Acoustic Cavitation as Process Intensifier: A Phenomenological Study

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Abstract

When an acoustic field is coupled to a liquid and transient cavitation is induced, it can significantly intensify ongoing processes, making them run faster, cheaper, better. Surface cleaning is a classic example that has been investigated in various studies over the years. Sonochemical reactors are increasingly being deployed in industry. Cavitational enhancement of mass transfer phenomena such as diffusion, dissolution and leaching has been quantified in literature, and its effect on heat transfer from fluids to adjoining solids has been reported as well. Nano-particle synthesis by "sono-fragmentation" is widely practised as a top-down alternative to bottom-up methods of nano-particle production with tons-per-day throughput. Cavitation-induced destratification has been investigated earlier in this laboratory as a method to keep cryogenic fuels well-mixed during storage on the ground. More recently, cavitation has been evaluated as a mechanism to remove ash, sulfur and alkalis from coal prior to combustion, thereby greatly mitigating the downstream propensity for slagging, fouling, corrosion and erosion. Practical applications abound, as the additional energy expenditure associated with the acoustic field is easily compensated by savings in process time and productivity enhancement.

Unification of these cavitation-induced effects in multiple domains is a worthwhile exercise in order that the effect may be fully understood and optimized. In particular, ultrasonic frequency is a tunable parameter that can have dramatic effects on the outcome. The transition from the cavitation regime to acoustic streaming (as frequency is increased from the ultrasonic to the megasonic regime) is one that needs to be characterized and managed with care. In many applications, acoustic streaming can provide a synergistic effect when deployed in conjunction with cavitation, as in, for example, a dual-frequency system that can operate in the high (> 100 kHz) and low (<100 kHz) rage. Alternatively, an intermediate frequency such 300 kHz which combines both cavitational and streaming features may be employed as well.

The definition of a "process intensification factor" and assessment of its dependence on ultrasonic frequency for various thermodynamic and transport phenomena constitutes a valuable contribution for practitioners, and this has been attempted in this paper. Based on the frequency dependence established, processes may be categorized with respect to their sensitivity to acoustic cavitation. This categorization enables optimum application of cavitational fields to achieve desired results with minimum expenditure of energy, and mitigation of undesirable side effects.

Keywords: Cavitation, Ultrasound, Process Intensification, Sono-fragmentation, Coal beneficiation, De-sulphurisation

Introduction

Application of ultrasound on liquids such as water leads to two types of physical mechanisms: acoustic cavitation and acoustic streaming. The former refers to the implosion of bubbles resulting in a shock wave that travels in all directions, while the latter is described by a flow that is unidirectional in nature along the normal to the transducer in the ultrasonic equipment. When a medium is exposed to sound waves of frequency above 18 kHz [1], it results in the propagation of oscillating compression and rarefaction cycles. When a local pressure gradient develops due to difference in ambient pressure and vapor pressure of the liquid, bubbles are formed [2]. These bubbles grow in size till they can no longer sustain themselves, leading to a violent bubble collapse which causes release of shock waves that traverse the medium. This is associated with a local increase of temperature and pressure, often reported to be up to 5000K and 1000 atm., respectively.

When the ambient pressure of a liquid is reduced adequately, it can boil without heating. This principle is used in an ultrasonic tank where the reduction of local pressure results in formation and implosion of bubbles, leading to

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release of shock waves throughout the medium [1]. Cavitation can be stable (occurs at lower intensities where the bubbles oscillate about their mean position) or transient (occurs at higher intensities where the bubbles grow and collapse violently). As rarefaction and compression occur in alternating cycles, bubbles form and grow during the former and collapse in the latter cycles. As the frequency increases, the number of bubbles formed increases correspondingly [3]. However, the size of the bubble decreases with increasing frequency and leads to reduced intensity of cavitation as the frequency increases. This explains the pronounced effect of cavitation intensity at lower frequencies.

