHV	low heating value, ($J\,kg^{-1}$)
m	mass, (kg)
N	number density, ($\#\,m^{-3}$)
P	pressure, (Pa)
$\dot{Q}$	heat loss, ($W\,m^{-3}$)
r	overall rate, ($mol\,m^{-3}\,s^{-1}$)
	bubble radius, (m)
$\dot{R}$	bubble velocity, ($m\,s^{-1}$)
$\ddot{R}$	bubble acceleration, ($m\,s^{-2}$)
R_G	gas constant, ($8.314\,J\,K^{-1}\,mol^{-1}$)
t	time, (s)
T	temperature, (K)
V	volume, (m^3)
w	molecular weight, ($kg\,mol^{-1}$)
W	energy density, ($J\,m^{-3}$)
$\dot{W}$	work, ($W\,m^{-3}$)
X	conversion per reactant
Y	mass fraction

Greek letters

β	generalized temperature exponent
δR	thickness of thermal boundary layer, (m)
ΔC	molar concentration difference, ($mol\,m^{-3}$)
γ	polytropic exponent
η	chemical efficiency
λ	thermal conductivity, ($W\,m^{-1}\,K^{-1}$)
μ	dynamic viscosity, (Pa s)
ρ	density, ($kg\,m^{-3}$)
σ	surface tension, ($J\,m^{-2}$)
τ	characteristic time, (s)
υ	stoichiometric coefficient
ω	angular frequency, ($rad\,s^{-1}$)

Subscripts

A	acoustic
B	bubble
d	diffusion of gas in liquid phase
di	diffusion of gas within the bubble
f	forward
G	gas phase
H_2O	water
k	specie in gas phase
L	liquid phase
n	natural
r	reverse
	at the bubble interface
0	Initial
∞	static ambient pressure

having grown to an unstable size during the rarefaction cycle, creating cavitation especially for high acoustic pressure amplitudes of about 1 bar and more [4]. Collapsing bubbles can emit light by sonoluminescence [3]. The collapse of bubbles near an adiabatic regime results in the generation of extreme conditions, e.g. temperatures of the order of several thousand degrees Kelvin and pressures of the order of several hundred atmospheres in localized zones, where reactions can occur by formation and recombination of free radicals (e.g. H, HO and HO_2 during the sonolysis of water), while the overall liquid environment remains near ambient conditions. Thus, phenomena caused by ultrasonic techniques have been proven to be useful in many liquids to enhance reactions traditionally implemented with high temperature and pressure processes [5]. Many parameters affect cavitation, e.g. acoustic parameters (ultrasonic frequency, acoustic intensity), solvent properties (surface tension, viscosity, vapor pressure, thermal conductivity, speed of sound) and operating conditions (temperature, pressure, dissolved gases). The physicochemical properties of CO_2 can change the pressure and the temperature associated with a collapse. Furthermore, CO_2 can change the reaction scheme inside the bubble.

Sonochemistry of CO_2 dissolved in liquid water has been studied by some authors from 20 to 2400 kHz at lab scale in closed vessels with a volume in the 10–1000 cm^3 range [6–10]. An interesting finding for CO_2 reduction is that the final products formed in CO_2 bubbles are mainly CO, H_2, O_2 and H_2O_2. In parallel to experimental studies with sonochemistry, some models based on the hot-spot theory have been developed to study bubble dynamics and the factors that affect sonochemistry [4,11–16]. However, very few models have studied the effect of dissolved CO_2 on the aqueous medium in the presence of sonochemical activity [17].

There are still several fundamental issues concerning the sonochemistry of dissolved gases and CO_2 in water, because direct measurement in a cavitation bubble is extremely difficult using traditional approaches [18]. The hot spot temperature and pressure as well as the composition of radicals and gas species in an oscillating bubble can be estimated more easily by modeling. The aim of this work is to model, for a single bubble, the close coupling of the mechanisms of bubble dynamics with the kinetics of gas phase reactions in the bubble that can lead to CO_2 reduction. The calculation of the concentration of free radicals and gases formed in the bubble is undertaken mainly in order to look at the effects of ultrasound frequency, pressure amplitude, initial bubble radius and bubble composition. Finally, a comparison is made between theoretical predictions and literature measurements.

2. Previous works in literature

The effects of several parameters on sonochemistry of CO_2 in liquid water have been studied by several authors [6–10] in controlled conditions (Table 1), e.g. gas dissolved as nuclei in water (especially N_2, Ar and He), temperature of liquid water, CO_2 concentration in gas phase and ultrasonic frequency.

At lab scale, Harada [7] and Harada and Ono [10] have shown that the decreasing rate of CO_2 follows the order Ar > He > N_2. Indeed, sonochemistry hardly occurs under polyatomic gases and does not proceed in general in a pure CO_2 atmosphere. Generally, the capacity of Ar to support sonochemistry has been explained by both its thermal capacity and its thermal conductivity compared to polyatomic gases. Thus, an insulating gas with low thermal conductivity contributes to the slowing down of thermal dissipation from cavitation zones to liquid water. Furthermore, using a dissolved gas that has a high specific heat capacity ratio is efficient for achieving higher temperatures during