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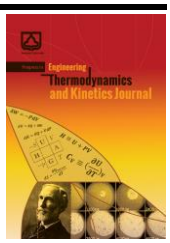

Research Article

The Influence of Ultrasonic Waves on Ice and THF Hydrate Formation

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ABSTRACT

In this study, the influence of ultrasonic waves on ice and THF/H_2O hydrate formation was investigated. Experiments were conducted under ambient pressure, with ultrasonic power ranging from 0 to 288 W and irradiation temperatures between 6 and 12 °C. The effects of ultrasonic irradiation at a frequency of 25 kHz on the induction time and nucleation temperature were experimentally examined. The results indicate that ultrasonic irradiation increases the nucleation temperature of the THF/H_2O solution while reducing the induction time. An optimal irradiation temperature was identified, corresponding to temperatures close to the equilibrium points of ice (0 °C) and THF/H_2O hydrate (4.4 °C), which were found to be the most favorable for ultrasonic application. At lower ultrasonic power levels, the formation of both ice and THF/H_2O hydrate was suppressed, primarily due to prolonged irradiation and additional heat generation. To mitigate thermal effects, ultrasonic irradiation at duty cycles of 50% and 70% was applied. The results demonstrate that ultrasonic irradiation with a duty cycle of 70% effectively promotes the hydrate formation process.

1. Introduction

Crystallization is a phase transition in which a liquid or gas transforms into a solid phase through the formation of ordered crystalline structures within a solution. The rate of crystallization is determined primarily by the degree of supersaturation and the physicochemical properties of the solution. Key parameters, including nucleus size, crystal morphology, induction time, and initial nucleation temperature, are strongly influenced by the

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degree of supersaturation, as well as the surrounding environmental conditions [1, 2]. The hydrate formation process shares strong similarities with conventional crystallization phenomena. Hydrates are ice-like crystalline structures in which guest molecules, either gaseous or liquid, are trapped within a hydrogen-bonded network of water molecules; these structures are commonly referred to as clathrate hydrates. Various gases, such as methane, ethane, propane, and certain refrigerants, such as tetrahydrofuran (THF) and cyclopentane (CP), are capable of forming clathrate hydrates. The most notable properties of gas hydrates include their high storage capacity, transportability, and potential applications in water desalination [3-11]. Gas hydrates can adopt different crystallographic structures, with most liquid hydrate formers, such as THF, preferentially forming structure II hydrates. The hydrate formation process involves two stages: nucleation and subsequent growth. During the nucleation stage, initial nuclei are microscopic and cannot be detected by the naked eye. As the temperature increases and additional hydrate particles form, the clusters of nuclei become visible and grow into macroscopic crystalline structures. Certain hydrate formers are considered cold storage materials due to their proper phase change temperature, substantial fusion heat, and formation at ambient pressure. These characteristics make them suitable for use in air conditioning systems, reducing peak demand for electric power and increasing the refrigeration coefficient. The selection of a thermal energy-storing material for air conditioning systems is crucial, and THF hydrate, with its phase change temperature close to room temperature, proves to be a viable option [7-16].

Some researchers have demonstrated that ultrasonic waves can enhance the crystallization process during hydrate formation and water freezing [17]. Ultrasonic irradiation is believed to influence the heat transfer coefficient, leading to an increased freezing rate [18]. During the crystallization process, the application of ultrasonic waves induces bubble formation, creating acoustic flow in the solution. Cavitation and bubble collapse contribute significantly to the formation of initial nuclei during the crystallization process [18-21]. Other works have demonstrated that acoustic waves affect the induction time and promote the nucleation process. Kiani et al. studied the application of ultrasonic irradiation during crystallization and reported that ultrasound effectively enhanced the rate of nucleation and crystal growth [22].

