Chapter

Sonochemistry: Applications in Biotechnology

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Abstract

Sonochemistry is a branch dealing with effects of chemical as well as sound wave as the name suggest. The sound waves are ultrasonic, i.e., high frequency waves (20 kHz can extent to 10 MHz and above) beyond the range of a human ear (20–20 kHz). Sonochemistry technology is incorporated into both mechanistic and synthetic studies. An important event called acoustic cavitation take place where microbubbles grow and under the influence of ultrasonic waves they collapse. Sonoluminescence is one of the outcomes of cavitation which leads to homogeneous sonochemistry. Sonochemistry has also entered one of the major developing field biotechnology from basic activation of enzyme to preparation of catalyst. It is also used for the fabrication of nanomaterial which comes under the liquid phase method. One disadvantage of nanomaterial preparation is the amount of time it consumes to show results. This can be eliminated when biotechnological research is conducted in conjunction with sonochemical application. Latest research results have proved that ultrasound irradiation is both time and cost-effective approach for any bio-processes like enhancement of emulsification and trans-esterification of fatty acids for bio-fuel products. Bio-process monitoring and dewatering of sludge have also been accelerated. This chapter contains introductory information on sonochemistry.

Keywords: sonochemistry, acoustic cavitation, nanoparticles, collides, medicine, water treatment, sonocatalyst

1. Introduction to sonochemistry

1.1 About sonochemistry

We are all familiar with the terms chemistry and sound when these two terms are put together into practice, a new field is developed called sonochemistry. This is quite new to us and is still a developing area of science. In simple words this field involves the study of effect of sound in chemical reactions in a given solution caused by acoustic cavitation [1, 2]. The basis of sonochemistry is use of lower range of ultrasound with higher power that causes significant physical and chemical changes. First commercial use of ultrasound dates back into 1917 by Langevin to measure the depth of water [1]. In 1927, Robert Williams Wood (1868–1955) and Alfred Lee Loomis (1887–1975) conducted an experiment to demonstrate effect of ultrasound in water [3]. Later in 1960s use of ultrasound entered industries

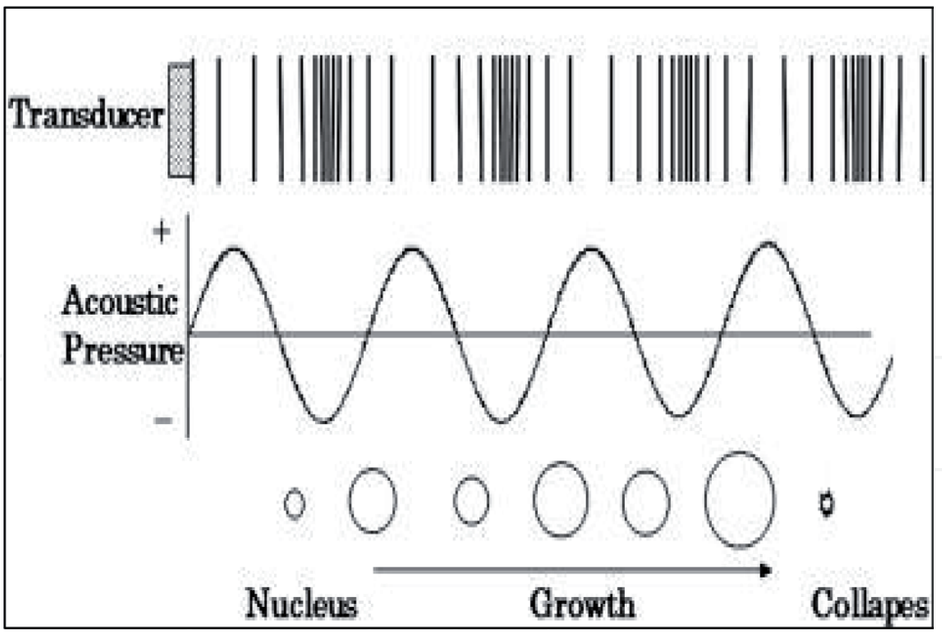

Figure 1.
Acoustic cavitation caused by ultrasound.

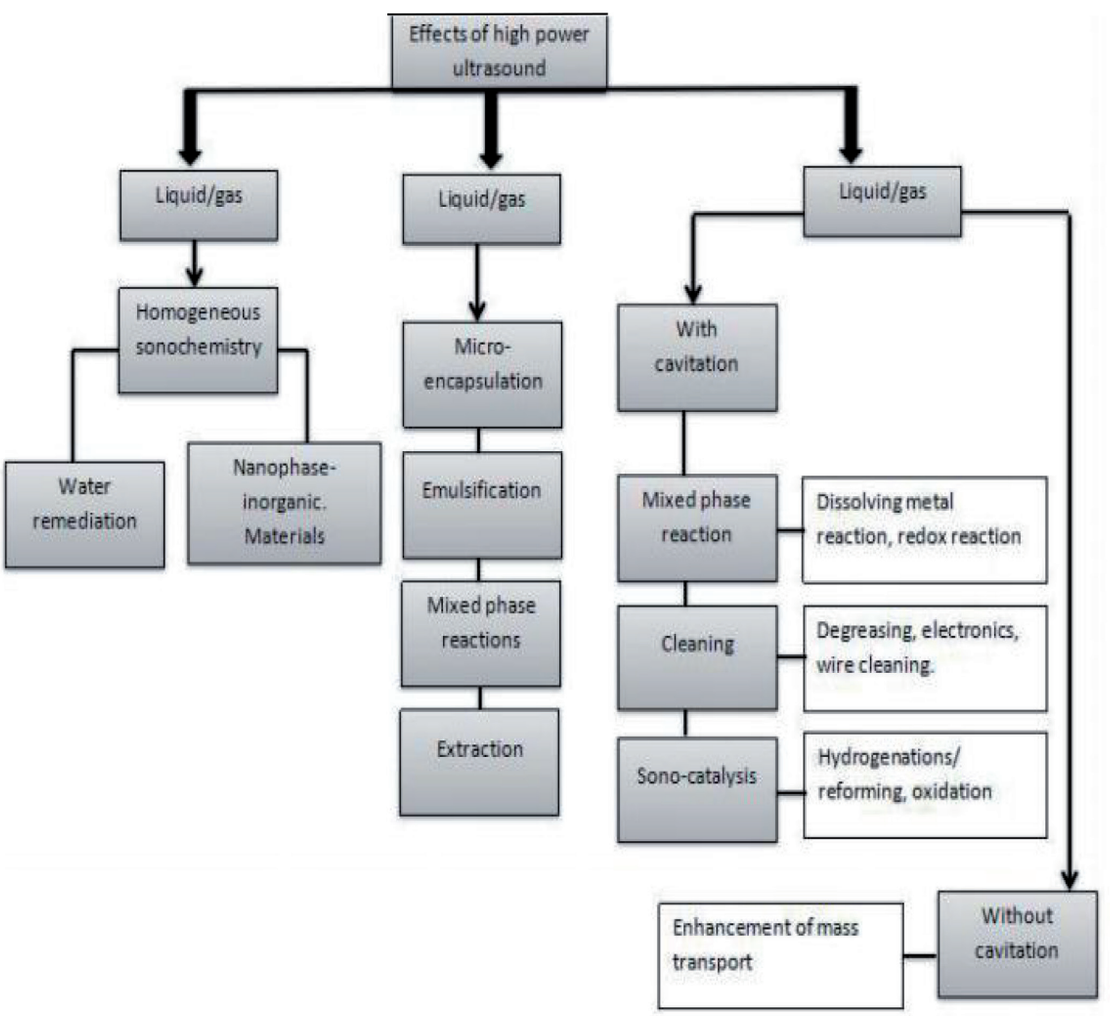

Figure 2.
Chemical and physical effects of ultrasound [4].

and soon became a means to accomplish advancement using technology. These methods were used in many chemical processes to either initiate or enhance the on-going reactions.

