

NANO BUBBLE CAVITATION FOR ENHANCED LIQUID AND GASEOUS FUEL PRODUCTION FROM BIOMASS

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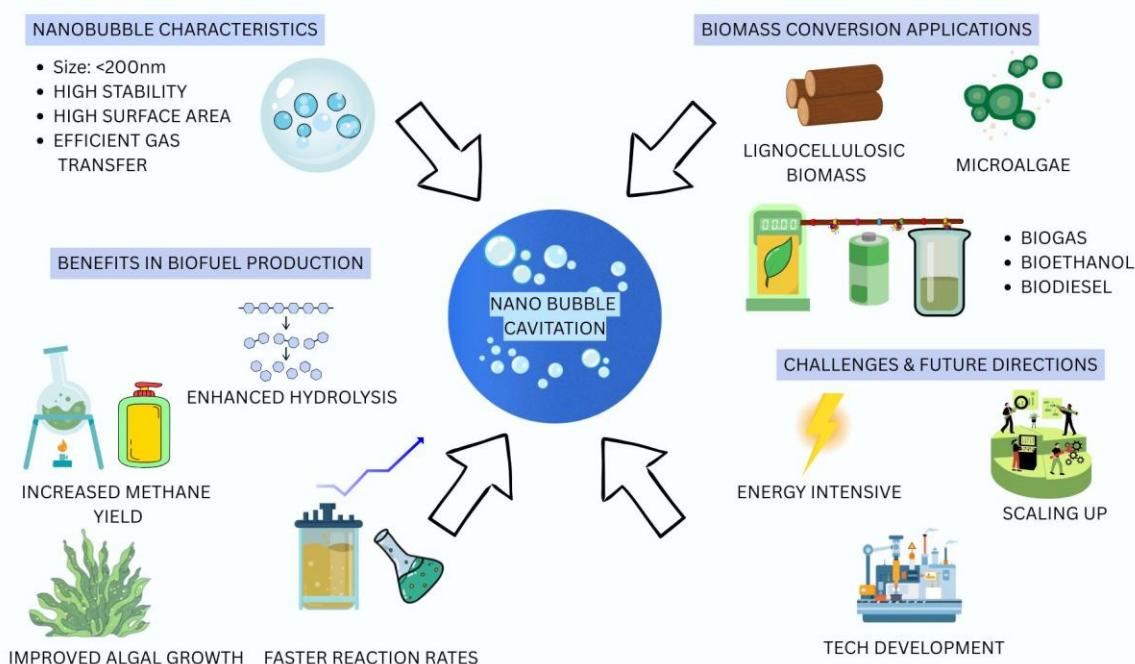
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ABSTRACT

The remarkable physicochemical characteristics of nanobubble technology, such as its nanoscale size, long-term stability, high specific surface area, strong zeta potential, and superior gas-liquid mass transfer efficiency, have made it a promising development in biomass conversion. Nanobubbles can stay in aqueous systems for long periods of time, allowing for improved interaction with chemical and biological processes, in contrast to traditional bubbles that rise and fall quickly. Along with a critical assessment of the main methods used to create nanobubbles, including electrolysis, cavitation, ultrasonication, membrane techniques, and fluidic oscillations, this review offers a thorough overview of nanobubble fundamentals, classification, stability mechanisms, and important physicochemical properties. The importance of nanobubbles in enhancing the production of liquid biofuels from lignocellulosic feedstocks and microalgae, and of gaseous biofuels (biogas and hydrogen), as well as in biomass pretreatment, is given special attention. Higher methane yields, better digestive kinetics, and higher algal productivity are the outcomes of nanobubble-assisted procedures that improve hydrolysis, microbial activity, enzymatic efficiency and gas solubility. The adaptability of nanobubble systems is illustrated through applications in fuel combustion, increased oil recovery, anaerobic digestion and algal bioreactors. Critical analysis is also given to the scale constraints, techno-economic difficulties, and sustainability issues related to energy-intensive production techniques. Overall, this review identifies important research gaps and future directions required for large-scale industrial implementation while highlighting nanobubble technology as a revolutionary tool for sustainable biofuel generation and biomass valorisation.

KEYWORDS: Nanobubble technology; Anaerobic digestion; Methane enhancement; Biofuel production; Lignocellulosic biomass; Sustainable energy

Graphical abstract:



Highlights

- Resolves the conflict between experimental stability of nanobubbles and classical theory by a

rigorous analysis of suggested stabilizing mechanisms.

- Gives a thorough connection between the characteristics of nanobubbles and their application in biofuel production, which is currently not available in any of the reviews.
- Identifies important physiochemical factors that affect the yields of gaseous biofuel (hydrogen & methane) during nanobubble assisted anaerobic digestion.
- Critically assesses the scalability and energy efficiency constraints of current nanobubble generation methods.
- Suggests a comprehensive framework for using nanobubbles in biofuel and biomass pretreatment systems.
- Identifies research gaps and potential paths for large scale, sustainable nanobubble engineering in bioenergy applications.

1. INTRODUCTION

Nanobubbles, typically identified as cavities of gas with typical diameters less than one micron, represent a new class of bubbles characterised by astonishing physicochemical properties. Unlike conventional bubbles that quickly ascend and rupture in aqueous environments, nanobubbles are stable for longer periods due to their nanoscale size and unique interfacial properties [1, 2]. These bubbles involve surface nanobubbles-gas pockets sticking to the solid-liquid interface and bulk nanobubbles, which are dispersed in the continuous liquid phase. However, although nanobubbles were believed to experience a fast dissolution according to classical theory, experimental observation indicated the presence of nanobubbles for hours or even days, implying a gap in theoretical understanding and further investigation in the mechanism of their formation and stability [3, 4]. However, generation of stable nanobubbles is still energy-intensive; besides, advanced generation techniques are required to make them more scalable and of better performance compared to those currently achieved [5, 6].

Despite these developments, there are still a lot of unanswered questions, especially when it comes to determining the primary mechanisms controlling the formation, persistence and interaction of nanobubbles with complex liquid systems, as well as how to reconcile classical thermodynamic predictions with experimentally observed nanobubble stability. Additionally, little is known about how physico-chemical factors such as temperature, pressure, ionic strength and gas type collectively affect the nanobubble behaviour in various application contexts. Biomass is a plentiful renewable resource with enormous potential for the production of chemicals and sustainable energy. Pretreatment is necessary because the hard lignocellulosic structure restricts effective conversion [7]. Because of its high interfacial area and stability, nanobubble-assisted pretreatment improves mass transfer and reaction efficiency. This strategy increases the availability of biomass for the synthesis of biofuels and value-added chemicals. In wastewater treatment, nanobubbles have proven to be incredibly useful, especially in processes such as enhanced oxidation, flotation, disinfection, and aeration [8]. Nanobubble-based technologies have been extensively studied to improve pollutant removal while enabling downsizing, shorter treatment times, and lower operating and maintenance costs. As a result, nanobubble technology is increasingly applied in water treatment, bioprocessing, microalgal cultivation, biomass pretreatment, oil-water separation, and biomedical systems [9, 10].

Nevertheless, challenges remain in the application of nanobubbles in biomass conversion and biofuel production, especially when it comes to process optimization, scalability, and integration with current bioconversion systems. The application of nanobubble technology in gaseous biofuel production is not explored to its fullest potential. However, major research gaps persist in understanding nanobubble formation mechanisms, stability under varying physicochemical conditions, and energy-efficient large-scale generation. Current techniques such as hydrodynamic cavitation, ultrasonication, electrolysis, and membrane dispersion often demand high energy or lack precision in bubble size control [5, 11]. These limitations constrain their optimal use in high-demand sectors like biofuel production from biomass.

