Supplementary Material with Paper No. ie-2009-016557 by Amrita Ranjan et al.

MATHEMATICAL MODEL FOR CAVITATION BUBBLE DYNAMICS AND ESTIMATION OF CONVECTION GENERATED THEREBY

As noted earlier, ultrasound manifests its physical and chemical effects through phenomenon of cavitation, which is nucleation, growth and impulsive transient collapse of gas bubbles driven by bulk pressure variation induced by ultrasound wave. The nuclei for cavitation are contributed by tiny gas bubbles already suspended in liquid or the gas pockets trapped in the crevices of the solid boundaries in the medium such as reactor wall or sonicator probe surface. Upon exposure to ultrasound, these pockets expand to form cavitation bubbles, as the bulk pressure falls below ambient in the rarefaction half cycle. In the subsequent compression half cycle, the bubble undergoes compression. These volume oscillations of the bubbles are in phase with bulk pressure variation, if the pressure amplitude of the ultrasound (or acoustic) waves is low. For high acoustic pressure amplitude, the inertial forces dominate the volume oscillations (or radial motion) of the bubbles. In this case, the bubble keeps on expanding even after the rarefaction cycle is completed. Moreover, the expansion is more than twice the original size. In the subsequent compression cycle, rapid spherical convergence of fluid elements imparts high kinetic energy to the bubble. The velocity of the bubble wall (or gas-liquid interface) can reach or even exceed the sonic speed in liquid medium. The compression of the bubble is adiabatic, and temperatures and pressures in the bubble reach extreme (~ 5000 K, ~ 500 bar). The radial motion of the bubble also gives rise to strong convection in the medium through two principal physical effects, viz. microturbulence and acoustic (or shock) waves. A brief description of these effects is as follows (Leighton, 1994):

Microturbulence: This is essentially oscillatory motion of liquid induced by radial oscillations of cavitation bubble. The velocity of this motion depends on the amplitude of the radial oscillations itself. For large amplitude or transient radial motion, the velocity of microturbulence is quite large so as to cause intense mixing. However, microturbulence is rather local phenomenon, i.e. its intensity is highest in the close vicinity of bubble and decreases very rapidly away from it.

Acoustic (or Shock) Waves: The acoustic or shock waves are consequence of the reflection of fluid elements from the gas-liquid interface, when the bubble wall comes to sudden halt during radial motion. This occurs at the point of minimum radius during transient collapse, when the bubble contains non condensable gas. The intensity of the wave also depends on the amplitude of the radial motion of the bubble. For large amplitude transient bubble motion, the amplitude of these wave can be as high as 50-100 bar; which is capable of causing physical changes (particle size reduction, degradation of large molecules etc.) in the medium. Similar to the microturbulence, the intensity of these waves is maximum in the vicinity of the bubble and diminishes away from it.

In the context of the present study, both of these effects can enhance the extraction of the lipids. A direct measurement of the magnitude of these effects is beyond the capabilities of the instrumentation used in this study, and hence, we rely on numerical simulations of radial motion of the cavitation bubbles to estimate magnitude of microturbulence and acoustic waves under different experimental conditions.

Influence of biomass particles on ultrasound wave propagation and cavitation bubble dynamics: The principal effect of presence of solid particles in the medium on wave propagation is scattering of the waves and effect on cavitation bubble dynamics is induction of an asymmetric collapse leading to formation of microjets. As far as scattering effect of biomass particles is concerned, it is expected to be negligible in the present case (Pierce,

1989) due to two reasons, viz. the concentration of the particles is very dilute, and secondly, the size of particles (~ 100 microns) is much smaller than the wavelength of ultrasound (6 cm). Effect of biomass particles on cavitation bubble dynamics is also expected to be minimal. The reasons for this are also two fold: first is same as stated earlier (low concentration of biomass particles), and secondly, extremely soft nature of the algal biomass. It has been proven in previous studies using high speed photography of cavitation bubbles (Brujan et al., 2001, 2001a) that solid particles with large elasticity modulus (or soft materials) do not induce asymmetric collapse leading to formation of microjets. Thus, radial motion of cavitation bubbles in the vicinity of soft solid boundaries is essentially spherically symmetric. It is in view of these previous studies that we have not taken into account the effect of biomass particles on ultrasound and cavitation bubble dynamics.