In ultrasonic-assisted crystallization, ultrasonic irradiation increases the mass transfer coefficient, facilitating the attainment of supersaturation in the solution [23]. The nucleation process is altered by ultrasonic irradiation. Likewise, it significantly reduces the degree of supercooling at high intensity [24-26]. Baogou et al. investigated the effects of ultrasonic irradiation at different temperatures and wave intensities during radish freezing. The results

indicated that the optimal conditions were achieved at a temperature around -0.5ºC and an intensity of 0.26 W/cm2. It was observed that approximately 7 seconds of irradiation were sufficient to improve nucleation [27]. Kiani et al. explored the effect of ultrasonic waves on the freezing process of water, sucrose solution, and agar gel samples. They discovered that ultrasonic waves induced nucleation at higher temperatures through cavitation. Ultrasonic waves were most effective when samples were irradiated at temperatures close to the nucleation temperature [28]. Additionally, ultrasonic waves can enhance fluid mixing, prevent crystal agglomeration [29], increase the formation rate, and change the byproduct elimination in chemical processes [30]. Park and Kim reported that ultrasonic irradiation in the range of 100–200W significantly affected gas consumption during methane hydrate formation. Furthermore, increased hydrate formation and reduced reaction time were observed at an ultrasonic power of 150W [17]. Guo et al. investigated the effects of ultrasonic waves on liquid mixing and agglomerated crystal breakage processes. Ultrasonic irradiation improved the efficiency of food and water freezing processes. The results showed a linear relationship between the nucleation temperature of food samples and the temperature of ultrasonic irradiation. However, prolonged use of ultrasonic waves is not always desirable [31]. Sadegh et al. studied the effect of compressional wave velocity on consolidated sediments with and without tetrahydrofuran using the pulse transmission method. They found that the P-wave velocity of consolidated sediments increases with increasing hydrate formation and confining pressure [32]. Pohl et al. investigated the effect of ultrasonic P wave velocity and attenuation measurements on pure tetrahydrofuran hydrates. They observed that while velocity increased, the waveform frequency content and amplitude decreased after the completion of the hydrate formation reaction, indicating an increase in P-wave attenuation following hydrate formation [33]. Since the processes of crystal formation and growth are similar in hydrate formation and freezing, ultrasonic waves are expected to exert a comparable influence on hydrate formation.

Gas hydrate formation or decomposition processes are considered from two points of view: equilibrium thermodynamics and the kinetics of these processes. While some researchers have studied the thermodynamics of hydrates, the study of the kinetics of hydrate formation and the parameters affecting this process is crucial. Some liquid hydrate formers, such as THF, TBAB (Tetra butyl ammonium bromide), and cyclopentane, can be suitable surrogates for gas hydrates, as they can form structures similar to gas hydrates. For example, nitrogen, as a natural gas hydrate former, can participate in the hydrate structure as a guest and form structure II. Also, liquid hydrate formation is possible under atmospheric pressure, whereas high pressure is required for gas hydrate formation.

In this study, ultrasonic waves were applied to investigate the formation of ice and THF hydrate under atmospheric pressure. The formation processes of ice and THF hydrate were performed at different ultrasonic powers and duty cycles (DC). The results indicated that ultrasonic waves can enhance the nucleation and growth processes. Furthermore, the obtained results were compared with conventional crystallization data, and the effect of different irradiation temperatures and powers on the formation process was investigated. Likewise, the optimal conditions were identified for both temperature and irradiation power. To mitigate the extra heat generated by ultrasonic wave irradiation, duty cycles were employed.

2. Experimental setups and methods

2.1. Apparatus I

An experimental apparatus is shown in Fig.1, consisting of three batch reactors, a cooling system, an ultrasonic generation system, and a data acquisition system. The reactors are constructed from double-walled stainless-steel cells, each equipped with three piezoelectric transducers mounted at the bottom. These transducers are controlled by an ultrasonic wave generator transmitting waves directly into the solution. To control the solution temperature, a 50:50 volumetric mixture of water and ethylene glycol circulates through a thermal jacket. As exothermic nucleation and hydrate formation occur, the solution temperature rises. Therefore, the cooling system maintains thermal stability to prevent dissociation. Two K-type thermometers are positioned to monitor the internal temperature distribution within each cell. Temperature data were logged at 10-second intervals.

The reactor volume is approximately 300 cm3. The test solution consisted of deionized water and THF at a 1:17 molar ratio. To investigate the impact of ultrasonic irradiation, waves with a frequency of 25 kHz and power outputs ranging from 0 to 240W were applied during both freezing and hydrate formation processes. To maintain consistent conditions, the operating parameters were kept constant throughout both processes. The initial solution temperature of 20°C was lowered by circulating the coolant at -10°C. Subsequently, induction times were recorded by applying the ultrasonic waves at specific desired temperatures (12, 10, 8, and 6 ˚C).