Recent studies have highlighted significant advancements in converting biomass to bioenergy using biochemical, thermochemical, and nanotechnology-based approaches. The biochemical conversion of agricultural and algal biomass has demonstrated high efficiency and sustainability potential, although challenges related to pretreatment and costs remain [12]. Additionally, chemical looping technologies have emerged as promising methods for transforming organic solid waste into energy, offering improved carbon efficiency and integrated CO₂ capture [13]. Furthermore, nano-engineered biomaterials and nano-biocatalysts have been shown to enhance enzymatic activity, stability, and overall biofuel yields by improving reaction kinetics and catalytic performance [14]. Despite these advancements, issues with mass transfer and overall process efficiency continue, underscoring the need for innovative solutions, such as nanobubble-assisted systems, to further enhance biofuel production.

The current review is innovative in this regard since it offers an integrated and application focused viewpoint that connects basic nanobubble characteristics with their functional functions in biomass conversion and biofuel production systems. This work notably highlights their synergistic impact in improving gaseous and liquid biofuel yields while also addressing issues with scalability, energy efficiency and process integration, in contrast to earlier assessments that mostly concentrate on nanobubble generation technologies. This review therefore provides an integrated analysis of nanobubble properties, generation methodologies, and emerging applications, emphasising their growing relevance in enhancing gaseous and liquid biofuel production and highlighting future directions for sustainable, scalable nanobubble engineering.

2. Types of bubbles

A bubble is generally defined as a gas that aggregates and stays in a surrounding medium that is divided by an interface. Bubbles are created in situ by physical, chemical or biological processes when gas is added to a liquid. For descriptive and application-oriented purposes, bubbles are typically divided based on size and approximate diameter [15]. Microbubbles are the largest type, usually measuring more than $100\mu\text{m}$ in diameter. They are plainly visible to the unaided eye and rise quickly to the liquid's surface because of buoyancy [16]. Sub-microbubbles about $1\text{--}10\mu\text{m}$ are regarded as an intermediate class between microbubbles and smaller-scale bubbles within their range [17].

According to the international standard, 'fine bubbles' refers to all bubbles smaller than $100\mu\text{m}$, including both microbubbles and ultrafine bubbles. Long-term suspension in liquids is made possible by ultrafine bubbles, which have a diameter of less than $1\mu\text{m}$ and very little buoyancy. A subclass of ultrafine bubbles, known as nanobubbles, is usually smaller than $100\text{--}200\text{ nm}$ and has been shown to last for a long time in aqueous environments. Systems with a mixed population of micro and nanoscale bubbles that combine traits from both size regimes are referred to as micro bubbles [18]. All things considered, the shift from macrobubbles to nanobubbles is characterised by a steady decrease in size and unique dispersion behaviour in liquid media. The size-based categorisation is commonly used to characterize bubble-generating methods and their uses in environmental engineering, chemical processing and water treatment.

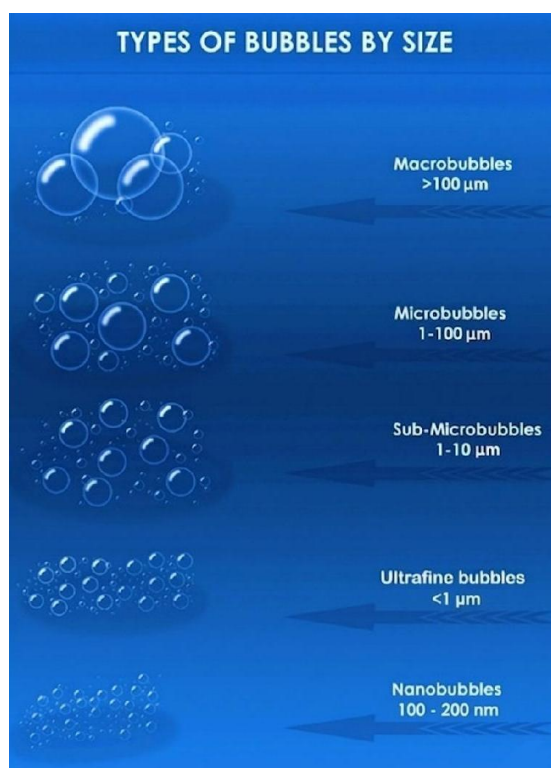


Fig 1. Types of Bubbles Categorised by Size

3. Fundamentals and types of nanobubbles

Nanobubbles are ultrafine gas cavities characterized by exceptional stability, persisting in aqueous systems for extended periods. Normally, bubbles rise in water and burst. But NB refuse because of its small size, the buoyant force is weaker when compared to microbubble [19]. The NB has strong hydrogen bonds observed by the ATR-IR (Attenuated Total Reflectance Infrared Spectroscopy). This shows that these bonds present on the NB surface form the thin layer surrounding the bubble called the interfacial film. Due to this gas exchange between the bubble become slow and greater stability [20]. NB are extremely efficient in transferring gas. Although nanobubble production is expensive due to the use of high-energy density techniques, it offers high mass transfer efficiency and superior performance [21].

The interfacial curvature of NB is quite large because of its radius. The young Laplace equation states that this curvature creates an internal pressure that is significantly greater than the atmospheric pressure. The encapsulated gas should become more soluble in the surrounding liquid due to the high internal Laplace pressure, which could speed up gas diffusion into the bulk. According to classical diffusion theories, NB should dissipate in a matter of microseconds to milliseconds. Nevertheless, NB duration on the order of hours to days is regularly reported by experimental observations, which is three to five orders of magnitude longer than what is predicted theoretically [18]. Hence, coming to the properties of NB's it includes some of the properties like buoyant force, zeta potential, Internal pressure, Surface tension, Bubble density, Specific surface area, rising velocity, and residence time.

Based on their location and manner of existence in liquid systems, nanobubbles are typically divided into two categories surface nanobubbles and bulk nanobubbles. Surface nanobubbles usually occur on hydrophobic or somewhat hydrophobic surfaces immersed in water, are tiny gas domains that stick to solid-liquid interfaces.

Surface Nano bubbles are spherical caps made of gas-filled pockets or sacs on surfaces whereas bulk NB are defined as spherical, gas-filled cavities that are produced in the liquid phase [22, 23]. Atomic force microscopy is frequently used to investigate surface nanobubbles, which are known to last for extended periods of time despite their tiny size. Contact line pinning and gas oversaturation close to the solid surface are frequently blamed for their stability [24].

4. Properties of nanobubbles

4.1 Zeta potential

When a colloidal particle travels in an electric field, the electric potential at its sliding or shear plane is referred to as the zeta potential. The work necessary to transfer a unit positive charge from infinity to the particle's surface without accelerating it is known as the surface electric potential. In essence, zeta potential is the potential difference between the surrounding dispersing medium at the sliding plane and the electric double layer (EDL) enclosing an electrophoretically mobile particle[25].

The stability of the nanobubbles increases with a higher zeta potential, whereas coagulation and stability will decrease with a lower zeta potential. Studies say that at neutral pH, the zeta potential values range between -20 and -30 mV[26]. Based on pH, the value of the zeta potential varies, leading to a change in the stability of the Nano bubble as represented in the (Fig2)[17].