Now that we are familiar with the topic next question is how sound effects the chemical reaction in a solution they are introduced into. Acoustic cavitation is responsible for the enhancement of these processes. When sound waves (ultrasound) are passed into solutions they generate mechanical vibrations along with acoustic streaming. These solutions in normal conditions contain dissolved gasses nuclei, which collapse under ultrasound field. This cavitation (oscillation and collapse) results in many physical changes like shockwaves, shear forces, turbulence, etc., along with physical changes it is an adiabatic process and generates very high temperature inside the bubbles for a short interval (**Figure 1**) [1, 2, 4].

1.2 Effects of sonochemistry

These are both chemical and physical effects in which chemical falls under homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid-liquid or liquid-solid systems, and sonocatalysis. Based on earlier studies, effects of ultrasound on slurries of inorganic solids are shown (**Figure 2**).

2. Application of sonochemistry

2.1 Nanostructured inorganic materials

Over the past few years sonochemical reactions have been chosen for a general approach towards the synthesis of nanophase materials. Due to distinct behaviour of nanosized material compared to the bulkier ones [5]. These small clusters have electronic structures with high density. Both gas phase and liquid phase techniques are used to synthesis them. With these different phase techniques and also their combination, the sonochemical approach is included [4, 5]. Various forms of nanophase material are generated by simply changing the reaction medium as shown (**Figure 3**).

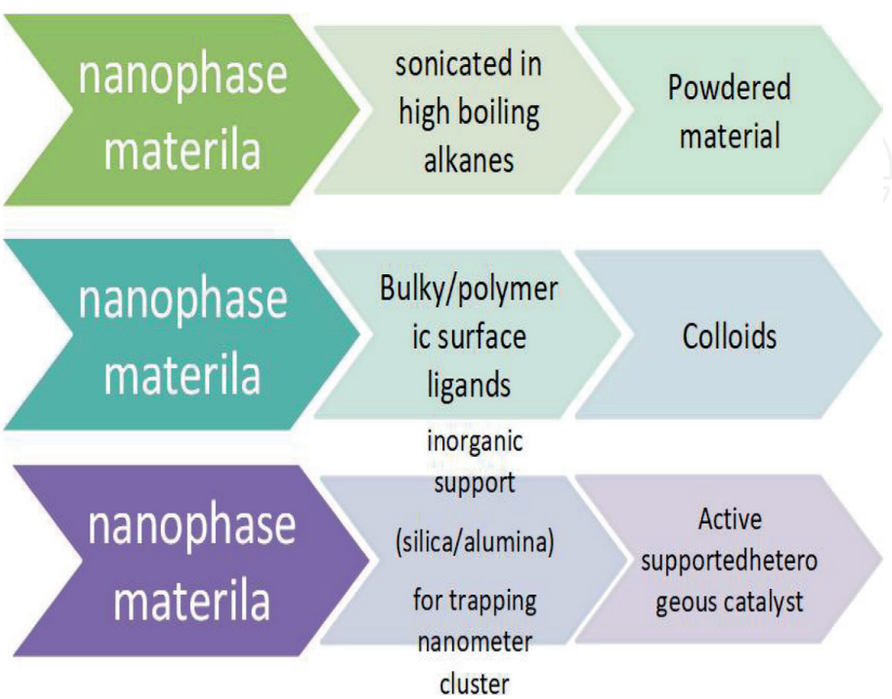

Figure 3.
Different forms of nanomaterial generated by changing reaction medium of the phase.

2.1.1 Different types of nano products obtained

Nanomaterials obtained using sonochemistry are of various forms. Different forms exist based on their usage. As an matter of interest, nano-sized particles serve as great source for action. This is the reason they are so popular. In **Figure 3** most common nano-product are listed. These materials are formed using different techniques and processes. Sometimes combinations of techniques are used in conjunction with sonochemistry. Also due to their diverse nature they consume different interval of time to become fully functional. Based on these categories the options are narrowed for their usage. Some of these materials are listed in **Figure 4** [4, 6].

2.1.1.1 Amorphous metals

A dull black powder was obtained by sonication of iron pentacarbonyl in decane at 0°C under continuous flow of argon. Amorphous nature was verified by different techniques like SEM, different scanning calorimetry, electron micro-diffraction, X-ray powder diffraction and neutron diffractions were used. EMD revealed a diffuse ring pattern (amorphous characteristic). The amorphous metals are formed as a result of extremely high cooling rate during acoustic cavitation. This was shown by DSC (noted transition temperature is 308°C). The size of the particles were in the range of 4–6 nm [4].

2.1.1.2 Alloys

The compositions of Fe/Co alloy can be controlled by changing the ratio of solution concentrations of both the individuals. They are readily available and are thermally stable at adequate bulk solution temperature. The solid-solution nature is determined by energy dispersive X-ray measurements. The products are homogeneous on a nano-scale. They are initially amorphous and after heat treatment at 400°C under H_2 gas for 2 h (**Figure 5**).

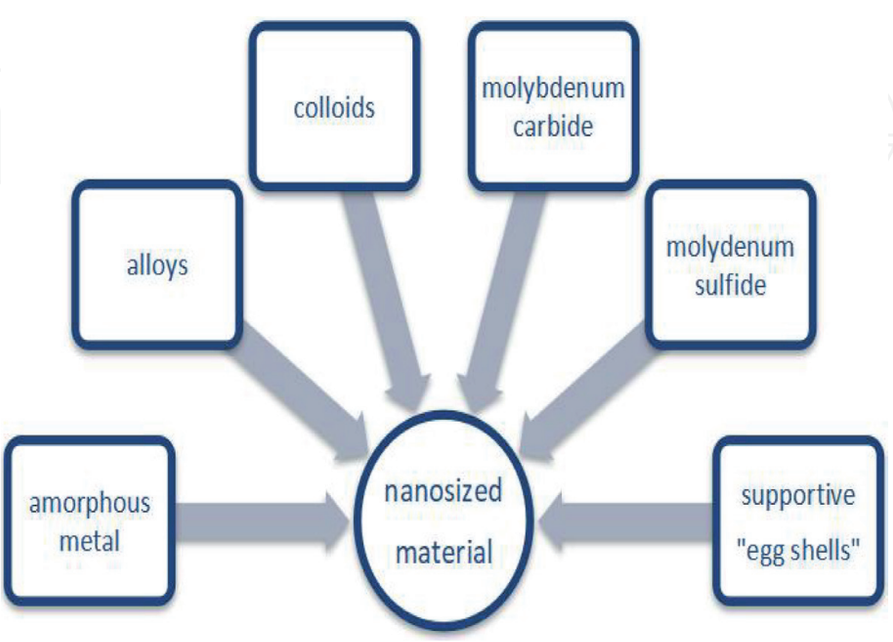

Figure 4.
Most common nanophase materials produced using sonochemical reactions.