For our analysis, we have chosen the following bubble dynamics equation (Lofstedt et al., 1995; Hilgenfeldt et al., 1996; Barber et al., 1997) which is essentially a modified form of the original Rayleigh-Plesset equation (Plesset, 1949) with inclusion of the compressibility effect (Prosperetti & Lezzi, 1986; Keller & Miksis, 1980):

$$R\frac{d^2R}{dt^2}+\frac{3}{2}\left(\frac{dR}{dt}\right)^2=\frac{1}{\rho}\big(p(R,t)-P_0-P(t)\big)+\frac{R}{\rho c}\frac{d}{dt}\big[p(R,t)-P(t)\big]-\frac{4\mu}{\rho R}\frac{dR}{dt}-\frac{2\sigma}{\rho R} \tag{A.1}$$

Various notations are as follows: R = radius of the bubble at any time; dR/dt = velocity of bubble wall; P_0 = ambient or static pressure in bulk liquid; ρ = density of bulk liquid; c = sonic speed in bulk liquid; μ = viscosity of the bulk liquid; σ = surface tension of bulk liquid. $p(R,t)$ and $P(t)$ are the pressures inside the cavitation bubble and the time variant pressure of the acoustic wave, respectively; and are written as:

$$p(R,t)=\left(P_0+\frac{2\sigma}{R_0}-P_v\right)\left(\frac{R_0^{\,3}-h^3}{R^3-h^3}\right)^{\gamma}+P_v \tag{A.2}$$

$$P(t) = P_A \cos(2\pi ft) = P_A \cos(\omega t) \tag{A.3}$$

Various notations are as follows: R_0 = initial or equilibrium radius of the bubble; P_0 = vapor pressure of bulk liquid; h = van der Waal's hard core radius; r = polytropic constant of bubble content; P_A = pressure amplitude of ultrasound wave; f = frequency of ultrasound wave; ω = angular frequency of ultrasound waves. With substitution as $dR/dt = s$, and expansion of the derivative terms on the RHS, equation A.1 gets transformed into two simultaneous ODEs as:

$$\frac{dR}{dt} = s \tag{A.4a}$$

$$\frac{ds}{dt} = \frac{1}{R\rho}\left[p(R,t) - P(t) - P_0\right] + \frac{1}{\rho c}\left[\frac{-3\gamma R^3 p(R,t)}{(R^3 - h^3)}\frac{dR}{dt}\right] + \frac{1}{\rho c}\omega P_A sin(\omega t) - \frac{4\mu}{\rho R^2}\frac{dR}{dt} - \frac{2\sigma}{\rho R^2} - \frac{3}{2}\frac{s^2}{R} \tag{A.4b}$$

The numerical solution of the equations A.4a and A.4b using Runge-Kutta adaptive step size method (Press et al., 1992), yields time series of R and dR/dt. The magnitude of the convective effects, viz. velocity of the microturbulence $\mu(r,t)$ and pressure amplitude of the shock waves $P_s(r,t)$ can be calculated as follows:

$$u(r,t) = \frac{R^2}{r^2}\left(\frac{dR}{dt}\right) \tag{A.5}$$

$$P_s(r,t) = \rho\frac{R}{r}\left[2\left(\frac{dR}{dt}\right)^2 + R\frac{d^2R}{dt^2}\right] \tag{A.6}$$

where r is the distance from bubble centre.

Simulation parameters: The physical properties of the mixture of chloroform and methanol have been approximated by using the linear mixing rule based on mole fractions of the components in the mixture. This is described in many textbooks on thermodynamics (for example Chapter 5 of Reid et al., 1987). Such an approach has been adopted in many previous papers on cavitation bubble dynamics (for example Storey & Szeri, 2000, 2001, Toegel & Lohse, 2002). Bubble dynamics models employing either linear or geometric mixing rule have successfully explained behavior of sonoluminescing bubble as well as trends in sonochemistry experiments.

Values of other physical parameters required for numerical solution of equations A.4a and A.4b are estimated as follows.

Frequency of the ultrasound waves (f) = 20 kHz (same as the frequency of the sonic processor); P_A = 1.5 bar (estimated using calorimetric techniques; Sivasankar et al., 2007); R_0 = 5 μm (taken as representative value; Mettin et al., 1997); γ = 1/3 (polytropic constant); h = R_0/8.86 (van der Waal's hard core radius); r = 1 mm (taken as representative value); c = 1054 m/s (for n-hexane) and 969 m/s (for chloroform-methanol mixture); σ =18.43 mN/m (for n-hexane) and 27.1 mN/m (for chloroform-methanol mixture); ρ = 660 kg/m^3 (for n-hexane) and 1485 kg/m^3 (for chloroform-methanol mixture); T = 298 K (or 25 °C); $\mu = 2.94 \times 10^{-4}$ Pa-s (n-hexane) and 5.8×10^{-4} Pa-s (chloroform-methanol). The vapor pressures (P_v) of the two solvents (in bar) are calculated using Antoine correlations (NIST Data Gateway, 2009):

$$n\text{-hexane: } \log_{10} P_v = 4.00266 - \frac{1171.53}{T_o - 48.784}$$

$$\text{chloroform} - \text{methanol: } \log_{10} P_v = 4.20772 - \frac{1233.129}{T_o - 40.953}$$

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