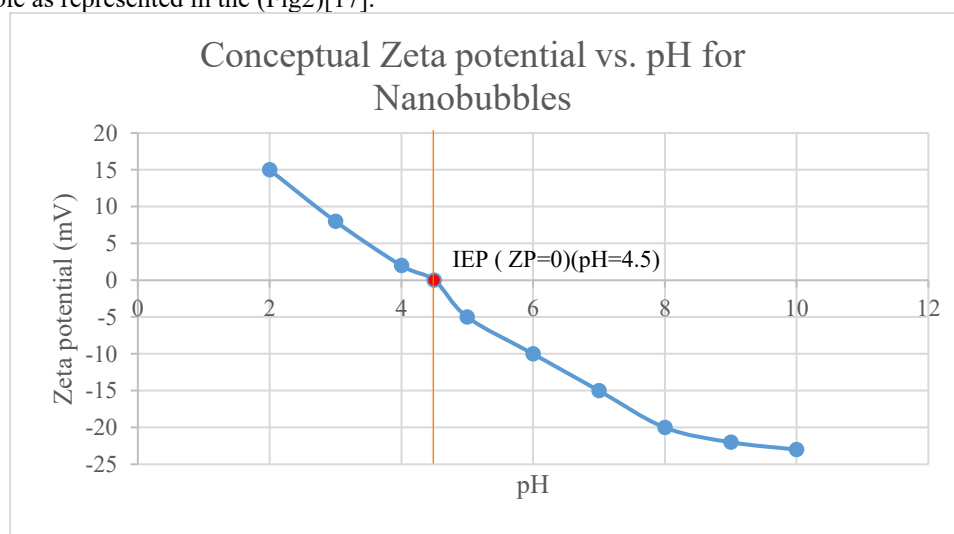


Fig 2. Effect of pH on Zeta Potential and Stability of Nanobubbles

The addition of nanoparticles in the solution increases the stability and generation of the Nanobubbles based on the various temperatures. Berkelaar et.al.,[27]reported that NB generation reaches its peak at 33°C. The generation of Nanobubbles was significantly improved by the initial introduction of titanium oxide nanoparticles. This is due to the heterogeneous nucleation effect showing better than homogenous nucleation. Additionally, the solution titanium dioxide supports the stability of the nanobubbles [28].

When nanobubbles are combined with gold nanoparticles, the interactions between the negatively charged gold nanoparticles and nanobubbles are size-dependent [27]. Larger nanoparticles demonstrate stronger interactions, which result in the disappearance of the original peaks that correspond to individual nanobubbles and nanoparticles in dynamic light scattering (DLS) measurements. Instead, a new peak that represents intermediate-sized complexes appears, indicating the formation of nanobubble-nanoparticle complexes. It is important to note that DLS measures the hydrodynamic diameter, which includes not only the core of the particles but also any surrounding interfacial layers or attached structures. Therefore, the observed shift in peaks does not reflect a change in the size of individual particles; rather, it indicates the formation of larger dynamic entities within the system. These complexes are formed due to interfacial interactions such as van der Waals forces and hydrophobic attraction, rather than being driven purely by electrostatic effects, which are detected as larger effective sizes in DLS analysis.

In a solution, nanobubbles attract oppositely charged ions, leading to the formation of a compact stern layer, followed by a more diffuse outer layer that is governed by electrostatic interactions. Together, these layers contribute to the net surface charge of the nanobubbles, enhancing their stability, ensuring uniform dispersion, and establishing zeta potential within the system.

4.2 Specific surface area

Specific surface area is the total surface area per unit of mass. Nanobubbles are nano-sized spherical particles with a high specific surface area. It is one of the characteristics of the nanobubbles generation that is correlated with the radius[6]. Among the SNB and BNB, the bulk nanobubbles exhibit a large specific surface area because surface area is inversely proportional to the radius [29].

4.3 Rising velocity

Rising velocity is the critical parameter in NB that directly influences their stability and residence time, which are critical for their performance in application and are characterised by the terminal velocity [30]. The equation arises from the Newtonian mechanisms applied to the fluid around a spherical object

$$\mu_t = \sqrt{\frac{\mu g d_b (\rho_l - \rho_b)}{3 C_D \rho_l}}$$

It involves the buoyancy, gravitational force, and drag force.

At terminal velocity,

$$F_B - F_G - F_D = 0$$

It is critical to use this model for commercial application even though it is simple. So some of the researchers proposed many models based on their experiments. Jamialahmadi et.al.,[31] considered it to be one of the best models, and it is expressed as

$$u_t = \frac{u_b u_t^w}{\sqrt{(u_b)^2 + (u_t^w)^2}}$$

$$u_b = \frac{1}{18} \frac{\rho_L - \rho_b}{\mu_L} g d_e^2$$

Based on this model, they experimented and concluded that rising velocity increases tend to increase the bubble size, depending on the diameter, and a decrease in rising velocity tends to reduce the bubble size leads to longer residence time.

4.4 Residence time

The duration between a bubble entering the reactor and popping at the air – water interface is known as the residence time. In industrial applications, residence time is a crucial factor that influences reaction kinetics, gas–liquid mass transfer efficiency, and overall process performance. It is mostly dictated by the size of the bubbles, the hydrodynamic circumstances, the liquid phase's physicochemical characteristics, and interfacial behaviour [30]. We can calculate the residence time with the height of the reactor and rising velocity when the NB are in a linear position by using the Reynolds' number. The dimensionless quantity used in fluid mechanics to predict the flow behaviour of fluid around an object, like a bubble, is called the Reynolds number.

$$Re = \rho u d \div \mu$$

If NB is in a nonlinear position, it never reaches the steady terminal velocity. As a result, especially under unsteady conditions, use of dimensionless numbers such as the bond number and motion number is preferred rather than Reynold number and the water number[29].

5. Techniques of nanobubble generation

Nanobubbles can be generated through a variety of physical and physicochemical techniques that rely on gas–liquid interactions under controlled conditions. Gas entrapment during liquid submergence, electrochemical processes, thermal stimulation by raising temperature, and pressure manipulation through quick depressurisation are some of the general mechanisms used in these generating techniques. By modifying interfacial energy, gas solubility, and local supersaturation conditions, facilitate gas nucleation and stabilisation of the nanoscale. Hydrodynamic processes like shear or oscillatory fluid motion cause bubble fragmentation and size reduction, while electrolysis-based methods use in situ gas production at electrode surfaces. While membrane-based methods regulate bubble size by forcing gas through nanoscale pores, ultrasonication creates nanobubbles through acoustic cavitation and bubble collapse. The choice of an appropriate generation method depends on factors like energy efficiency, scalability, gas type and the intended use of nanobubbles.

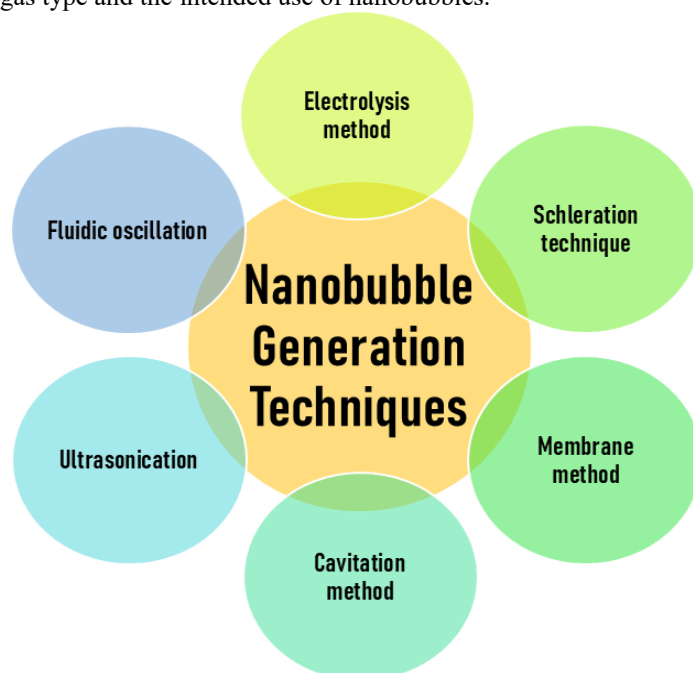


Fig 3. Overview of Major Nanobubble Generation Techniques

5.1 Electrolysis method

Electrolysis is an electrochemical method employed for the formation of nanobubbles (NB), where in gas evolution occurs at the electrode-electrolyte interface as a result of redox reactions. Water electrolysis generates hydrogen at the cathode and oxygen at the anode, whereas nanobubbles emerge when dissolved gas attains supersaturation [32, 33]. The production and properties of nanobubbles are primarily influenced by applied voltage, current density, electrolyte concentration, electrode material, and duration of electrolysis. Elevating voltage and current density augments gas evolution and nucleation, leading to increased NB generation rates and reduced bubble diameters [33, 34]. Increased electrolyte concentration enhances conductivity and diminishes energy consumption; however, elevated salt concentrations may lead to larger bubble formation due to coalescence [34]. The characteristics and spacing of electrodes determine nucleation sites and efficiency, whereas the duration of electrolysis influences the stabilization of bubble size over time.