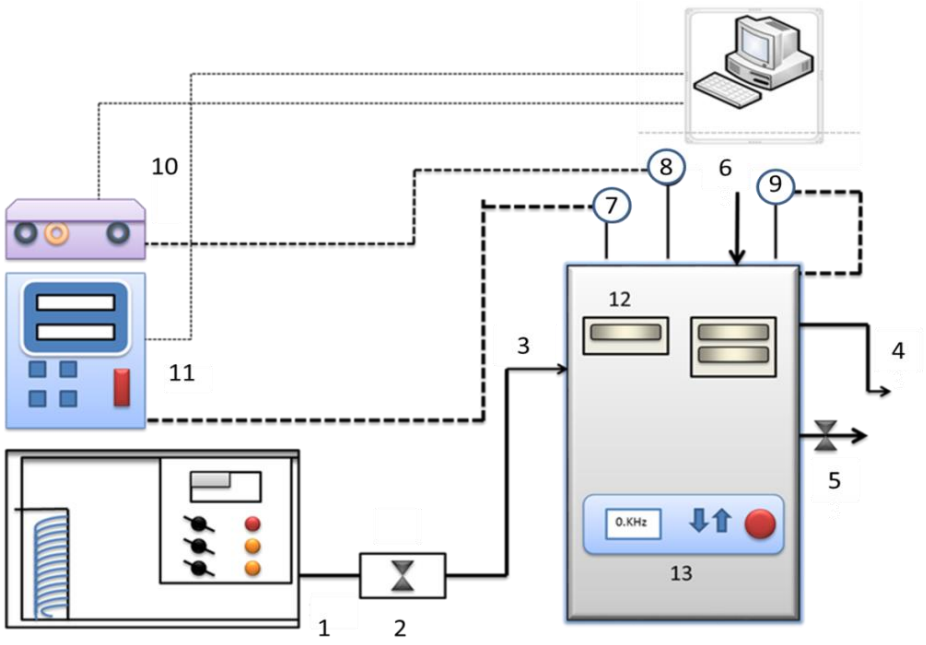


Figure 1. Schematic of experimental setup 1. Cooling system, 2. Coolant pump, 3. Coolant input, 4. Coolant output, 5. Vent, 6. Entrance, 7. Thermocouples, 8. Hydrophone, 9. Thermocouples 10. Oscilloscope, 11. Data logger, 12. Display temperature, 13. Display frequency and power.

2.2. Apparatus II

The experimental setup was optimized to ensure uniform power distribution within the cell and to investigate the effects of wave irradiation duration on nucleation temperature and induction time. The schematic of this configuration is shown in Fig 2. The system comprises three 100 cm3 double-walled stainless-steel cells. A piezoelectric transducer is mounted at the base of each cell to generate ultrasonic waves, with output power adjustable from 0 to 480 W via the generator. To precisely control the duration of irradiation, a dedicated control circuit was installed between the generator and the transducers. This modification aimed to maximize the repeatability and reproducibility of experimental results across the three reactors under the same operating conditions.