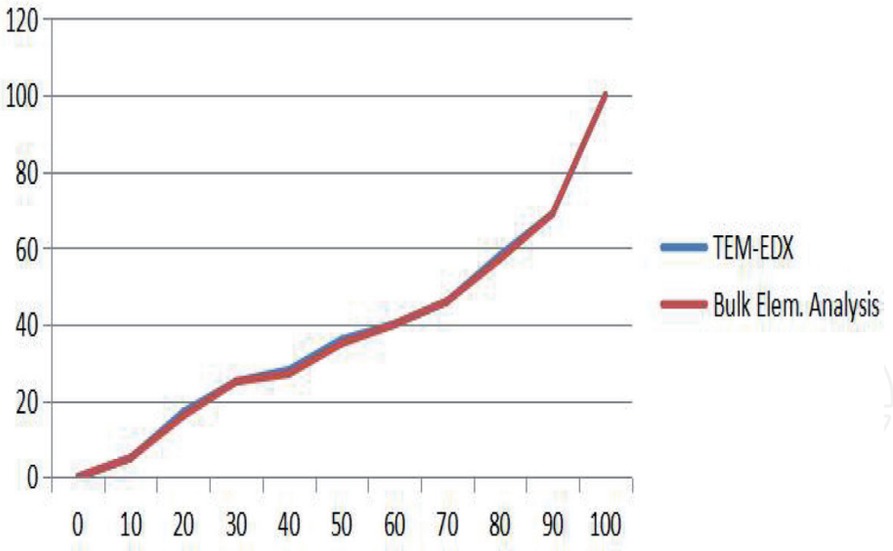

Figure 5.
Bulk and EDX analysis of Fe/Co alloy prepared sonochemically from respective precursors [4].

2.1.1.3 Colloids

Colloids of ferromagnetic materials are made by exhaustive grinding of magnetite (Fe_3O_4) in ball or vibratory mills for many weeks. Wide range of particles (based on size) is produces due to presence of surfactants. A new method is developed using high intensity ultrasound to produce stable colloids of iron. In this method volatile organo-metallic compounds are decomposed sonochemically. In presence of polyvinylpyrrolidone, the size of colloidal iron particles are in range of 3–8 nm whereas in presence of oleic acid they are in uniformly distributed at 8 nm [4] (**Figure 6**).

2.1.1.4 Molybdenum carbide

Sonochemical decomposition of molybdenum hexacarbonyl in hexadecane by ultrasound irradiation produces a black powder. When this powder is heated for

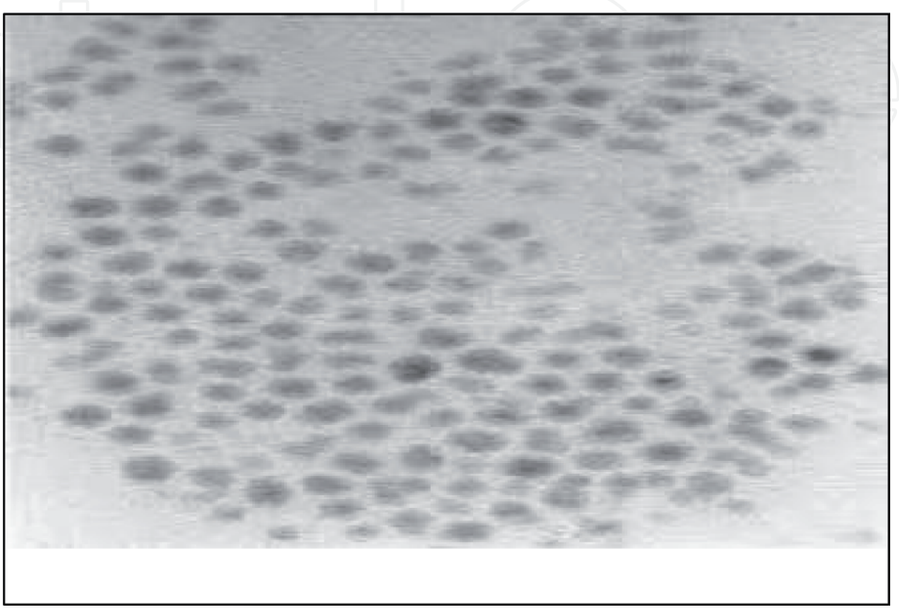

Figure 6.
Transmission electronic micro-graphic view of sonochemically prepared iron colloid (stabilized by oleic acid) [7].

12 h under He flow at 450°C. SEM revealed the extremely porous surface and TEM confirmed the size of particles of the porous aggregate, i.e., 3 nm diameter [4].

2.1.1.5 Molybdenum sulfide

Due to its layered structure, MoS_2 is also called as the standard automotive lubricant. It is prepared by high intensity ultrasound irradiation of molybdenum hexacarbonyl and sulfur in 1,2,3,5-tetramethylbenzene. Under the flow of He the amorphous product was heated at 450°C to get crystallized MoS_2. The sonochemically prepared MoS_2 has much greater edge and defect content than conventionally prepared ones as the layers must bend, break or otherwise distort to fit outer surface of the 15 nm particle size [4] (**Figure 7**).

2.1.1.6 Supportive "egg shells"

When eggshells with uniform-sized nanoparticles of metals are deposited on the outer surface of supports, potential advantages for catalyst preparation increases greatly compared to non-uniform particles. Ultrasonic irradiation of decane solutions of iron pentacarbonyl, $Fe(CO)_5$, in the presence of silica gel produces a silica-supported amorphous nanostructured iron-iron particles on the outer surface of are formed during cavitation. By changing the initial composition of iron precursor, its loading on SiO_2 can be verified. TEM confirmed the high dispersion of iron particles (3–8 nm) produced by sonolysis of $Fe(CO)_5$ on the SiO_2 surface [4].

2.2 Synthesis of bio-materials

Protein micro-spheres are one of the most notable bio-materials. The development of aqueous sonochemistry for bio-materials synthesis is still an on-going

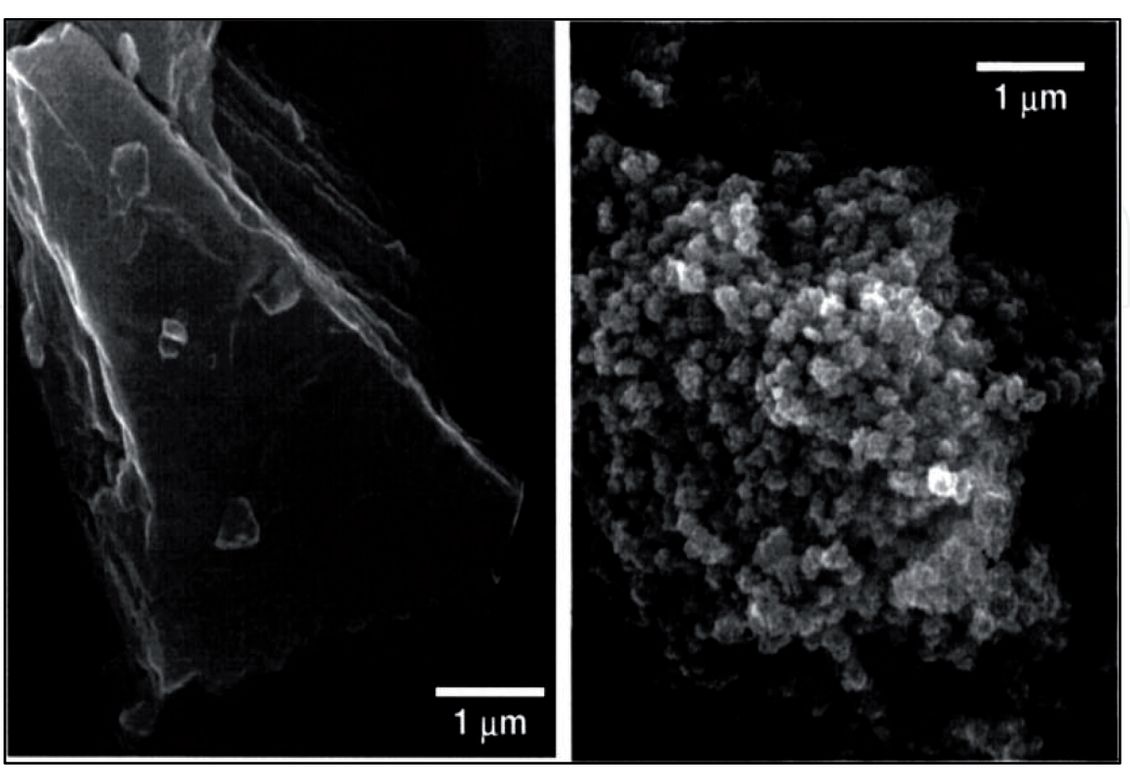

Figure 7.
Conventionally prepared MoS_2 (left) and sonochemically prepared MoS_2 (right) [8].