Furthermore, the type of gas affects nanobubble (NB) features; hydrogen nanobubbles usually appear in larger quantities, whereas oxygen nanobubbles have enhanced stability owing to their increased solubility [32]. Nanobubbles are generated through electrochemical nucleation in conditions of gas supersaturation, and methods like pulsed voltage can diminish bubble size and inhibit coalescence [35]. Despite this, the process possesses disadvantages, such as elevated energy consumption. Electrode contamination, restricted scalability, and applicability to particular gases only. Systematic control of operational parameters is essential for the efficient and consistent creation of nanobubbles.

5.2 Schlieren technique

It is an optical visualisation method to detect small changes in refractive index in transparent media. When NB form they slightly change the refractive index. A researcher can see patterns that correspond to a region with a bubble. According to experimental findings, the generated NB separates or splits from the cloud rather than remaining as a single large cluster. In electrolysis-based generation using a double-layered system (DLS), the initial nanobubble size typically ranges between 60 and 80 nm. Due to continued gas absorption and coalescence effects, this average size can increase to about 250 nm after 15 minutes of sustained electrolysis. The spontaneous combustion event traps O₂ and H₂ inside the bubbles, contributing to their stability and influencing optical signatures [36]. According to Lee et al., [37], to track these refractive index changes and provide real-time monitoring of nanobubble nucleation and growth, optical methods, including phase contrast microscopy and interferometric imaging, are frequently used. Furthermore, electrochemically produced nanobubbles can last far longer than predicted by traditional diffusion theory when optical viewing and high-speed imaging are combined, suggesting the existence of a stabilising interfacial mechanism at the nanoscale [38].

5.3 Membrane method

The membrane-based method is a highly regulated approach in generation of nanobubbles (NB), where compressed gas is driven through nanoscale pores in a porous membrane into a liquid phase, resulting in bubbles at the pore outlets. The membrane effectively functions as a network of homogenous orifices, allowing the formation of bubbles with a relatively limited size distribution. During bubble formation, gas emerges with a diameter equal to the pore size. However, as gas injection continues, the bubble increases due to diffusion and expansion. Simultaneously, hydrodynamic drag forces generated by the liquid flow rise until they overcome surface tension forces, resulting in bubble separation. As a result, the ultimate bubble size is frequently larger than the pore diameter, often by 8-9 times, demonstrating that pore size is an important element in determining nanobubble dimensions [22].

In addition to pore size, gas pressure and transmembrane pressure ratio (typically 1.1-2.0) are crucial for stable bubble formation, as inadequate pressure cannot overcome liquid entry barrier, while excessive pressure can cause bubble coalescence [33]. Another crucial component is liquid flow velocity, as higher flow increases shear stress at the membrane surface, resulting in smaller bubbles owing to rapid detachment, whereas lower flow rates potentially reduce monodispersity through coalescence. The physiochemical parameters of the liquid, such as surface tension and viscosity, also influence bubble formation; for example, hydrophobic membrane surfaces have been shown to promote the development of smaller bubbles [34]. Despite its benefits, which include precise size control, great responsibility, and the capacity to manufacture monodispersed nanobubbles with membranes such as shirasu porous glass (SPG), the method has some disadvantages. These include membrane fouling and clogging, particularly in complex liquids the need for precise pressure regulation, relatively low gas throughput, and inconsistencies in reported relationships between pore size and bubble size under various hydrodynamic conditions [22, 34].

5.4 Cavitation method

Cavitation-based techniques are frequently used to produce microbubbles and nanobubbles, as these methods generate rapid pressure changes in a liquid medium. Although the phenomenon has been studied since the early 18th century, the term "cavitation" was first introduced in 1895 [37]. Cavitation processes are primarily governed by two mechanisms -acoustic cavitation and hydrodynamic cavitation—while nano-bubble-assisted cavitation (NBC) has emerged as a more advanced approach.

Acoustic cavitation, also referred to as ultrasonic cavitation, is produced by the propagation of high-frequency sound waves through a liquid medium. These waves generate alternating cycles of compression and rarefaction, leading to the formation, growth, and collapse of bubbles. The rapid collapse of these bubbles produces extreme

localized conditions, including high temperature, pressure, and the generation of reactive oxygen species. These effects contribute to the physical disruption of biomass structures and enhance biochemical reactions [32, 33]. Furthermore, the collapse of larger bubbles under intense shear or ultrasonic forces can result in the formation of smaller and more stable nanobubbles. Techniques such as ultrasonication, high-pressure shearing, and microfluidic mixing are commonly employed to enhance this process [38].

Hydrodynamic cavitation, in contrast, is induced by pressure variations generated when liquid flows through constrictions such as venturi tubes, orifice plates, or rotor systems. As the liquid accelerates through these constrictions, pressure decreases below the vapor pressure, resulting in the formation of vapor-filled cavities. These cavities collapse upon pressure recovery, releasing energy in the form of shear forces, microjets, and reactive radicals. Compared to acoustic cavitation, hydrodynamic cavitation is more energy-efficient and better suited for large-scale applications, although the intensity of bubble collapse is relatively lower [22]. Nano-bubble-assisted cavitation (NBC) differs fundamentally from conventional cavitation mechanisms. In NBC, pre-existing nanobubbles present in the liquid act as stable nucleation sites for cavitation. Due to their high stability and large specific surface area, nanobubbles reduce the energy barrier required for bubble formation and promote more uniform cavitation activity. This results in controlled nucleation, thereby enhancing interactions between biomass substrates, reactive species, and mass transfer processes [15].

Nucleation plays a critical role in distinguishing NBC from acoustic and hydrodynamic cavitation. NBC utilizes pre-existing nanoscale gas domains to lower the cavitation threshold and modify collapse behaviour. In contrast, acoustic and hydrodynamic cavitation relies on external energy input to initiate bubble formation. Consequently, NBC produces more stable and sustained cavitation effects, which are particularly advantageous for biomass conversion processes requiring efficient mass transfer and controlled disruption of biomass structures.