Cavitation intensity depends on a number of factors [4]. While the force of cavitation is inversely proportional to the cube of frequency, other properties of the medium such as surface tension, vapour pressure, temperature, viscosity and density play a key role as well. For example, altering the temperature results in change in ambient pressure and the gradient developed becomes higher leading to higher cavitation effects. Similarly, lowering the viscosity leads to a better response of the liquid to bubble growth and collapse, and increases cavitation effects in turn. Each of these properties can be altered depending on the medium used for bubble growth and collapse.

The objective of this work is to study the "intensification" effect of ultrasound-assisted processes. Although ultrasound has been used for several decades in diverse fields to improve processes [5], the pace of applications has accelerated in recent times. Cavitation can have two types of effects on a chemical reaction: it can either accelerate the reaction, or promote reactions which would not have occurred otherwise. The latter happens due to the dissociation of sonicated water into hydrogen ions and hydroxyl radicals which, in turn, leads to multiple back reactions and formation of new products. The mechanical effects associated with cavitation are also of significance in a number of systems. The formation and collapse of bubbles at a surface leads to a sudden inflow of liquid at the surface, and since this inflow occurs at high local temperature, pressure and velocity, it is an important mechanism in ultrasonic surface cleaning applications. Cavitation has also found abundant applications in wastewater treatment, rupture of cells, synthesis of nano-particles, etc. While some processes may be highly sensitive to cavitation, some might need a combination of cavitation and acoustic streaming to demonstrate intensification effects which are noteworthy. A consolidated understanding of the role that cavitation plays in process-intensification in a variety of heterogeneous systems would be useful in identifying system-specific parameters which can be tuned for optimization.

Cavitation as a process-intensifier: Applications

a. <u>Heat-Transfer enhancement in furnace tubes</u>

Dhanalakshmi et al. [6] studied the effect of ultrasound-assisted heat transfer enhancement in furnace tubes. This work focused on the heat transfer characteristics of water flowing in a tube exposed to heat in the presence and absence of ultrasound. It was found that the critical parameter in the process is the ratio of characteristic ultrasonic field velocity and prevailing flow velocity. Though heat transfer enhancement due to ultrasonic exposure depended very much on the flow conditions, i.e., the Reynolds number, heat transfer enhancement rate (HTER) at 20 kHz frequency increased till a Reynolds number of 500 was reached; it decreased as Reynolds number increased from 500 to 1200 and showed no significant change thereafter. This study was done with 3 different frequencies – 20 kHz, 33 kHz and a combination of 20 and 33 kHz. While 20 kHz showed much better HTER compared to 33 kHz, 20+33 kHz was slightly better than 20 kHz alone. This illustrates that while 20 kHz alone is a first-order effect, using a combination of frequencies introduces a second-order effect. They concluded that the cavitation technique for heat transfer enhancement is ineffective for higher flow rates, but showed considerable improvement for controlled laminar flow regimes.

b. <u>Degradation of Methyl Violet</u>

High-intensity, low-frequency ultrasound is widely used to augment sono-chemical reactions. The sono-chemical hotspots formed due to cavitational implosion lead to disintegration of water molecules into H^+ and OH^- radicals. These recombine to form hydrogen peroxide, molecular hydrogen and a number of other radicals and species. Methyl violet dye is released as an industrial waste and is extremely harmful to plant and aquatic life owing to its highly toxic characteristics. The main aim of this study was to boost decolorization of methyl violet using ultrasound

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[6]. The experiments were conducted in both tank-type and probe-type sonicators, and utilizing frequencies ranging from 20 kHz to 1 MHz. The main steps involved preparation of Fenton's reagent, mixing with dye dissolved in water and irradiating with ultrasound for 150 minutes. The results showed that in the presence of Fenton's reagent, ultrasonic irradiation of the contaminated sample led to near-complete removal of dye from the water. The effect of frequency is interesting to note because as the frequency increases, decolorization of water is faster, and reaches near-completion although the increase in rate is not significant when the frequency exceeds 430 kHz. At higher frequencies, the cavitation effect decreases and is dominated by acoustic streaming, the large density of bubbles leads to higher gas-liquid interfacial area and hence greater contact with OH radicals, resulting in higher reaction rates. The rate of decolorization also increased with increasing power.