research area particularly of micro-encapsulation. High intensity ultrasound is used on simple protein solutions to make both air-filled micro bubbles and non-aqueous liquid-filled micro-capsules. Micro-spheres are stable for months and can be intravenously injected to pass unimpeded through the circulatory system due to their smaller size compared to erythrocyte scan. The particle size can be determined as a function of sonication time, suggesting the disintegration of the aggregates on longer exposure to ultrasound radiation [4, 9] (**Figures 8–10**).

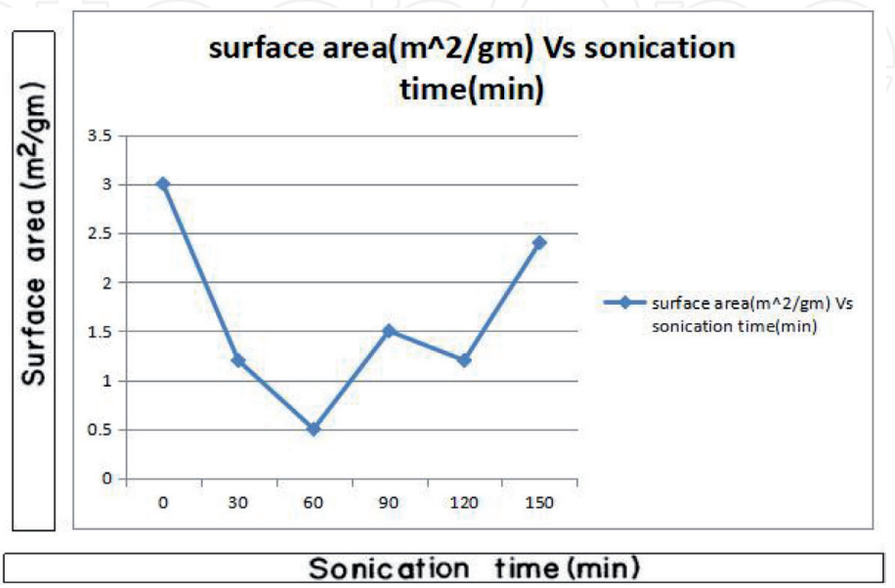

Figure 8.
The variation of surface area of micro-spheres with time is represented in the above graph [4, 9].

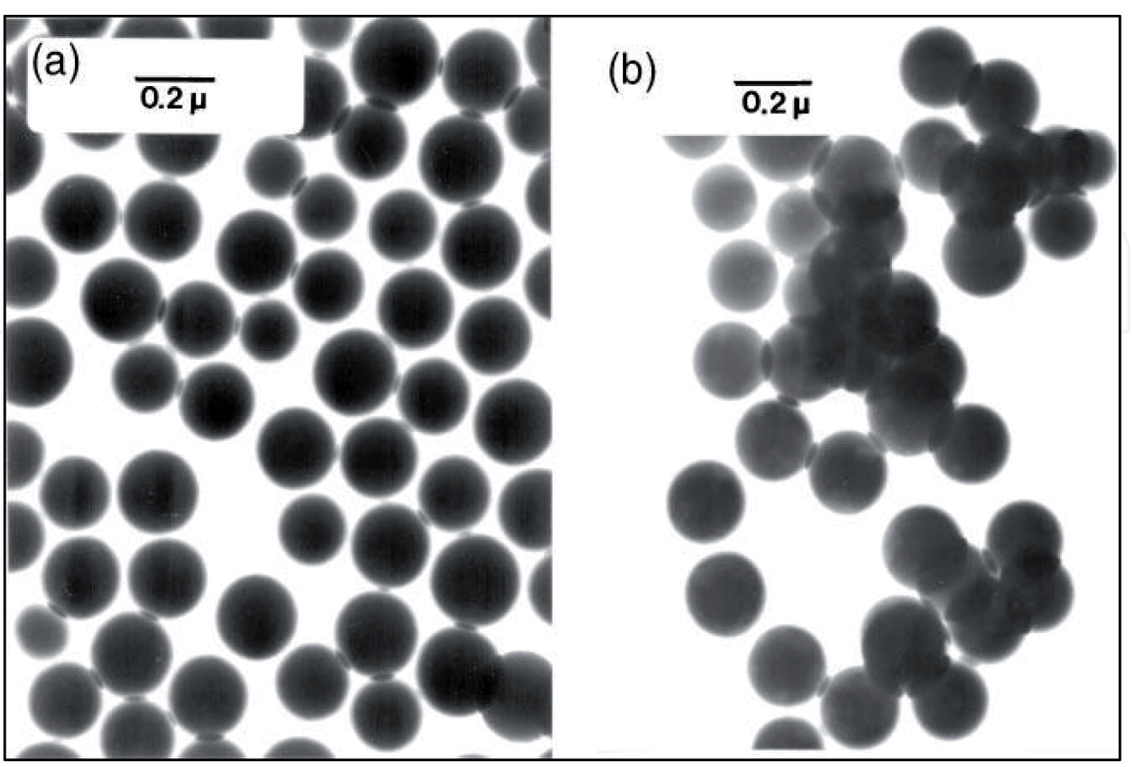

Figure 9.
TEM micro-graphs of (a) as-prepared Stober's silica in the size range of 150–200 nm and (b) the silica micro-spheres irradiated with ultrasound for 2 h in decalin medium [9].