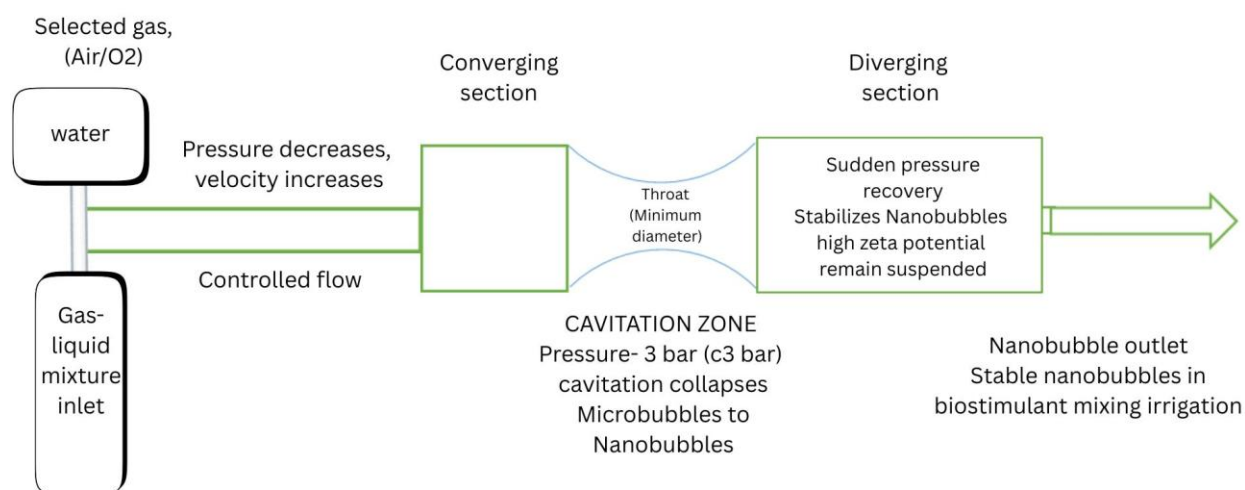


Fig 3. Mechanisms of Cavitation-Based Nanobubble Formation

5.5 Ultrasonication

Ultrasonication is a common method for generating nanobubbles, employing acoustic cavitation events triggered by high frequency sound waves (often 20 kHz-1 MHz). As ultrasonic waves traverse a liquid media, they generate localized pressure variations through cycles of alternating compression and refraction. In the rarefaction phase, negative pressure promotes the nucleation and expansion of gas cavities, but subsequent compression results in their rapid collapse. A collapse of transient cavitation bubbles generates strong localized energy; leading to the splitting of microbubbles into stable nanoscale bubbles [39-41].

The efficacy of nanobubble production using ultrasonication is significantly influenced by critical operating factors. Ultrasound frequency is important in influencing cavitation behaviour low frequencies (20-50 kHz) encourage transient cavitation, resulting in violent bubble collapse and increased nanobubble production, while higher frequencies (>100 kHz) facilitate stable cavitation, producing oscillating but less destructive bubbles [42, 43]. Ultrasonic power directly affects cavitation intensity; increasing power enhances the rate and concentration of bubble nucleation, although it may also enlarge the average bubble size due to coalescence effects [39, 44]. The duration of sonication influences both concentration and size distribution, initially increasing the quantity of nanobubbles, which may thereafter stabilize or diminish due to coalescence and dissolution processes [45].

A major impact is the kind and concentration of dissolved gas, which serve as cavitation nuclei. Increased gas content amplifies cavitation intensity and facilitates nanobubble formation, but gas characteristics like solubility and diffusivity affect bubble growth and stability [41, 42]. The kind of ultrasonic equipment such as horn type (probe) or bath type systems affects energy distribution and cavitation efficiency, with probe systems often generating more intense localized cavitation than bath systems [43, 46].

Apart from its efficacy, ultrasonication possesses numerous limits. The procedure is energy demanding, particularly at elevated power levels and extended sonication durations, potentially constraining large scale implementations [46]. Regulating bubble size distribution is difficult due to the dynamic characteristics of cavitation, and repeatability may fluctuate based on reactor design and operational parameters. Moreover, excessive ultrasonic intensity may result in bubble coalescence or destabilization, hence diminishing nanobubble output over time. The increase in temperature during sonication is a significant concern, since it can modify gas solubility and cavitation dynamics [40]. Ultrasonication offers a flexible and effective method for nanobubble formation; however, cautious regulation of operational parameters is crucial to maximize bubble size, concentration and stability for particular applications.

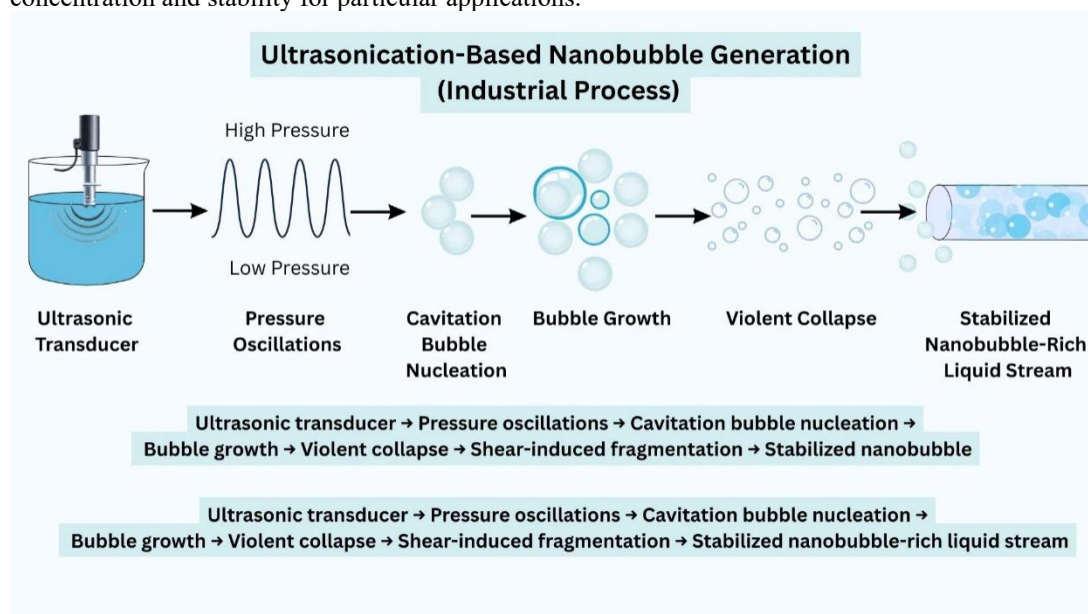


Fig 4. Ultrasonication-Driven Cavitation Mechanism for Nanobubble Generation

5.6 Fluidic oscillation

A fluidic oscillator is a no moving parts valve that uses a feedback loop to change a steady gas liquid flow into an oscillating flow. The operational flow conditions and the length of the feedback channel control the oscillation frequency [47]. Bubble size can be successfully controlled by adjusting this oscillation frequency; lower frequencies produce larger bubbles, while higher frequencies encourage the creation of smaller bubbles due to faster flow switching and increased shear forces [48]. When compared to traditional sparging systems, the oscillatory motion produces periodic pressure variations that improve bubble stability and gas liquid mass transfer efficiency by promoting bubble breakup and suppressing coalescence [49].

The combined influences of oscillation frequency, liquid velocity, gas flow rate, ore size, surface wettability, and liquid viscosity define the ultimate bubble size and concentration [48]. Specifically bubble size is correlated with the oscillating flow's pulse width, which is determined by the fluid velocity to oscillation frequency ratio. This suggest that bubble shrinkage is favored by higher frequencies and lower liquid velocities [50]. Instead of the slow bubble growth seen under constant flow circumstances, oscillatory flow hydrodynamically causes fast gas separation from membrane pores, resulting in jet like ("bullet") bubble ejection. Surface characteristics also affect this process because hydrophilic materials make it easier for a thin liquid coating to develop, which decreases gas adherence and encourages the release of smaller bubbles. Because oscillatory flow is non- steady state, this behavior differs from classical models like Tate's law [51].

