Physics of ultrasound and cavitation: A brief overview

Before proceeding to literature review on ultrasound-assisted bioalcohol synthesis, we have given herewith some basic information on concepts and principles of ultrasound and cavitation. This section may help readers (especially those who are not conversant with the science of ultrasound and cavitation phenomena) build necessary background for perceiving and interpreting the subsequent sections on critical analysis of the ultrasound assisted biomass pretreatment and bioalcohol synthesis.

1.1 Ultrasound wave phenomenon

As noted earlier, sound wave passes through a compressible medium in the form of a longitudinal wave comprising of alternate compression and rarefaction phases. Propagation of the ultrasound wave causes sinusoidal variation in bulk pressure as well as density of the medium. A simple mathematical expression that represents the variation in bulk pressure with passage of ultrasound is:

\[ P(t) = P_0 - P_A \sin(\omega t) = P_o - P_s \sin(2\pi ft) \]  \hspace{1cm} (1)

where, \( P_o \) is the hydrostatic pressure in the medium, \( P_A \) is the pressure amplitude of the ultrasound wave, \( \omega \) is the angular frequency of the ultrasound wave, while \( f \) is the absolute frequency and \( t \) is time in sec. The pressure amplitude of the ultrasound wave is governed by
net power input to the ultrasonic device and the area of the transducer through which ultrasound is generated. The pressure amplitude of the ultrasound wave also determines the oscillatory velocity of the fluid elements. Basic relations between these physical quantities are given in our previous publication.\(^1\) Ultrasound wave undergoes attenuation (or reduction in pressure amplitude due to energy loss) during its passage through the medium. This effect is attributed to three mechanisms, viz. frictional (or viscous) loss, thermal loss and acoustic damping due to bubbles.\(^2,3\) Viscous dissipation or attenuation is essentially due to absorption of the momentum of the ultrasound wave by the medium due to finite viscosity and this loss is manifested in terms of unidirectional circulatory currents set up in the medium (known as acoustic streaming). The gas bubbles present in the medium also scatter the ultrasound waves that cause severe attenuation. Presence of gas bubbles in the liquid also alters the compressibility of the medium, as a result of which the speed of sound in the medium reduces.

1.2 Cavitation Bubble Dynamics

Ultrasound manifests its physical and chemical effects through phenomenon of cavitation.\(^4,5\) Cavitation essentially refers to nucleation, growth, oscillations and implosive transient collapse which results due to the variation in bulk pressure induced by propagation of ultrasound wave through the medium. In ultrasonic cavitation (also known as acoustic cavitation), the liquid medium is usually stagnant during propagation of the ultrasound wave through it. However, in some processes (especially those operating on continuous basis), the liquid medium could be flowing. In this case, variation of bulk pressure can also be created by changing the flow geometry that induces variation in the velocity of the flow. This type of cavitation is termed as hydrodynamic cavitation. Occurrence of acoustic or hydrodynamic cavitation requires presence of nuclei in the bulk liquid medium. The cavitation nuclei could be tiny free-floating gas bubbles already present in the liquid or the gas pockets trapped in the
crevices of the solid boundaries in the liquid medium. These gas pockets can grow in response to reduction in ambient pressure with passage of acoustic wave. In case of hydrodynamic cavitation, the cavitation nuclei are also contributed by the gas bubble generated due to release of dissolved gas, as the bulk pressure in the flow falls with rise in velocity. Depending on the level of energy dissipation in the medium, vaporous cavitation can also occur in the medium in case of both acoustic and hydrodynamic cavitation that results in generation of vapor bubbles.

1.3 Radial motion of cavitation bubbles

As noted earlier, transient implosive collapse of the cavitation bubbles creates intense energy concentration on extremely small spatial and temporal scale. This phenomenon has been extensively studied with help of mathematical models for the radial motion (or volumetric oscillations) of the cavitation bubbles. Modeling of cavitation bubble dynamics is a major area of research in physical acoustics with voluminous literature (more than 1000 papers with both experimental and theoretical approach) published in past five decades. In this section we very briefly summarize the major contributions in this area for the readers who are not well conversant with this subject matter. The mathematical models for cavitation bubble dynamics described in this section have been developed for the acoustic or ultrasonic cavitation, but these are equally applicable for the hydrodynamic cavitation. For more information on cavitation bubble dynamics, we would like to refer the interested readers to comprehensive treatises by Young (1989) or Leighton (1994).