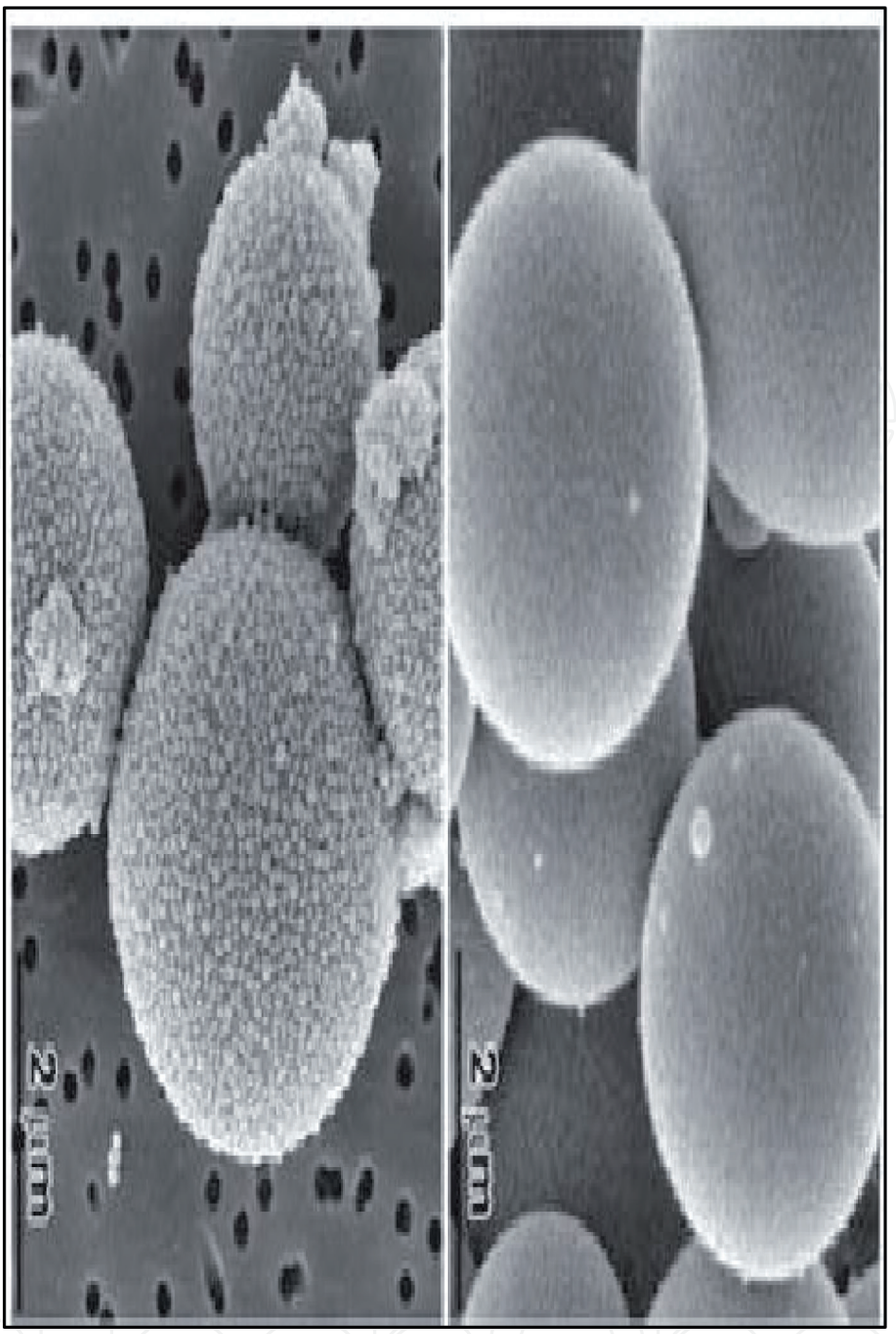

Figure 10.
SEM images of micro-spheres prepared by sonication of bovine serum albumin [10].

Protein micro-spheres have a wide range of biomedical applications. They are also used as a echo contrast agents for sonography [11], magnetic resonance imaging contrast enhancement [12–14], oxygen or drug delivery [15] sono-chemically produced hemoglobin micro-bubbles, hollow and solid spheres and micro-spheres.

2.3 Modification of inorganic materials

Ultrasound is widely used to accelerate chemical reactions in liquid-solid heterogeneous systems. This sonochemical enhancement has become a synthetic technique for heterogeneous organic as well as organo-metallic reactions [4, 16, 17]. These reactions mostly include metals like such as Mg, Li and Zn and also apply to

reactive inorganic salts and to main group reagents. Less work has been done with unreactive metals.

2.3.1 Surface cavitation

Cavitation near extended liquid-solid interfaces and cavitation in pure liquids, both are very different [4, 17]. Micro-jet impact and shockwave damage are responsible for effects caused by cavitation near surfaces. The special symmetry of the liquid particle in motion during cavity collapse often induces a deformation within the cavity. The potential energy of the expanded bubble is converted into kinetic energy of a liquid jet that extends through the bubble's interior and penetrates the opposite bubble wall. As most of the energy is converted to accelerate jet, the velocity attained is in hundreds of m/s. Such energy concentration can caused extreme damage to the boundary surface (**Figure 11**).

The later one, i.e., cavitation in pure liquid, mechanism of cavitation-induced surface damage invokes shockwaves created by cavity collapse in the liquid [4]. Micro-jets and shockwaves on the surface, creates the localized erosion responsible for ultrasonic cleaning and. These effects can generate newly exposed highly heated surfaces and even eject metal from the surface [18].

2.3.2 Inter-particle collision

For ultrasonic frequencies greater than 20 kHz, damage associated with micro-jet formation cannot occur for solid particles smaller than 200 mm. This takes on a special importance for sonochemistry [19]. This is the reason, they are preferred as catalysts. Passing shock waves over particles in close proximity to one another results in high-velocity inter-particle collisions. Right angled collision can drive metal particles at sufficiently high velocities to cause melting effect at the collision point [4]. Energy generated is determined by the volume of melted region under the

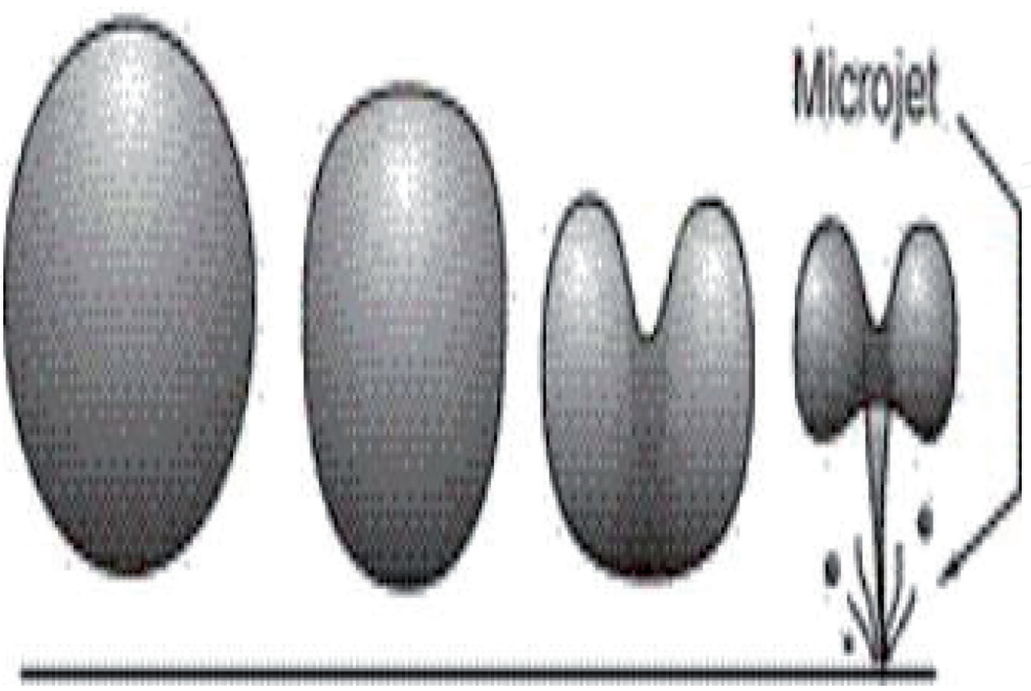

Figure 11.
It shows the collapse of a bubble later expanded to a liquid jet (cavitation near surface).

impact of collision. A lower estimate of the velocity of impact was several hundred m/s, or roughly one half the speed of sound! [4] (**Figures 12** and **13**).

2.3.3 Ultrasound on heterogeneous catalysts

These kinds of catalysts are rare and expensive. Using ultrasound activation of less reactive is less costly. The effect occur in three distinct stages

1. During formation of supported catalysts.

2. Activation of performed catalysts.

3. Enhancement of catalytic behavior during its reaction

Increases in turnover rates were usually observed upon ultrasonic irradiation even though they were rarely more than 10 folds but were appropriate. The hydrogenation of alkenes by Ni powder is enormously enhanced by ultrasonic irradiation [4]. At a macroscopic scale, the initially crystalline surface are agglomerated into small particles by ultrasound irradiation. This effects is due to inter-particle collisions caused by cavitation-induced shockwaves, revealed that there is a striking decrease in the thickness of the oxide coat after ultrasonic irradiation. It is the removal of this passivating layer [4, 7] (**Figure 14**).