c. <u>Sono-fragmentation of coal</u>

This study [6], focused on the breakage of coal particles suspended in a solution. Frequencies spanning from low (<100 kHz), intermediate (100-400 kHz) and high (> 400 kHz) were studied. The ground coal was mixed with three different reagents (hydrogen peroxide, acetic acid and ethanol) separately and sonicated at the chosen power and different frequencies. The results obtained showed that particle breakage was higher at lower frequencies, while particle agglomeration set in at higher frequencies. A combined effect of both the phenomena was observed at intermediate frequencies. Particle breakage was found to be a function of both frequency and time. Longer time of sonication, up to 5 minutes, led to reduced particle size, and particle breakage gradually decreased between 5 to 10 minutes of ultrasonic exposure. Particle size reduction with respect to frequency followed the order: 25 > dual > 132 >192 >470 >1000 kHz.

d. <u>Destratification</u>

Thermal stratification refers to the variation in temperature at different levels of a stored fluid. This is a challenged posed by cryogenic liquids due to boil off losses associated in handling, storage and transport. The work reported in [7] studies the potential effect of ultrasound on thermal destratification. Experiments were initially conducted in a storage tank with water and later extended to cryogenic liquids. This was done by heating the top layer of a tank containing water while the bottom layer remained at room temperature. This system was irradiated with ultrasound and the temperature was measured at all levels creating a complete temperature profile along the height of the vessel at different points of time. A range of frequencies starting from 25 kHz to 470 kHz were used to study the destratification effect. Of all the frequencies chosen, the highest frequency of 470 kHz provided maximum breakage of thermal layer and destratification. When the power input and the storage pressure was increased, 470 kHz system showed drastic increase in stratification Index compared to other lower frequencies. However, dual frequency mode of operation such as 58/192 kHz, which combines the effect of cavitation and streaming, provides better mixing as opposed to using a high frequency tank in isolation.

e. <u>Effervescent atomization</u>

When an effervescent gas is mixed in with a liquid inside a chamber in such a way that bubbles are formed inside a nozzle, it is known as "effervescent atomization". This is used in spraying of fuel as liquid droplets in the combustor and leads to instantaneous formation of vapor. The objective of this study [8] was to produce very fine droplets from an effervescent atomizer, with the assistance of ultrasound. Ultrasound was used to break the bubbles formed by the aerator and distribute their size homogeneously. Experiments were carried out with 20 kHz frequency and showed that ultrasound helped in breaking up of larger sized bubbles into smaller ones. At lower power (of less than 40% input power), bubbles undergo shape change without fragmentation. Although acoustic streaming plays a role in elongation of bubble in the direction of the streaming force, the main mechanism involved in this process of bubble break up is cavitation, and the spray obtained is qualitatively superior when compared to traditional methods employed for effervescent atomization.

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f. <u>Coal beneficiation studies</u>

The high percentage of sulphur and ash content found in Indian coals make them suitable for techniques such as ultrasonic coal wash. This method, employed at different frequencies to remove ash and sulphur from Indian coals, forms the main basis of the study reported in [9, 10]. Along with different frequencies, both aqueous- and reagent-based ultrasonic coal washing methods were explored. 20 kHz, 25 kHz, 58/192 kHz dual-mode and 430 kHz frequencies were used for the study. While the 20 kHz frequency was transmitted via a probe-type sonicator, the rest of the equipment was tank-type. For de-ashing experiments, the sieved coal was sonicated for 15 minutes and subjected to three-level decantation using a fabricated settling column. Ash, being heavier, settles faster than coal. Three layers are then separated and analyzed for ash content. The de-sulphurisation experiments involved sonication of the sample, filtration, washing, drying and analysis as their main steps. For de-ashing, the lowest frequency gave the best size reduction owing to cavitational bubble collapse and subsequent breakage of coal particles. Higher frequencies showed lesser rupture of particles due to streaming being the dominant mechanism in such systems. However, ash removal percentage was optimum at 132 kHz and this behavior may be attributed to the simultaneous presence of streaming and cavitation producing a balanced effect. For de-sulphurisation of coal, the lowest frequency systems showed excellent contact of oxidizing agents produced by ultrasound with fine coal particles, leading to higher removal of pyritic and organic sulphur compared to the high-frequency systems. The rate of removal was, however, more than 90% in all cases, proving the viability of ultrasonic coal wash as an option for de-sulphurisation of coal.