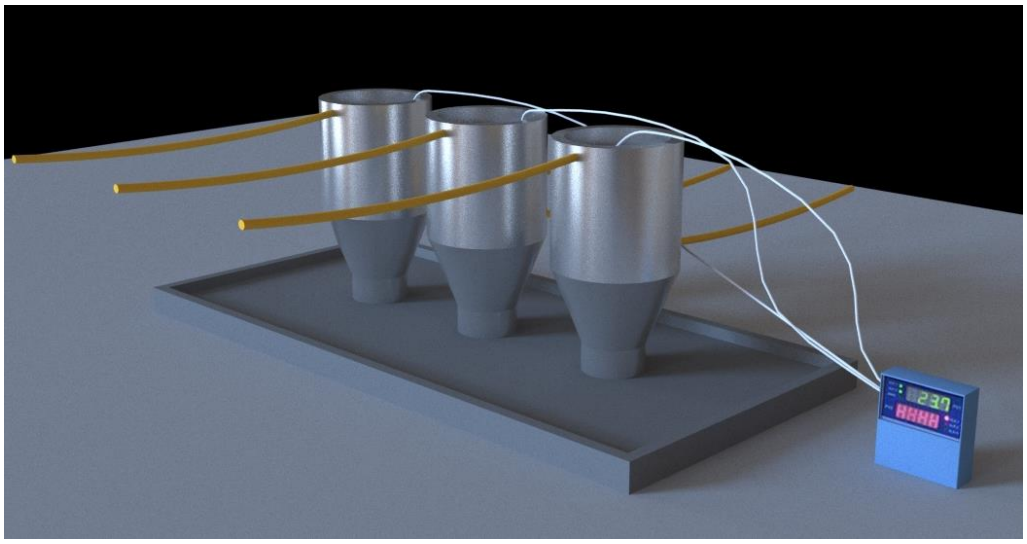


Figure 2. Schematic of ultrasonic setup II, 1. Coolant input, 2. Coolant output, 3. Double-walled cells, 4. Piezoelectric, 5. data logger.

3. Results and discussion

3.1. Effect of the ultrasonic waves on nucleation temperature and induction time

In Fig. 3, the morphology of THF hydrate is shown both with and without ultrasonic waves. The results demonstrate a noticeable alteration in the morphology of THF hydrate in the presence of ultrasonic irradiation.

(a) (b)

Figure 3. THF hydrate a. With UL, b. Without UL.

The experiments were performed using two different systems to examine the effect of ultrasonic waves on the freezing rate of deionized water and THF hydrate formation. In the first apparatus, the impact of various initial solution temperatures (ranging from 6 to 12℃) was investigated.

Table 1 presents experimental results for hydrate formation (HF) and freezing (F) with and without an ultrasonic system, maintaining a constant power of 240W.

Table 1. Experimental results for hydrate formation (HF) and freezing (F) with and without an ultrasonic system at a constant power (240W).

Temperature of irradiation (℃)	$T_{induction}$ (℃) HF	$T_{induction}$ (℃) F	T_{max} (℃) HF	T_{max} (℃) F	Irradiation duration (Sec.) HF	Irradiation duration (Sec.) F
Control	2.9	0.8	3.1	2.6	0	0
12	3.2	1.5	4.6	2.1	810	110
10	3.6	1.3	4.96	4.6	530	4480
8	3.7	2.1	4.98	4.35	380	230
6	4.8	3.02	5.8	4.8	170	100

The temperature profiles for water freezing and hydrate formation at an ultrasonic power of 240W are illustrated in Figs. 4 and 5, respectively. In both figures, a distinct rise in solution temperature is observed upon the onset of nucleation, attributed to the release of latent heat. This abrupt temperature spike marks the nucleation point. The results indicate that the induction time is temperature-dependent, with significantly shorter periods observed at lower temperatures (6 and 8°C). Furthermore, ultrasonic irradiation was found to effectively promote the kinetics of both water freezing and hydrate formation.