2.4 Lignocellulosic biomass

Lignocellulosic biomass is a natural renewable chemical feedstock that is used to produce high value-added chemicals and platform molecules. There is variety of aspects concerning the valorization of lignocellulosic biomass into desirable products. For biomass conversion, few of the existing technologies require high temperatures

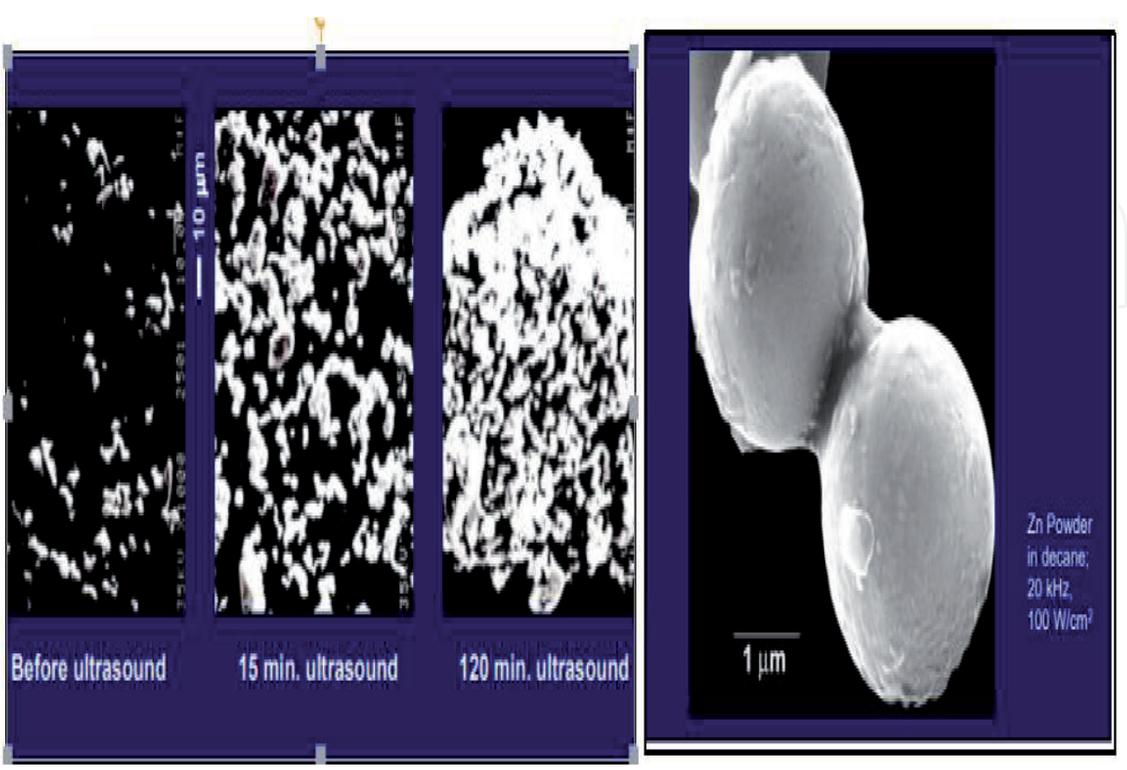

Figure 12.
Cavitation effect on surface morphology (left), inter-particle collision (right).

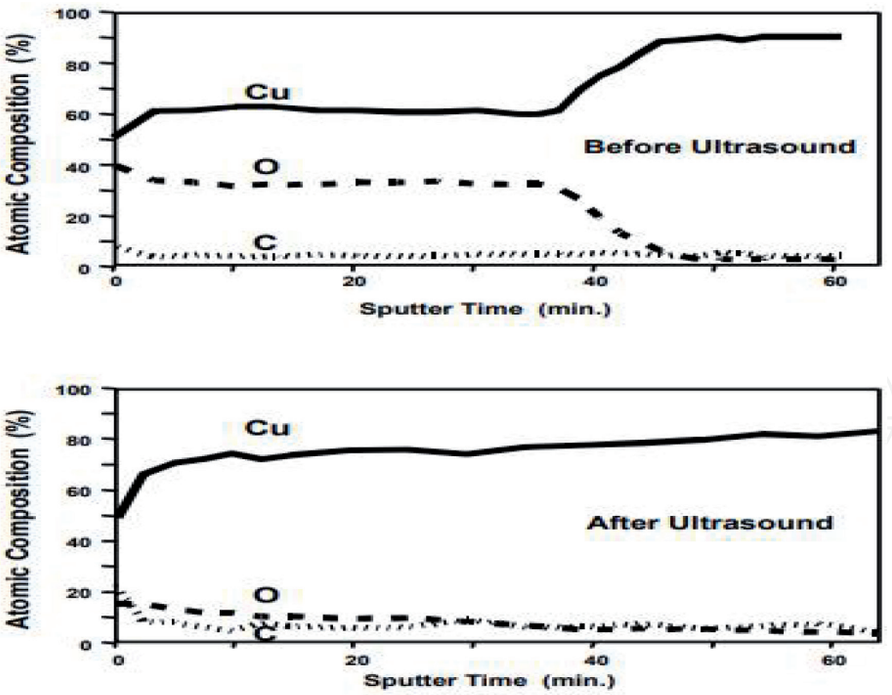

Figure 13.
The effect of ultrasonic irradiation of Cu powder slurries on the surface composition. 50 min. Sputter time is roughly 1 mm depth [4].

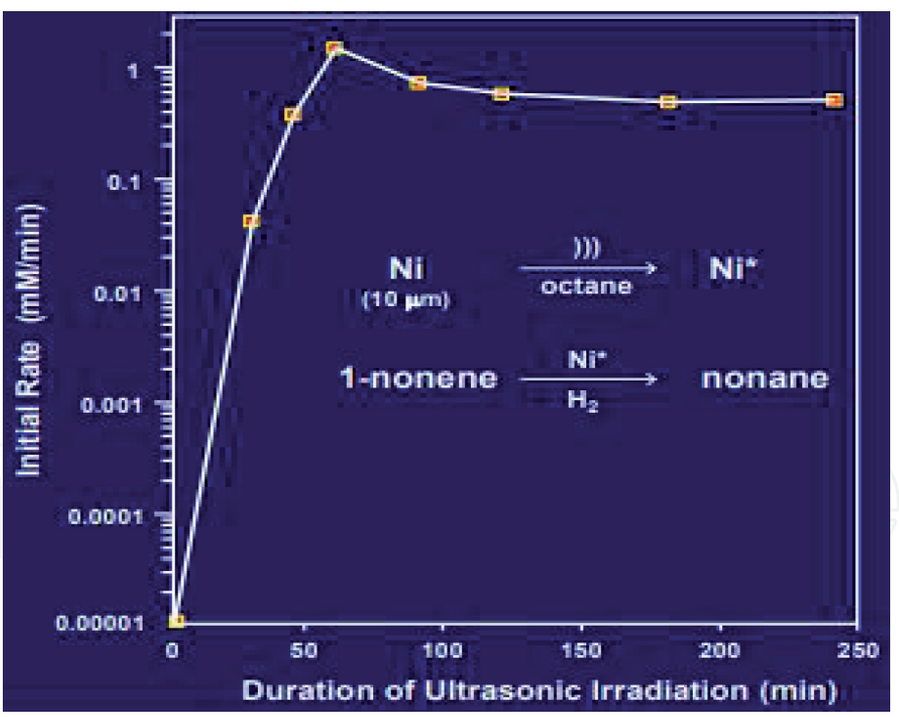

Figure 14.
Sonochemical activation of Ni powder.

and pressures. To fulfill the extreme conditional requirement, key technological innovations based on more economical and environmental methodologies are being explored both in academic laboratories and in industry. Sonocatalyst constitutes a substitute means offering innovative strategies to improve biomass (**Figure 15**).