The nature of the radial motion (or volumetric oscillations) of the cavitation bubble depends on the pressure amplitude of the acoustic wave. Two forces, viz. inertial force and pressure force, govern the radial motion of the cavitation bubble. For relatively small acoustic pressure amplitudes – typically smaller than the static pressure in the medium, the volume oscillations of the bubble are of small amplitude – driven mainly by the pressure forces, and
essentially in phase with the acoustic wave. Volumetric oscillations of the cavitation bubble become large-amplitude as well as non–linear for larger acoustic pressure amplitudes—typically greater than static pressure in the medium. In this case, the radial motion of the bubble comprises of an initial explosive growth, in which the bubble radius grows at least two times or higher of its initial value. The growth phase is followed by a transient collapse and few after–bounces. In this case, the radial motion of the bubble is dominated by the pressure forces.\textsuperscript{8}

Lord Rayleigh presented the first–ever mathematical analysis of an empty cavity collapsing under constant static pressure.\textsuperscript{9} Subsequent researchers improved the analysis of Lord Rayleigh, which included accounting for the effects of surface tension and viscosity of liquid, and presence of non–condensable gas and solvent vapor inside the bubble. This analysis resulted in the popular Rayleigh–Plesset–Noltingk–Neppiras–Poritsky equation for radial motion of bubble which is as follows:\textsuperscript{10–12}

\[ R \frac{d^2 R}{dt^2} + \frac{3}{2} \left( \frac{dR}{dt} \right)^2 = \frac{1}{\rho} \left[ \left( P_o + \frac{2\sigma}{R_o} - P_v \right) \left( \frac{R_o}{R} \right)^{3\gamma} + P_v - \frac{2\sigma}{R} - \frac{4\mu}{R} \frac{dR}{dt} - \left( P_o + P(t) \right) \right] \] (2)

The above equation did not account for liquid compressibility, which becomes a dominant factor as the bubble wall velocity becomes closer or even exceeds the sonic velocity in the medium during the final moment of transient bubble collapse. The first model for cavitation bubble dynamics accounting for liquid compressibility effect was proposed by Gilmore \textsuperscript{13} on the basis of Kirkwood-Bethe hypothesis.\textsuperscript{14} Major subsequent contributions in this area are from Keller and Kolodoner\textsuperscript{15}; Keller and Miksis\textsuperscript{16} and Prosperetti and Lezzi\textsuperscript{17}. These analyses have resulted in more rigorous forms of models for radial motion of cavitation bubbles. Two most popular equations for cavitation bubble dynamics among scientific community are:

(1) Keller and Miksis equation:\textsuperscript{15, 18}
(2) Bubble dynamics equation proposed by Lofstedt et al.\textsuperscript{19} and Barber et al.\textsuperscript{20}:

\[
\left(1 - \frac{\dot{R}}{c}\right) R \frac{dR}{dt} + \left(1 - \frac{3 \dot{R}}{c}\right) \frac{3 \dot{R}}{2} = \frac{1}{\rho} \left[ P_g - P_o - P(t) \right] + \frac{\dot{R} dP_g}{\rho c \, dt} - 4 \nu \frac{\dot{R}}{R} - 2 \frac{\sigma}{\rho R} \tag{3}
\]

\[
R \frac{dR}{dt} + \frac{3 \dot{R}}{2} = \frac{1}{\rho} \left[ P_g - P_o - P(t) \right] + \frac{\dot{R} dP_g}{\rho c \, dt} - 4 \nu \frac{\dot{R}}{R} - 2 \frac{\sigma}{\rho R} \tag{4}
\]

1.4 Modeling of the sonochemical and sonophysical effects

Ultrasound waves as well as radial motion of cavitation bubbles driven by these waves induce physical and chemical effects in the reaction system or in general liquid medium. The physical effect associated with ultrasound and cavitation is essentially generation of intense micro-mixing in the system as a result of strong micro-convection generated through various mechanisms.

1.4.1 Sonochemical effect

The chemical effect associated with ultrasound and cavitation (popularly known as sonochemical effect) is generation of highly reactive chemical species, some of which are radical species, which can induce/accelerate numerous chemical reactions in the medium, generated through thermal dissociation of gas and vapor molecules present in the bubble at the moment of transient collapse.\textsuperscript{4, 21, 22}