g. <u>Alkali leaching of coal</u>

The alkali content in coal has been a cause of concern with regard to deposition of fly-ash on heat transfer surfaces. The sodium and potassium salts leave the char and react with calcium, magnesium and alumino-silicates leading to the formation of a sticky layer. This sticky layer aids in the deposition of tiny fly-ash particles on the surface of boilers, on super heater tubes and elsewhere in the system. Ultrasound has been effectively used in removal of alkali from coal. Extensive studies have been undertaken to characterize ultrasound-assisted alkali leaching of coal. This technique involves preparing a solution of ground coal, chosen reagent and water, followed by sonication for a short period of time. Analysis is done using ICP. While preliminary studies [11] involved a combination of low- (25 kHz) and high-frequency (430 kHz) systems, further studies done on low-frequency cavitation systems involved 25 kHz, 40 kHz, 58 kHz and 68 kHz. Though the results were satisfactory for potassium leaching, removal of sodium was low. This was followed up with further leaching using a range of ultrasonic and megasonic frequencies, namely 58 kHz, 132 kHz, 58/132 kHz dual, 360 kHz and 1 MHz. The results showed the presence of different types of alkali salts in coal, with only the water-soluble salts being removed. The reaction is diffusion-controlled as observed by fitting the data to a "shrinking core" model. 360 kHz worked best for removal of both sodium and potassium owing to the right mix of cavitation and streaming. While cavitation aids in breakage of coal matrix and particle fragmentation, streaming accounts for efficient leaching of alkali that occurs subsequently.

Cavitation as a process-intensifier: Mechanistic Understanding

The following Table 1 summarizes the observed intensification effects of ultrasonic fields on various physico-chemical phenomena:

Table 1: Consolidated representation of process intensification under the influence of ultrasound

No.	Process	Procedure	Frequency	Observations
a	Heat-Transfer enhancement in furnace tubes	• To compare of heat transfer characteristics of water flowing in a tube exposed to heat in the presence and absence of ultrasound.	20,33, 20+33 kHz	• Order of HTER was as follows: 33 kHz > 20+33 kHz combined > 20 kHz. • While 20 kHz alone was a first-order effect, combination of 20 kHz and 33 kHz was found to have a second-order