Heterogeneous sonocatalysis as an emerging advanced oxidation process (AOP), is a potential treatment method for water and has removed persistent organic compounds in the in past few decades [21].

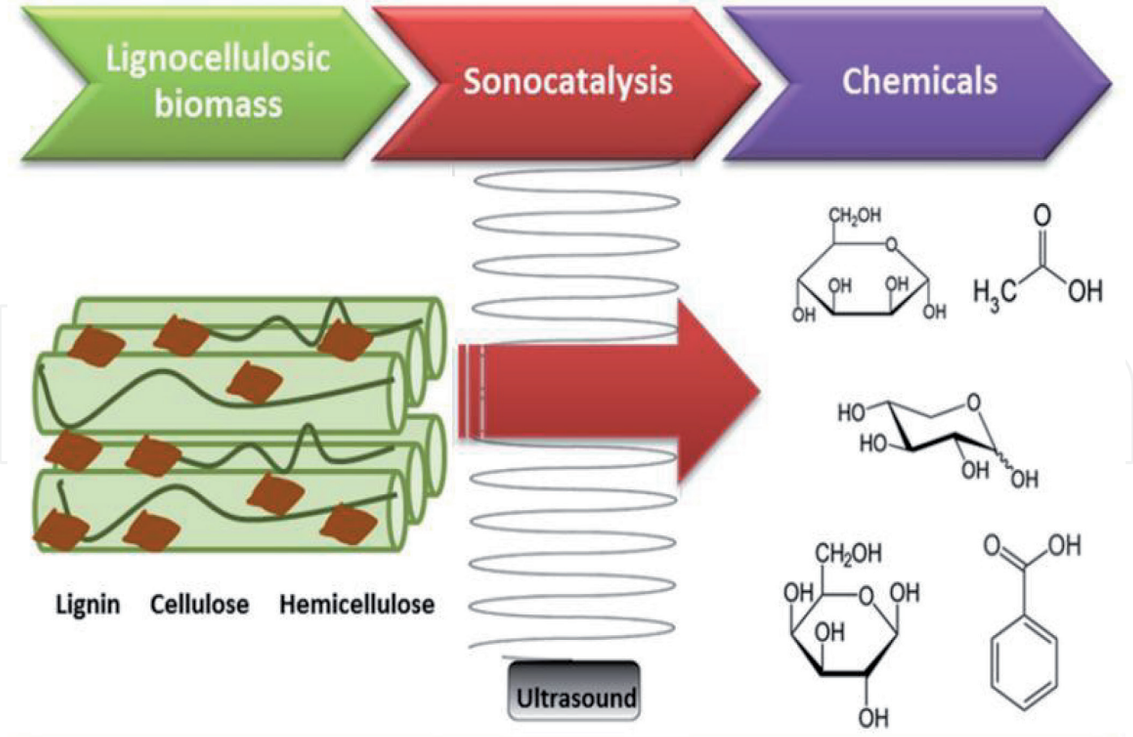

Figure 15.
Biomass valorization [20].

2.5 Sonoluminescence

Sonoluminescence is a phenomenon that occurs when a small gas bubble is acoustically suspended and periodically driven in a liquid solution at ultrasonic frequencies, resulting in bubble collapse, cavitation, and light emission.

Sound waves are aimed at an air bubble trapped in a flask. The sound waves cause the bubble to oscillate furiously

- The bubble starts out at a size around 5 μm.
- It expands to itself up to 50 μm (roughly). At this large size there is a near-vacuum inside the bubble because of the relatively few air molecules present. This low-pressure near-vacuum region is surrounded outside the bubble by a much higher-pressure region.
- A catastrophic collapse of the bubble to between 0.1 and 1 microns occurs.
- During this compression phase a flash of light emerges from the bubble.

The conversion of low energy density sound waves into light requires a concentration of energy by a factor of 1 trillion (**Figure 16**).

2.6 Sludge treatment

Sludge treatment in waste-water treatment plants are one of the most difficult challenges. This new technology of treating water with ultrasound is quite helpful. Ultrasound treatment promote hydrolysis during sludge treatment.

The basic principal is based on the destruction of bacterial cells and organics. Bacterial cells release their contents, which are then available for consumption by

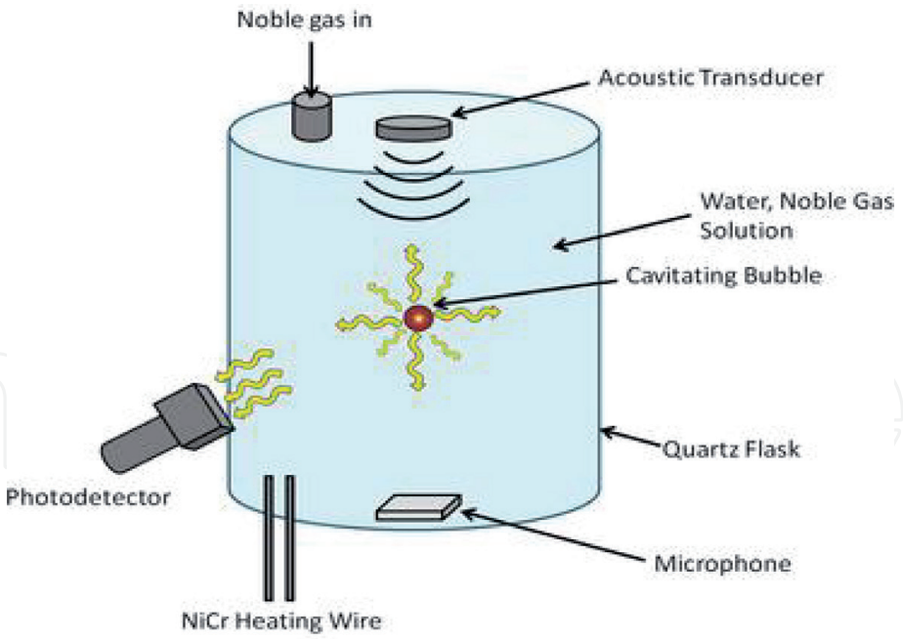

Figure 16.
A setup similar to the following is required to create a bubble that can sonoluminescence.

other species. The organics are broken down into smaller fractions which can be readily biodegradable.

When an ultrasonic field is applied to a liquid medium, microbubbles are produced during the cavitation process. These cavitation bubbles implode under extreme high temperature and pressure. The force of the bubble implosions breaks up sludge particles when applied in sewage sludge treatment. The extent of the intended effects depends on the high or low intensity of the applied ultrasonic field [22].

3. Sonochemistry in market

3.1 Industrial level

When it comes to an industrial level of production, cost efficient and avoiding wasteful reactions is considered primary when we talk about catalysts, maximum efficiency is the main concern and it can vary depending upon the metals or any other precursors used. Heterogeneous catalysts containing two metals often show unusual activity or selectivity for a wide range of industrially important reactions. Due to these reasons, catalytic studies of alloys, e.g., Fe/Co (as mentioned in the applications), was made using sonochemistry. Dehydrogenation of hydrocarbons is the important and desirable reaction, and hydrogenolysis (to methane generally) is a wasteful side-reaction in industries because of its high activity (more than required) as hydrogenolysis catalysts for commercial usage [4].