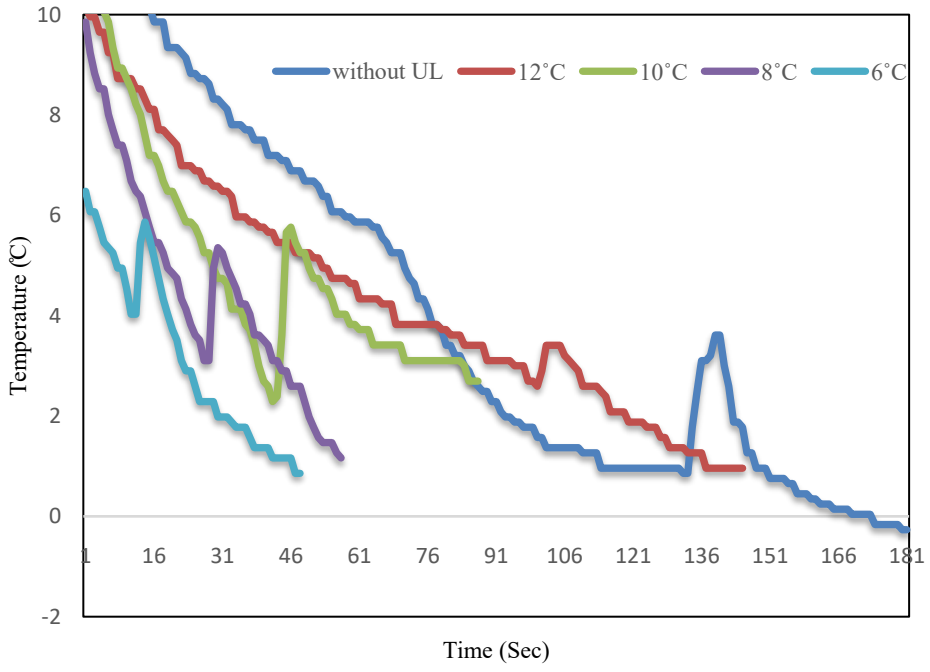


Figure 4. The temperature profile of water freezing (240W).

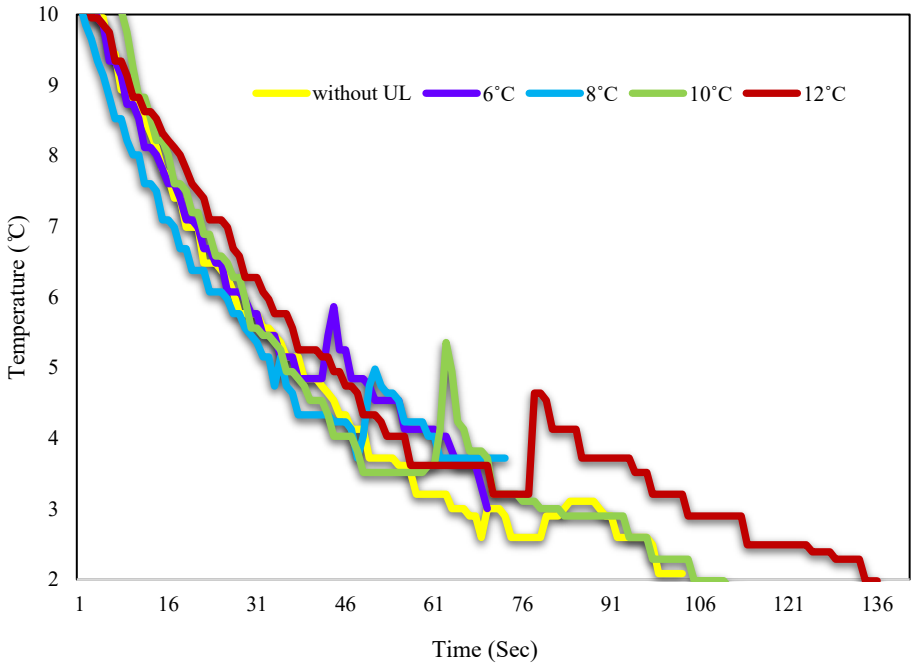


Figure 5. The temperature profile of hydrate formation (240W).

Because of the substantial reactor volume in the first apparatus, maintaining thermal homogeneity proved challenging. However, employing variable ultrasonic power and periodic irradiation was found to significantly improve temperature uniformity within the solution. As depicted in Fig. 2, a modified setup utilizing three stainless-steel cells with transducers located at their base was employed to isolate the effects of periodic irradiation and transducer power. Additionally, the surface roughness of the cell walls was observed to play a critical role in determining the nucleation temperature and formation rate. Distinct differences in freezing behavior and nucleation kinetics were observed between ultrasonic-assisted and quiescent systems. Moreover, adjusting the recycle valve of the refrigerator under optimal conditions enhanced both process stability and thermal uniform distribution. In Figs. 4 and 5, the effects of initial temperature on the formation process of THF/H2O solution were investigated. Experiments were conducted at temperatures of 6, 8, 10, and 12 °C to identify the optimal operating conditions. The thermal profiles indicate that lower temperatures—specifically those approaching the equilibrium points of ice (0°C) and THF hydrate (4.4°C)—yielded the most favorable formation kinetics under ultrasonic irradiation.