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		• Critical parameter found to be ratio of ultrasonic flow velocity and prevailing flow velocity.		effect.
b	Degradation of Methyl Violet	• To boost decolorization of methyl violet using ultrasound. • Preparing Fenton's reagent, mixing with dye and irradiating with ultrasound were the main steps involved.	25, 132, 430 kHz, 1 MHz	• Decolorization increases with increasing frequency and reaches near completion at 430 kHz. • At higher frequencies, though cavitation effect is reduced, there is a higher density of bubbles leading to better contact with OH radicals and higher reaction rates.
c	Sono-fragmentation of coal	• To mix ground coal with three different reagents and sonicate at the chosen frequency. • Results were analyzed quantitatively using a laser particle counter and qualitatively in SEM.	25, 132, 58+192, 190, 470 kHz, 1 MHz	• Lower frequencies show effective particle breakage while particle agglomeration happens at higher frequencies. • Particle size reduction with respect to frequency (kHz) followed the order: 25 > 58+192 > 132 >192 >470 >1000.
d	Destratification	• To study the effect of ultrasound on thermal destratification. • A tank filled with water is heated at the top, while the bottom is maintained at room temperature. The system is exposed to ultrasound and the temperature profile is obtained.	25, 40, 58, 68, 132, 192, 58+192, 172+192, 470 kHz	• 470 kHz provided maximum breakage of thermal layer and destratification. • When the power input and the storage pressure was increased, 470 kHz system showed a dramatic increase in Stratification Index. • Dual frequencies, which combine effect of cavitation and streaming, provided better mixing compared to high or low frequencies.
e	Effervescent atomization	• To produce very fine droplets from an effervescent atomizer, with the assistance of ultrasound • Ultrasound was used to break the bubbles formed by the aerator and distribute them homogeneously	20 kHz	• At lower frequency, ultrasound helped in breaking up of larger sized bubbles into smaller ones. • The main mechanism involved in bubble break-up is cavitation, and the spray obtained is qualitatively superior.
f	Coal beneficiation studies	• To study aqueous and reagent-based ultrasonic coal wash • For de-ashing, the sieved coal is subjected to sonication followed by a three-level decantation. • De-sulphurisation was done by sonication, followed by titration for analysis	20, 25, 58+192, 430 kHz	• For de-ashing, the lowest frequency gave the best size reduction owing to cavitational bubble collapse and subsequent breakage of coal particles. • For de-sulphurisation of coal, the low-frequency systems showed excellent contact of oxidizing agents produced by ultrasound.
g	Alkali leaching of coal	• To sonicate ground and sieved coal for a fixed period of time after mixing with reagent. • Samples are tested using ICP.	25, 40, 58, 68, 132, 58+132, 360 kHz, 1 MHz	• Low frequency ultrasound alone was not effective for alkali leaching. • When a medium frequency system such as 360 kHz is used, combined effect of cavitation and streaming produces best results for removal of

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				both sodium and potassium from coal.

When an acoustic field is coupled to a liquid medium, two phenomena are induced--- cavitation and acoustic streaming—and two effects are created—physical and chemical. The interaction between these can be quite complex. However, some general insights emerge from a cause-and-effect analysis:

- When first-order physical effects are pronounced-- for example, in particle breakage and in aerosolization of liquids-- low-frequency cavitational effects are dominant..
- However, when second-order physical effects, such as diffusion and leaching, the combined effect of cavitation and acoustic streaming is superior to that produced by either mechanism acting alone.
- Convection and mixing may be intensified by either cavitation or acoustic streaming, since they operate by different but equally effective mechanisms. While cavitational fields literally "throw" parcels of fluid around, streaming induces a unidirectional flow of the fluid away from the transducer, which can set-up convection rolls that assist redistribution.
- Higher frequencies lead to greater density of smaller-sized bubbles, thus increasing net effective interfacial area. Chemical reactions that rely upon surface contact between reacting species and radicals are therefore maximally enhanced at such frequencies at the higher end of the ultrasonic spectrum (or lower end of the megasonic range).
- When particle agglomeration is desirable, such as in separation of contaminants from effluents, higher frequencies are ideal for promoting it, while lower frequencies will actually break-up agglomerates.
- Acoustic field effects on transport phenomena—momentum, mass and heat—are very similar when the dominant mechanisms are the same.
- In the case of chemical reactions, while the localized high-temperatures and high-pressures associated with cavitation can increase local rates, frequency and length of contact between reacting species can be more directly affected by streaming effects. Thus, a frequency-blended field may be more appropriate.
- In general, streaming enhancement factors scale as square of frequency, while cavitational-enhancement effects scale as $1/f^3$. Both scale linearly with input power (amplitude) until a lower threshold value at which the field collapses. When both effects are exerting a combined influence, the frequency exponent will range from +2 to -3, depending on which influence is dominant. When multiple frequencies are used in series, as opposed to being integrated into the same tank or same stage, a cleaner separation of effects can be achieved, and this is the recommended mode of operation.

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