Despite its benefits, fluidic oscillation's performance in creating nanobubbles is limited by a number of factors. While actual nanobubble production requires higher frequencies in the kHz range, requiring device downsizing, the majority of current systems operate at relatively low fundamental frequencies (1-100 Hz), limiting bubble sizes to the micrometer range (~20 μm) [48]. Furthermore, there are still many obstacles to overcome, including managing higher harmonics, scaling up the technique for industrial applications, and ensuring uniform flow distribution across membrane pores. However, fluidic oscillation is regarded as a potential and scalable method for nanobubble generation because of its low energy consumption, lack of mechanical wear, and improved mass transfer efficacy.

In conclusion, depending on the intended use, several nanobubble generating methods show unique benefits and drawbacks. No single generator is always the best from a performance standpoint; instead, the choice is based on

processes specifications including energy input, gas transfer efficiency, and bubble size distribution. The most promising techniques for large scale applications are hydrodynamic cavitation and membrane-based generation because of their comparatively higher scalability and continuous operating capacity. On the other hand, even while ultrasonication and electrolysis methods are successful in creating nanobubbles with regulated properties, their industrial viability is frequently constrained by high energy consumption and operating expenses. Because hydrodynamic cavitation-based systems can increase mass transfer and reaction kinetics in complex liquid environments, they are especially useful for biofuel and biomass related applications.

6. Application of nano bubble in biofuel production

The performance of nanobubbles in biomass conversion processes is largely dependent on the physicochemical mechanisms controlling their behaviour. gas supersaturation, heterogeneous nucleation, and cavitation-induced fragmentation-a process in which dissolved gas molecules group together to form nanoscale cavities-are the main causes of nanobubble formation. A structured interfacial water layer, a high negative surface charge (zeta potential), and a dynamic equilibrium between gas diffusion into and out of the bubble are some of the reasons for their unusual stability, which defines classical diffusion theory [22, 52].

Nanobubbles undergo controlled collapse in response to external perturbations like pressure changes or cavitation conditions, producing localized energy in the form of shockwaves, microjets, and reactive oxygen species (such as OH radicals). This collapse is enough to produce both mechanical and chemical effects, despite being less violent than traditional cavitation bubbles. These include partial lignin oxidation, biomass structure disruption, and increased porosity that improves hydrolysis efficiency and enzyme accessibility. Additionally, stronger interactions between biomass substrates, enzymes, and microbial systems are facilitated by the high surface area and extended residence time of nanobubbles, which enhance gas-liquid mass transfer and ultimately improve depolymerization and biofuel conversion efficiency.

6.1 Gaseous biofuel

Gaseous biofuels, especially biogas, are renewable energy sources made by biologically converting organic materials. Because they are compatible with current energy infrastructure and emit fewer greenhouse gases than fossil fuels, they are increasingly seen as sustainable substitutes[53]. Biogas mainly consist of methane and carbon dioxide, which are typically produced by anaerobic digestion, a biochemical process in which microorganisms break down biodegradable substrates without oxygen, allowing for waste stabilisation, the recovery of renewable energy, and the reduction of emissions[54, 55].

In D. Wang et.al.,[4] investigation, he conducted AD under three conditions; Ultra fine bubble water, tap water and deionised water. In terms of daily methane production, the reactor with air. Ultra fine bubble water (UFBW) achieve peak value (44.21 mL/g) compared to the other treatments. It confirms that the UFBW addition enhances the methane concentration. Among these, the micro-oxygen environment created by UFBW plays the important role in hydrolysis, acidification and methanogenesis. Overall, the synergistic effect of UFBW and micro-oxygen appears to promote the AD process.

Tobacco stalks have drawn interest among the numerous agricultural residues investigated for anaerobic digestion because of their lignocellulosic content, abundance as a post-harvest waste, and lack of competing uses, making them a suitable feedstock for biogas production[56]. In many tobacco-cultivating regions, tobacco stalks are frequently burned away, which pollutes the environment; their usage to produce bioenergy offers both waste valorisation and environmental benefits. compared to other crops, they are more viable as a mono substrate or in a co-digestion system, because they contain significant structural carbohydrates (cellulose and hemicellulose) that are suited for microbial digestion and have fewer inhibitory chemicals than tobacco leaves[57].

Tobacco stalks contain three major components: cellulose, hemicellulose, and lignin. Anaerobic digestion (AD) converts lignocellulosic material of stalks into biogas. Among these components, about 40 – 50 % of methane is obtained from cellulose. The most crucial step in the anaerobic process is the preparation of feedstock. Research has shown that cellulose accounts for a significant portion of methane yield, and reducing particle size during feedstock preparation increases surface area and microbial access, enhancing digestion efficiency. The ideal feed to inoculum ratio for maximising methane production from tobacco stalk decomposition was determined by [56]. When the Tobacco stalk stayed below 10% increases, the microbial activity and transport functions were avoided [58]. According to Reansuwan et.al.,[59] research, hydrogen nanobubble water (H₂-NBW) can further improve anaerobic digestion performance by boosting microbial activity and speeding up the breakdown of lignocellulosic materials, which will increase methane outputs and improve digestion kinetics. In this research, H₂ NBW increases the generation of methane by the following values.

Tobacco stalk + 0 % H₂ NBW = 230.6 ± 6.1

Tobacco stalk + 60 % H₂ NBW = 262.2 ± 6.4

Nearly tobacco stalk + 100 % H₂ NBW results 202.4 ± 7.2, which is less than the control.

In addition to being superior in biogas yield, organic matter removal, energy recovery, and process stability, two-stage AD may address the drawback of the single-stage system's extreme acidity. Salinity is one of the factors that inhibits the formation of biogas from food waste in this study. NBW is utilised with N₂ NBW and Air NBW to produce hydrogen and methane. Nitrogen is particularly used because it will not support the growth of aerobic organisms. Nitrogen guarantees that enhancement occurs without the introduction of reactive oxygen species by

enhancing gas – liquid mass transfer. It increases the interaction between substrate microbes to promote hydrolysis and acidogenesis. The overall results of Hou Tingting are given in Table 1.

Overall, rather than isolated effects noted in various researches, the improvement of gaseous biofuel production by nanobubbles can be attributable to multiple interconnected mechanisms. First, because of their large surface area and extended residence duration, nanobubbles greatly improve the efficiency of gas-liquid mass transfer, increasing the availability of vital gases like carbon dioxide, hydrogen, and oxygen for microbial metabolism. Second, localized reactive species (such as hydroxyl radicals) produced by the collapse of nanobubbles can partially degrade complex organic substrates, improving their biodegradability and speeding up conversion during anaerobic digestion. Additionally, by fostering a suitable microenvironment, nanobubbles enhance microbial activity and stability. Their contact with microbial cells is improved by their negative surface charge (zeta potential), which encourages cell adhesion and nutrition exchange. These enhanced mass transfer, production of reactive species, microbial stimulation and improved transport phenomena all work together to increase the yields of gaseous biofuel.

Table 1. Effects of Nanobubble Water on Hydrogen and Methane Production Under Different Operational Conditions[60]

Condition / Parameter	Air-NBW (overall system)	N₂-NBW	Air-NBW under salinity (0–30 g NaCl/L)	Air-NBW – Enzymatic activity	Air-NBW – ETS activity	NBW pre-domesticated inoculum (2nd cycle)	KOH substitution for NaOH
Observation / Effect	Highest H ₂ and CH ₄ yields	Enhanced hydrolysis/acidogenesis only	Increased H ₂ and CH ₄ yields at all salinities	Enhanced at both stages	Increased ETS activity	Higher CH ₄ yield and inoculum activity	Improved methanogenesis and process stability
Improvement Compared to Control (DW)	H ₂ ↑ 38% , CH ₄ ↑ 24% , Energy recovery ↑ 23%		H ₂ ↑ 21–65% , CH ₄ ↑ 14–43%			CH ₄ ↑ 33% , Inoculum activity ↑ 27%	Shorter start-up, higher CH ₄ yield
Explanation / Mechanism	Air-NBW enhances both stages of AD due to micro-oxygen generated from nanobubble collapse.	Promotes substrate breakdown; inert gas maintains anaerobic conditions, but no direct methanogenesis stimulation	Micro-oxygen from Air-NBW enhances enzymatic activity under salt stress	Improved enzyme-mediated hydrolysis and methanogenesis confirmed.	Promotes electron transfer related to H ₂ and CH ₄ synthesis.	NBW acclimatisation improves microbial resilience and activity.	K ⁺ alleviates Na ⁺ inhibition on methanogens, enhancing salt tolerance.