Following the determination of the optimal operating temperature, the second phase of experiments investigated the impact of varying ultrasonic power intensities under continuous irradiation. Figure 6 illustrates the thermal profiles of the THF/H2O solution at power levels of 72, 180, and 288 W under continuous irradiation. It was found that while the delay between

ultrasonic irradiation and the appearance of the first nuclei is influenced by the ultrasonic power, no direct linear correlation was observed between power intensity and either induction time or nucleation temperature. As seen in Fig. 6, the highest nucleation temperature was recorded at 288 W, while a power of 180W setting proved to be the most effective for the overall kinetics, significantly enhancing the freezing process and minimizing the induction time. Notably, the application of ultrasonic irradiation consistently promoted hydrate formation across all tested power levels compared to quiescent conditions.

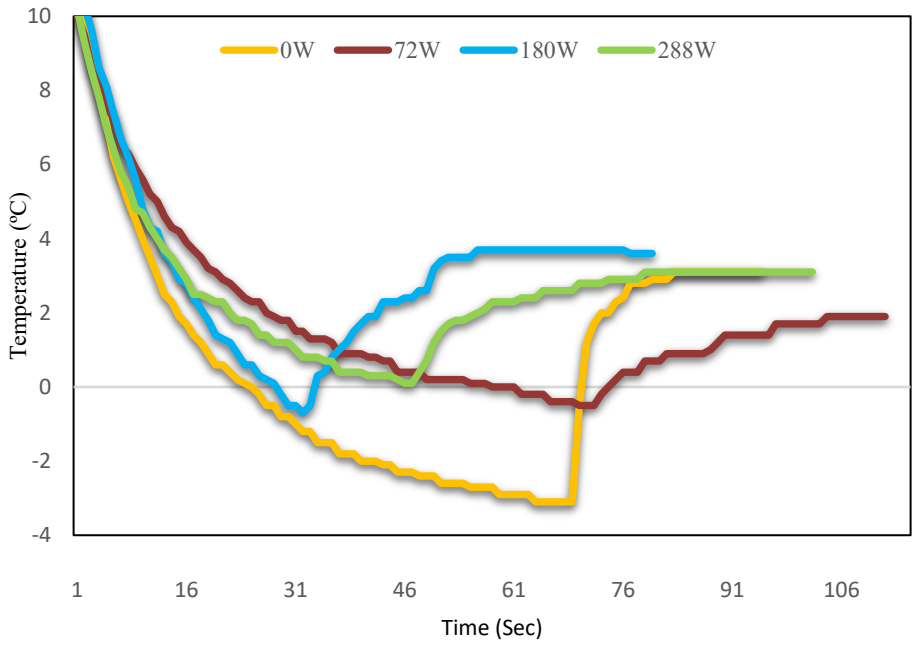


Figure 6. Temperature profiles of the solution at different powers (continuous irradiation).

It should be mentioned that the continuous flow of ultrasonic waves leads to thermal decomposition and dissociation of the formed hydrate and ice. The application of ultrasonic waves induces an exothermic reaction during crystallization, resulting in heat elevation within the solution. Under special conditions, this thermal accumulation affects the nucleation process and hydrate stability, with a portion of the generated heat being mitigated by cavitation and a cooling system. Consequently, to enhance efficiency, ultrasonic irradiation with varying duty cycles is periodically applied. The temperature profiles of the THF/H2O solution at duty cycles (DC) of 70% and 50% are indicated in Figs. 7 and 8, respectively. As shown in Fig. 7, the effect of power on hydrate formation is more pronounced at high power (288W) than at lower levels (72W) with a duty cycle 70%. Furthermore, using a DC 70% helps mitigate excessive heat

accumulation caused by cavitation and continuous wave propagation. Subsequently, the effect of a 50% duty cycle on the formation of ice and hydrate was studied. As shown in Fig. 8, the thermal behaviors differ significantly; with intensities of 72W and 180W demonstrating a notable reduction in nucleation time, whereas the 288W settings showed negligible improvement.