Several previous authors have dealt with the physical explanation to the sonochemical effect induced by ultrasound and cavitation. As a result of sinusoidal variation in the bulk pressure in the liquid medium produced due to passage of ultrasound wave through the medium, the cavitation bubbles grow (from the nuclei) in the rarefaction half cycle of ultrasound, when the pressure in the medium falls sufficiently below the ambient or static pressure. As stated earlier, if the pressure amplitude of the ultrasound wave is higher than the static pressure in the medium, the radial motion of the bubble is dominated by inertial forces and bubble undergoes an explosive growth to several times its original size. During this expansion, liquid at the bubble interface evaporates with diffusion of the vapor molecules.
towards the core of the bubble. However, as the bubble gets compressed in the compression half cycle of ultrasound, not all of the vapor present in the bubble can condense and return to the liquid medium. A review of literature treating vapor transport across bubble interface during radial motion and the entrapment of vapor in the bubble during transient collapse has been provided in our earlier paper.23

The general analysis of the vapor transport in the cavitation bubble was presented by Storey and Szeri 24. This analysis relaxed all of the assumptions and simplifications made in previous analyses. Storey and Szeri 24 showed that in the compression phase of radial bubble motion, counter diffusion of the vapor molecules occurs with condensation at the bubble wall. The principal result of the study of Storey and Szeri 25 was that water vapor transport in the bubble is a two–step process, i.e. diffusion to the bubble wall and condensation at the wall. Thus, it is influenced by two time scales, viz. time scale of diffusion ($t_{\text{diff}}$) and time scale of condensation ($t_{\text{cond}}$) 26, and their magnitudes relative to the time scale of bubble dynamics, $t_{\text{osc}}$.

During the transient motion of cavitation bubble, the velocity of the bubble wall (or the bubble-liquid interface) reaches or even exceeds the sonic velocity in the medium. At this stage, $t_{\text{osc}} \ll t_{\text{diff}}$ condition is reached, and the vapor molecules have insufficient time to diffuse to the bubble wall for undergoing phase change or condensation. The bubble composition gets essentially “freezed” with fixed and uneven distribution of vapor molecules in the bubble. In other words, the vapor present inside the bubble is essentially “trapped” in the bubble. In addition to diffusion limitation, another mechanism which also contributes to trapping of vapor molecules inside the bubble, is the non–equilibrium phase change at the bubble wall. In the final moments of bubble collapse, the time scale of bubble oscillations becomes lesser than the time scale of phase change or vapor condensation. As a consequence, all of the vapor molecules approaching the bubble wall cannot “stick” to the bubble wall for
undergoing a phase change. Storey and Szeri\(^\text{24}\) have shown in their analysis that the vapor entrapment in the cavitation bubble occurs predominantly due to diffusion limitation than condensation limitation. As the temperature and pressure inside the bubble reach extreme at transient collapse, the vapor molecules trapped inside the bubble undergo thermal dissociation along with the gas molecules resulting in generation of spectrum of chemical species (with relatively smaller molecular weight) including some radical species. In view of the results of Storey and Szeri\(^\text{24, 26}\), Toegel et al.\(^\text{27}\) developed a simple diffusion limited model, which has become immensely popular among the sonochemical community. This model, based on ordinary differential equations, has distinct merits of being simple yet physically realistic. The essential equations and thermodynamic data of the diffusion limited ordinary differential equation (ODE) model are given in Tables 1 and 2.\(^\text{28}\) The main components of this model are: (1) Keller–Miksis equation for radical motion of cavitation bubbles, (2) Equation for the diffusive flux of solvent vapor through the bubble wall, (3) Equation for heat conduction across bubble wall and (4) Overall energy balance treating the cavitation bubble as an open system. The transport parameters for the heat and mass transfer are determined using Chapman–Enskog theory with Lennard–Jones 12–6 potential at the bulk temperature of the liquid.\(^\text{29-31}\) With assumption of fast condensation of vapor molecules at bubble interface and prevalence of equilibrium, the thermal and diffusive penetration depths are estimated using dimensional analysis as follows:\(^\text{32}\):

\[
l_{\text{diff}} = \min \left( \frac{R}{\pi}, \sqrt{\frac{RD_i}{|dR/dt|}} \right) \tag{5}
\]

\[
l_{th} = \min \left( \frac{R}{\pi}, \sqrt{\frac{R\kappa}{|dR/dt|}} \right) \tag{6}
\]

An important assumption made for estimation of the sonochemical effect is the prevalence of chemical equilibrium in the bubble all through radial motion. This assumption is based on the relative time scales of reactions kinetics inside the bubble and the timescale of
bubble dynamics. The temperature and the pressure in the bubble reaches extreme (~ 5000 K and ~ 50 MPa) at the point of maximum compression triggering chemical reactions with large kinetic constants. Moreover, the concentrations of different chemical species in the bubble are very high due to extremely small volume. As a result, the rates of various reactions occurring between chemical species present in the bubble are extremely fast, due to which chemical equilibrium prevails in bubbles all along during the radial motion.\textsuperscript{23,33}