6.2 Liquid biofuel

In the transportation industry, liquid biofuels and renewable fuels made from biomass sources like vegetable oils, animal fats, sugars, starches, and lignocellulosic materials are mostly utilised as substitutes for liquid biofuels derived from petroleum.[60]. The major types of liquid biofuels include bioethanol, biodiesel, and bio-oil that can be generated through various biochemical processes such as thermochemical process, fermentation, transesterification and pyrolysis. Compatibility with current fuel infrastructure, lower greenhouse gas emissions, and increased energy security through the use of locally accessible renewable resources are just a few benefits of liquid biofuels[61].

Because of their high photosynthetic efficiency, quick growth rate, and capacity to store a lot of lipids, carbohydrates and proteins, algae have become a prospective feedstock for third-generation biofuel. In contrast to conventional terrestrial crops, microalgae and macroalgae can thrive in wastewater or non-arable land with sunlight and CO₂ as their main inputs, and they do not compete with food production. Based on the growth environment and management, algal cultivation methods are broadly classified into open and closed systems. By greatly enhancing mass transfer and microbial activity, nanobubbles technology presents prospective improvements for the production of algae and biofuel.

In comparison to conventional aeration techniques, Silva et.al.,[62] showed that nanobubble aeration can yield a 55.03% increase in particular metabolite concentrations and a 10% higher elimination of soluble chemical oxygen demand. More effective gas exchange and substrate utilisation are made possible by the technology's special characteristics, which include nanometric size, high internal pressure and extended liquid suspension. This is further supported by Yuan et.al.,[63], who point out that nanomaterials can boost microbial growth by lowering reactive oxygen species and increasing photosynthetic efficiency. The technology of nanobubbles has demonstrated exceptional promise in enhancing the generation of biofuel from microalgae. By encouraging efficient CO₂ dissolution, O₂ stripping, and biomass suspension, the stable nanobubbles in algal cultures improve mass transfer efficiency and raise algal density and productivity [64, 65]. Compared to microbubbles, the uniform nonporous membranes of airlift-loop bioreactors (ALB) can produce bubbles as small as 100 nm, which allows for efficient mixing and low energy usage [65]. Additionally, to further increase process efficiency, nanobubbles and nano-additives help flocculate and separate microalgal biomass before producing biodiesel and bioethanol [66]; [62].

The concepts of oil-water, water-gas, and oil-gas separation are used for purification by a number of oil refinery firms. NBs are employed in this procedure to use flotation to separate oil from suspended particles. A large number of NBs have been produced using the gas-injection technique. Air bubbles in the water cause oil droplets to float toward the top and gather there. It improves the efficiency of separation and lowers the generation of hydrogen sulfide gas, which is caustic, explosive, and harmful to humans. This method is now useful in a variety of separation operations, including oil refineries, petrochemical plants, and natural gas separation facilities[67].

The following tables 2,3,4 confirms that CO₂ nanobubbles improve oil recovery by increasing the adsorption of polymers and surfactants due to their high electrostatic potential. Additionally, nanobubbles speed up the mass transfer of CO₂ into the liquid phase, resulting in brief CO₂ oversaturation that facilitates CO₂ easier passage through narrow shale rock pores. Dissolved CO₂ can improve oil displacement by causing two-phase oil-gas production when nanobubbles gradually decompose. According to core flooding tests, CO₂ NB experiences minor pressure compression and heat expansion but maintain their stability at the nanoscale size under reservoir conditions. Overall, the study shows that by boosting CO₂ transit, stability, and interaction within confined reservoirs, CO₂ nanobubbles enhance oil recovery performance.

6.3 Comparative performance of nano-bubble cavitation across biomass types

The structural and compositional properties of the feedstock have a major impact on how well nano-bubble cavitation (NBC) converts biomass. Optimizing process efficiency requires a comparative understanding across various biomass categories. NBC mainly improves depolymerization through improved mass transfer and mechanical disruption in lignocellulosic biomass, which is made up of complex and resistant polymers like cellulose, hemicellulose, and lignin. Lignin restricts enzymatic accessibility; however, partial delignification and increased substrate accessibility are encouraged by nanobubble-assisted cavitation, which enhances hydrolysis efficiency [15, 68].

Algal biomass, on the other hand, is more susceptible to disruption due to its lower lignin content and simpler cellular structures. Compared to lignocellulosic biomass, NBC produces higher conversion efficiencies by improving cell membrane rupture and facilitating the release of intracellular components like lipids and proteins with comparatively little energy input [22, 69]. An intermediate scenario where structural heterogeneity and fluctuating lignin content affect NBC performance is agricultural residues. Although nanobubble cavitation promotes degradation and increases porosity, biomass composition and pretreatment conditions have a significant impact on overall efficiency [15].

NBC improves microbial accessibility, organic matter solubilization, and floc disruption in sludge-based biomass, especially from wastewater treatment systems. Improved mass transfer and biodegradability, not just structural depolymerization, are the main advantages of these systems [70]. Overall, biomass composition, structural complexity, and recalcitrance have a significant impact on NBC's efficacy. Because their matrices are more easily accessible, algae and sludge-based systems react more quickly, while lignocellulosic biomass needs more

thorough treatment. This emphasizes how crucial it is to tailor nanobubble-assisted procedures to particular biomass types in order to increase the efficiency of biofuel conversion.

Table 2. Performance Comparison of CO₂ Nanobubble-Assisted Flooding on Enhanced Oil Recovery[71]

Parameter	Control (Water + CO ₂ Flooding)	CO ₂ -NBs + 0.1 wt% CTAB	CO ₂ -NBs + 0.2 wt% CTAB	Improvement / Observation
Ultimate oil recovery (%)	~49	71	72	~45% improvement over control
Recovery plateau (Pore Volumes, PVs)	—	2.0–2.5	2.0–2.5	Similar plateau for both NB cases
Gas–oil ratio (Breakthrough, PVs)	~1.7	~2.7	~2.7	Delayed breakthrough with NBs
Pressure stabilisation (bar g)	~8.2	37.3	38.2	Significantly higher pressure stability
Operational implication	Baseline flooding	Improved oil recovery and delayed gas breakthrough	Similar trend	Promising for large-scale EOR applications

Table 3. Performance Comparison of Air Nanobubble-Assisted Oil Removal Using Polymer Flocculation[71]

Parameter	Control (Regular Air Sparging)	Air-NBs + 0.1 wt% Polymer	Air-NBs + 0.2 wt% Polymer	Improvement/ Observation
Oil removal efficiency (%)	62	96	98.5	~55% improvement compared to control
Saturation pressure (bar)	4	4	4	Same operating pressure
Bubble size range	0.5–2 mm (macro bubbles)	Nanobubbles (<1 µm)	Nanobubbles (<1 µm)	NBs provide a higher surface area-to-volume ratio
Flocculation polymer usage (wt%)	0.2	0.1	0.2	Less polymer is needed for similar or higher efficiency.
Oil removal kinetics	—	20% faster than control	20% faster than control	Faster removal rate with NBs
Operational implications	Regular air bubbles escape rapidly	Enhanced electrostatic interaction, improved flocculation	Higher efficiency, lower polymer demand	Improves sustainability and cost-effectiveness