3.1.1 Preparation of nanostructured alloys

All catalysts were treated under H_2 gas flow at 400°C for 2 h which causes crystallization before the catalytic studies. The catalytic selectivity is shown in **Figure 1**. Two different products were formed in the cyclohexane reaction. The first one is benzene from the dehydrogenation reaction and other one is aliphatic hydrocarbons from the hydrogenolysis. Fe/Co alloys are all active catalysts for cyclohexane conversion the activity is higher for Co and decreases with increase in Fe content. Compared

to pure metals, alloys generated much more dehydrogenation products. When 1:1 ratio of alloys was used, it had the highest selectivity along with higher dehydrogenation activity. The sonochemical preparations inevitably produce catalysts with small amounts of surface carbon and hence with high dehydrogenation selectivity compared to less selectivity of conventionally prepared ones [4] (**Figures 15** and **16**).

3.1.2 Preparation of nanostructured molybdenum carbide

To compare the activity, dehydrogenation versus hydrogenolysis of cyclohexane served as the standard reaction using a flow catalytic micro-reactor. Commercial ultrafine powders of platinum and ruthenium were also used remove surface contaminants under identical conditions, after heating at 400°C for 3 h under H_2 flow to. At all reaction temperatures examined, benzene was the only product formed for both samples and their activities were comparable and no hydrogenolysis product was detected. Results showed that for dehydrogenation of alkanes, sonochemically prepared nanostructured molybdenum carbide has electivity similar to Pt rather than to Ru [4, 23] (**Figures 17** and **18**).

3.2 Biofuel production

Ultrasonication has recently received attention as a novel bio-processing tool for process intensification in many areas of downstream processing. Ultrasonic intensification (periodic ultrasonic treatment during the fermentation process) can result in a more effective homogenization of biomass and faster energy and mass transfer to biomass over short time periods which can result in enhanced microbial growth. Ultrasonic intensification can allow the rapid selective extraction of specific biomass components and can enhance product yields which can be of economic benefit [24]. During lipid extraction from biomass, the physical effects of ultrasonication

	Hydrogenolysis	Dehydrogenation
Products	Methane	Benzene
Surface structure	Sensitive	Insensitive
Active site	Ensemble of metal atoms	Single metal atom
Active catalysts	Ru,Os,most metals	Pt

Figure 17.
Catalytic dehydrogenation versus hydrogenolysis.

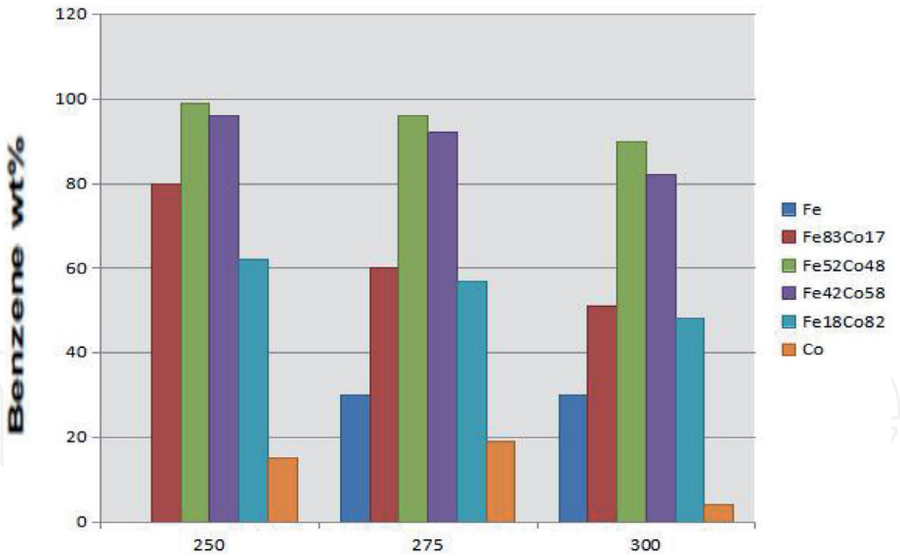

Figure 18.
Selectivity for cyclohexane dehydrogenation (to benzene) over hydrogenolysis (to methane) by sonochemically prepared Fe/Co alloy.

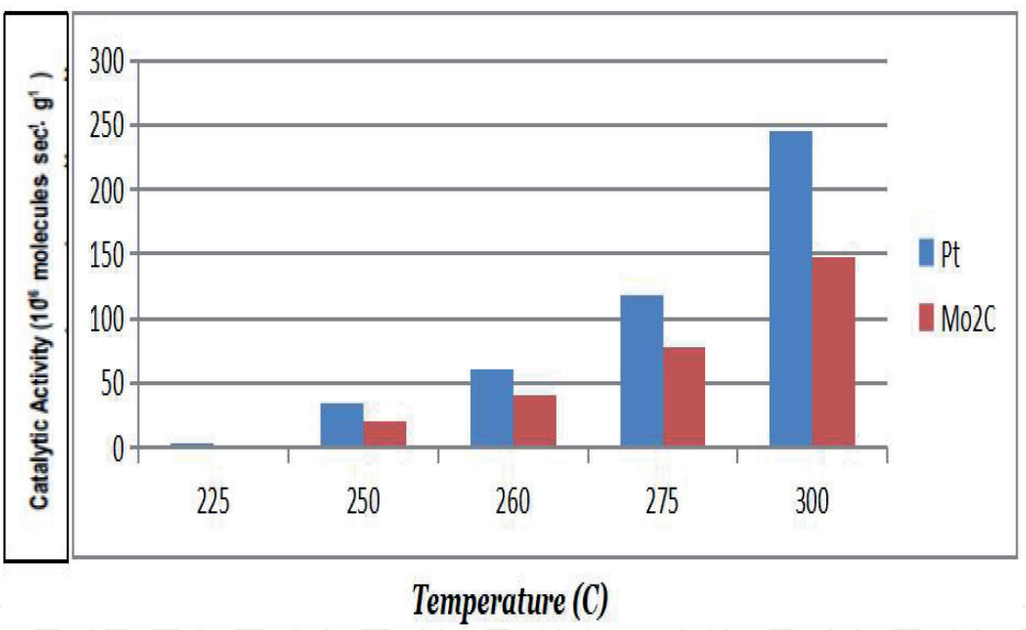

Figure 19.
Catalytic activity of sonochemically prepared Mo_2C compared to Pt.

can significantly enhance the lipid yield. Micro-turbulence can lead to a more efficient mixing of the biomass and solvent (without induction of shear stress), while shock waves can cause rupture of the cell wall. Ultrasound can also generate intense local turbulence in the medium, pushing the extracted lipids away from the surface of the microbial cells, and thus, maintaining a constant concentration gradient for continuous diffusion of lipids from the cells [24] (**Figure 19**).

4. Conclusion

A diverse set of applications of ultrasound to enhancing chemical reactivity has been explored, with important applications in mixed phase synthesis, materials chemistry, and biomedical uses. Bubble collapse in liquids results in an enormous

concentration of energy from the conversion of the kinetic energy of liquid motion into heating of the contents of the bubble. The enormous local temperatures and pressures so created provide a unique means for fundamental studies of chemistry and physics under extreme conditions. For example, the sonochemical decomposition of volatile organo-metallic precursors in high boiling solvents produces nanostructured materials in various forms with high catalytic activities. Nanostructured metals, alloys, carbides and sulfides, nanometer colloids, and nanostructured supported catalysts can all be prepared by this general route.

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