1.4.2 Physical effects of cavitation bubble

Ultrasound and cavitation render several physical effects on a reaction system. The main manifestation of all of these results is generation of intense micro–convection and micro–mixing in the reaction system. A brief description of all physical effects of ultrasound and cavitation is given below \textsuperscript{2-4, 7}:

Micro–streaming: This is essentially small amplitude oscillatory motion of fluid elements around a mean position, which is induced by propagation of ultrasound wave. For a typical ultrasound wave with pressure amplitude of 120 kPa in water ($\rho = 1000$ kg/m$^3$, $C = 1500$ m/s), the micro–streaming velocity = 0.08 m/s.

Acoustic streaming: Due to finite viscosity of the medium through which ultrasound waves propagate, the momentum of the wave is absorbed by the medium. This is manifested in terms of low velocity unidirectional currents of the fluid known as acoustic streaming.\textsuperscript{34, 35} Acoustic streaming also generated due to obstruction of the oscillatory motion of the fluid elements in the vicinity of solid boundaries in the medium. This phenomenon results in setting up of unidirectional current parallel to the boundary.

Microturbulence: The oscillatory motion of fluid induced by volume oscillations of the bubble is called microturbulence. During expansion of the cavitation bubble, the liquid surrounding the bubble is displaced away from bubble interface. In the compression phase, fast contraction of the bubble generates “void” around it, and the liquid is pulled towards the
bubble as it fills this void. The velocity of microturbulence, is obviously a function of the amplitude of bubble oscillation. The phenomenon of microturbulence is observed only in the close vicinity of the bubble, and diminishes very rapidly away from it.

**Acoustic (or shock) waves:** As noted above, the liquid gushes or spherically converges towards the bubble interface during the contraction phase. The compression of the bubble is mostly adiabatic and the pressure inside the bubble rises rapidly if the bubble contains non-condensable gas such as air. At the point of minimum radius (or maximum compression) during radial motion, the velocity of the bubble wall becomes zero. At this moment, the velocity of the fluid elements converging towards the bubble interface also reduces to zero – almost instantly – which creates rise in pressure (due to conservation of momentum). This generates a high pressure shock wave that propagates through the medium. The bubble may undergo rebounce due to the pressure exerted by the non-condensable gas inside the bubble.

**Microjets:** During radial motion driven by ultrasound wave, the initial spherical geometry of the bubble may be disturbed due to non-uniformity of pressure gradients surrounding it. These non-uniform gradients are induced by phase boundaries, either solid–liquid, gas–liquid or liquid–liquid, due to which the motion of liquid in the vicinity of the cavitation bubble is hindered. Under influence of non-uniform pressure gradient, the bubble undergoes asymmetric radial motion with the portion of bubble exposed to higher pressure collapsing at a faster rate than rest of the bubble. Such asymmetric motion results in formation of a high speed liquid jet. The direction of this jet depends on the type of phase boundary. For a “rigid” boundary such as metal surface, the microjet is directed towards the boundary. For a “free” boundary such as gas-liquid (typically air-water) interface, the microjet is directed away from the boundary. The velocities of these microjets are in the range of 120–150 m/s.
References:


Table S.1: Essential equations (ODE’s) of the diffusion-limited ODE model

<table>
<thead>
<tr>
<th>Model Component</th>
<th>Equation</th>
<th>Initial Value</th>
</tr>
</thead>
</table>
| 1. Radial motion of the cavitation bubble | \[
\left(1 - \frac{dR}{dt}\right) \frac{d^2R}{dt^2} + \frac{3}{2} \left(1 - \frac{dR}{dt}\right) \left(\frac{dR}{dt}\right)^2 = \frac{1}{\rho_1} \left(1 + \frac{dR}{dt}\right) (P_i - P_t) + \frac{R \frac{dP}{dt} - 4 \nu \frac{dR}{dt} \frac{dP}{dt} - 2 \sigma}{\rho_c} \frac{dR}{dt} + dR \frac{dR}{dt} \frac{dP}{dt} \]
| Internal pressure in the bubble: | \[P_i = \frac{N_{net}(t) kT}{4\pi(R^3(t) - h^3)/3}\] | At \(t = 0\), \(R = R_0\), \(dR/dt = 0\) |
| Pressure in bulk liquid medium: | \[P_t = P_0 - P_s \sin(2\pi\theta)\] |
| 2. Diffusive flux of solvent (methanol) molecules | \[
\frac{dN_S}{dt} = 4\pi R^2 \frac{\partial C_S}{\partial r} \bigg|_{r = h} \approx 4\pi R^2 D_S \left(\frac{C_{S,R} - C_{S}}{l_{diff}}\right)\]
| Instantaneous diffusive penetration depth: | \[l_{diff} = \min\left(\frac{RD_S}{dR/dt} \frac{R}{\pi}\right)\] | At \(t = 0\), \(N_S = 0\) |
| 3. Heat conduction across bubble wall | \[
\frac{dQ}{dt} = 4\pi R^2 \frac{\partial T}{\partial r} \bigg|_{r = h} \approx 4\pi R^2 \lambda \left(\frac{T_0 - T}{l_a}\right)\]
| Thermal diffusion length: | \[l_a = \min\left(\frac{R\kappa}{dR/dt} \frac{R}{\pi}\right)\] | At \(t = 0\), \(Q = 0\) |
| 4. Overall energy balance | \[C_{V,m} \frac{dT}{dt} = \frac{dQ}{dt} - P_dV/dt + \left(h_s - U_s\right) dN_s/dt\]
| Mixture heat capacity: \([i = N_2/O_2/Solvent]\) | \(C_{V,m} = \sum C_{V,i} N_i\) |
| Molecular properties of solvent: | \[h = \left(1 + \frac{f_i}{2}\right) kT_0\] | At \(t = 0\), \(T = T_0\) |
| Enthalpy: | \[
U_s = N_s k T \left(3 + \sum \frac{\theta_s/T}{\exp(\theta_s/T) - 1}\right)\]
| Internal energy: \([i = N_2/O_2/Solvent]\) | \[
C_{V,s} = N_s k \left(f_i/2 + \sum \left(\frac{\theta_s/T}{\exp(\theta_s/T) - 1}\right)\right)\] | Heat capacity of various species \([i = N_2/O_2/Solvent]\): |
Table S.2: Thermodynamic data for the diffusion limited model

<table>
<thead>
<tr>
<th>Species</th>
<th>Degrees of freedom (translational + rotational) $(f_i)$</th>
<th>Lennard–Jones force constants $\sigma(10^{-10} \text{ m})$</th>
<th>Characteristic vibrational temperatures $\theta(\text{K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>5</td>
<td>3.68</td>
<td>92</td>
</tr>
<tr>
<td>O$_2$</td>
<td>5</td>
<td>3.43</td>
<td>113</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>6</td>
<td>3.626</td>
<td>481.8</td>
</tr>
<tr>
<td>Ar</td>
<td>3</td>
<td>3.42</td>
<td>124</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>6</td>
<td>2.65</td>
<td>380</td>
</tr>
</tbody>
</table>

* Data taken from Toegel$^{28}$, Hirschfelder et al.,$^{29}$ Reid et al.,$^{30}$ Condon and Odishaw,$^{31}$ Davis$^{36}$.

**Notations:** $R$ – radius of the bubble; $dR/dt$ – bubble wall velocity; $c$ – velocity of sound in bulk liquid medium; $\rho$ – density of the liquid; $\nu$ – kinematic viscosity of liquid; $\sigma$ – surface tension of liquid; $\kappa$ – thermal conductivity of bubble contents; $\lambda$ – thermal diffusivity of bubble contents; $\theta$ – characteristic vibrational temperature(s) of the species; $N_S$ – number of solvent molecules in the bubble; $N_{N_2}$ – number of nitrogen molecules in the bubble; $N_{O_2}$ – number of oxygen molecules in the bubble; $t$ – time, $D$ – diffusion coefficient of solvent vapor; $C_S$ – concentration of solvent molecules in the bubble; $C_{S,G}$ – concentration of solvent molecules at the bubble wall or gas–liquid interface; $D_S$ – diffusion coefficient of solvent; $Q$ – heat conducted across bubble wall; $T$ – temperature of the bubble contents; $T_o$ – ambient (or bulk liquid medium) temperature; $k$ – Boltzmann constant; $h$ – molecular enthalpy of solvent; $U_S$ – internal energy of solvent molecules; $f_i$ – translational and rotational degrees of freedom; $h$ – van der Waal’s hard core radius; $P_o$ – ambient (bulk) pressure in liquid; $P_A$ – pressure amplitude of ultrasound wave; $f$ – frequency of ultrasound wave.