Table 4. Performance and Emission Impacts of Air Nanobubble–Enhanced Diesel Fuel[71]

Parameter	Control (Regular Diesel)	Air-NB-Enhanced Diesel	Improvement / Observation
Fuel type	Diesel (without NBs)	Diesel containing air-NBs	—
Generator running time (for equal fuel mass)	Baseline	~16% longer	Improved combustion efficiency
Reference comparison (Petroleum, from [28])	—	14% improvement	Slightly higher performance with diesel
CO₂ emission reduction (%)	—	~9% lower	Indicates more complete combustion
CO emission reduction (%)	—	~11% lower	Reduced incomplete combustion
Combustion mechanism	Conventional external combustion of droplets	Simultaneous internal (due to entrained air-NBs) and external combustion	Enhanced oxidation from oxygen-rich NBs
Operational implication	Standard fuel	Higher efficiency and cleaner exhaust	Promising for sustainable fuel applications

7. Nano bubbles in biomass pretreatment & conversion

As we discussed earlier about the techniques, acoustic cavitation is the term for the microscopic bubble holes created by ultrasonic waves when they travel through a liquid medium. These cavities quickly expand and contract. The structure of the cellulose and hemi-cellulose in the biomass is somewhat disrupted by the extreme localised pressure and temperature created when these bubbles burst. Gogate et al., [72] have used ultrasonic frequencies between 10 and 100 kHz to treat lignocellulosic biomass. The yield of reducing sugars increased by 19% when pine sawdust was processed with ultrasonication, for instance, proving that nano bubbles substantially improve the hydrolysis efficiency and sugar recovery from biomass [73].

In nanobubble-assisted pretreatment, hydrodynamic or acoustic techniques, like a venturi tube or orifice plate, create minuscule gas cavities (less than 200 nm) [68]. Reactive radicals like OH and O₂ are formed when these nanobubbles collapse, producing tremendous localised heat (10,000 K) and pressure (~1000 atm) [74, 75]. By oxidising and breaking down lignin, these radicals improve the effectiveness of enzymatic hydrolysis and relax the structure of biomass, making NB pretreatment a more environmentally friendly option than traditional techniques [74, 75]. According to Zhu et al., [76], NB technology increased the lignocellulosic biomass hydrolytic acidification and delignification efficiency, producing noticeably higher sugar yields than untreated samples. In a similar vein, Masuda et al., [77] found that ozone nanobubbles' efficiency broke down lignin and altered its structure by reducing the hemicellulose content of wood meal from 42.8% to 35.9% and the cellulose amorphous fractions from 62.3% to 56.6%. While preserving cellulose integrity, the presence of oxygen-rich radicals from NBs speeds up partial delignification.

8. Sustainability aspects

Eco-friendly production method, energy-efficient processes, and minimum environmental toxicity are essential to the sustainability of nanobubble (NB) technology. Large-scale usage of NBs raises questions regarding their environmental impact and long-term viability, despite the fact that they show considerable potential in biomedical, food, and water treatment applications. Existing techniques for NB synthesis, like sonication and cavitation, are still expensive and energy-intensive. In order to reduce manufacturing costs and the carbon footprint, scientists are creating renewable energy-driven NB generation techniques and low-energy microfluidic systems.

Nanobubbles can increase the effectiveness of biological reactions, decrease resource waste, and precisely supply oxygen and other gases within bioreactors [78]. The frequency of bioprocess maintenance can be decreased by the stability of nanobubbles. Stable reaction conditions help bioreactors last longer, experience less stress, and require less maintenance, which lowers the facility's overall carbon footprint and promotes sustainability [10]. For example, the use of MNB offers significant promise for environmental sustainability in addition to water treatment because of its improved time-cost efficiency and reduced chemical use. The usage and application of NBs for water purification are still restricted, despite a large body of research and experimental data.

The purpose of Tsai et al., [79] study to provide a summary of the body of literature currently available on nanobubbles and their uses in the water industry. This study will highlight upcoming trends in the utilisation of nanobubbles and offer insights into current advancements and the state of NB research. The ability of production systems to conform to techno-economic feasibility is what determines their sustainability. This element is still being discussed today in relation to algae-based biorefineries and the application of cutting-edge technologies to them. Following safety procedures and regulatory standards is necessary while using NBT in industrial settings. TEA and the life cycle effects of NBT should be taken into account under various planned uses, such as food and water treatment, in order to guarantee economic sustainability [9, 80].

9. Future perspective

Micro-nanobubbles have gained increasing attention in recent years due to their distinctive properties. Up to now, research has focused on the methods of Micro nanobubbles(MNB) formation, such as the production of bubbles that displace air, create bubbles that form the air, and produce bubbles by electrolysis. It is commonly known that MNB generators are used in thermal jet printing, medicine administration, water purification, mineral buoyancy, and lowering ship resistance[81].The in-depth study of NBs and their effects on long-term use is one of NBT's future hopes. The current cost of NBT needs to be reduced to at least competitive levels with MB or fine bubble producers in order to attract more potential customers and boost market penetration. Since the CCUS procedure is costly, it would be encouraging for algal bioprocesses if air NBs could be successful at 2%–3% CO concentration.[82]. Based on the Compound Annual Growth Rate (CAGR) report for 2021–2031, the demand for nanobubbles (NBs) in fishing, agriculture, and aquaculture has risen by around 5%. Nations across the Asia-Pacific region, as well as the United States, Europe, and the Middle East, are increasingly exploring the diverse applications of nanobubble technology. This growing global focus positions NBs as a promising frontier for future scientific and technological advancements.

10. CONCLUSION

Nanobubbles represent one of the fastest-developing frontiers in nanotechnology, possessing special physicochemical properties: long-term stability, high surface area, strong zeta potential, and efficient gas transfer capability. Such features have enabled their promising applications in a wide range of areas, from environmental remediation and water treatment to biomedical delivery systems and biofuel production. The longevity of nanobubbles, despite classic predictions of their rapid dissolution, is credited to surface interfacial films and nanoscale effects that impede gas diffusion. Furthermore, integration with nanoparticles along with surface modification has been demonstrated to enhance nanobubble stability and functionality, thereby expanding their practical deployment.

Ongoing research continues to improve nanobubble generation techniques, including electrolysis, cavitation, ultrasonication, and membrane methods, in overcoming challenges related to energy consumption, scalability, and controlled size distribution. Recent developments also emphasise the synergistic role of nanobubbles in enhancing microbial activities, enzymatic processes, and mass transfer rates in industrial and environmental systems.

The promising results of recent studies underline nanobubbles as a game-changing tool with immense potential to transform industries associated with wastewater treatment, agriculture, aquaculture, and renewable energy. However, future research has to overcome the challenges of cost-effective large-scale production and a deep understanding of the dynamics of nanobubbles under changing physicochemical conditions with minimal environmental impact. Addressing these aspects will be critical to fully harnessing the versatile functionalities of nanobubbles in sustainable technological solutions.

CRediT authorship contribution statement

Vignesh Sathiyamoorthi: Writing – original draft, Vasanth Mohan: data collection, Yamunasri Palanisamy: review and editing, data collection, Balachandar Dananjeyan: review and editing, Ramesh Desikan: review and editing, Babu Rajendra Prasad: review and editing, Vijayakumary ponniyan: review and editing, Parimala devi Rathinasamy: framework, conceptualization, review and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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