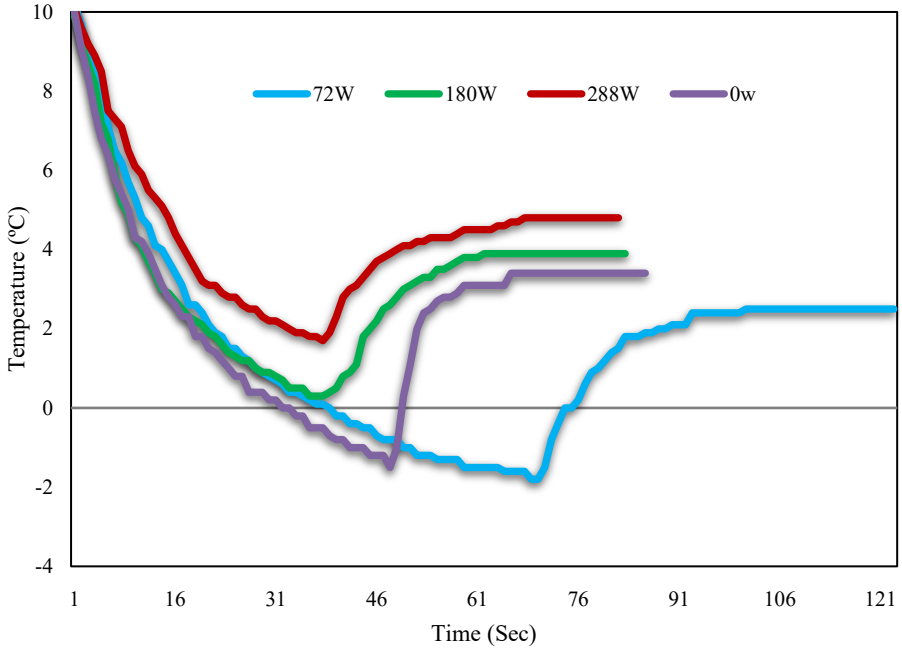


Figure 7. Temperature profiles of THF hydrate formation vs. time at DC 70%.

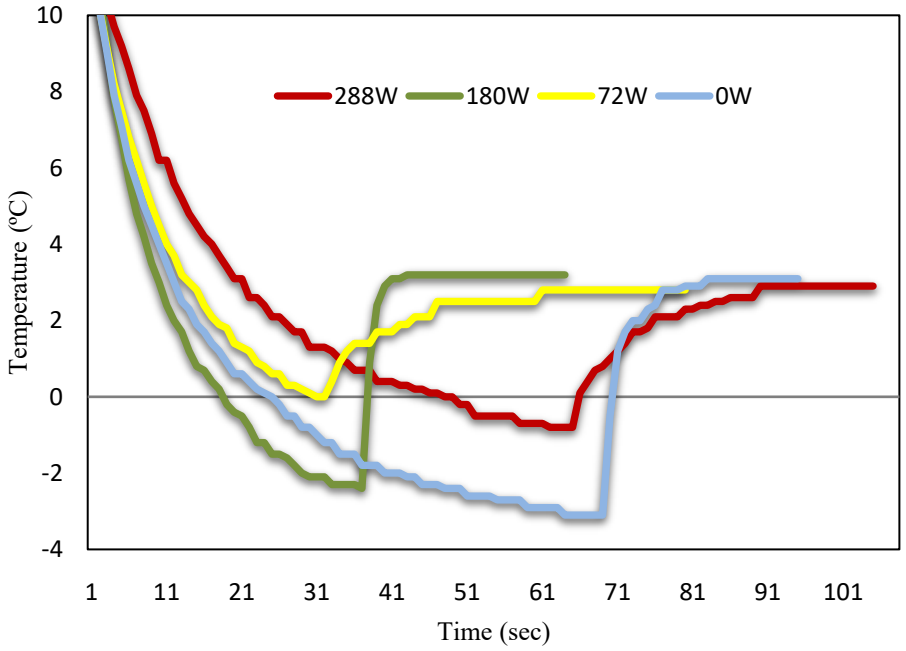


Figure 8. Temperature profiles of THF hydrate formation vs. time at DC 50%.

The induction times associated with the continuous ultrasonic irradiation, with duty cycles of 70% and 50% for hydrate formation, are presented in Fig. 9(a-c). For a better comparison, the relationship between induction time and power level across these different modes is summarized in Fig. 9(d).

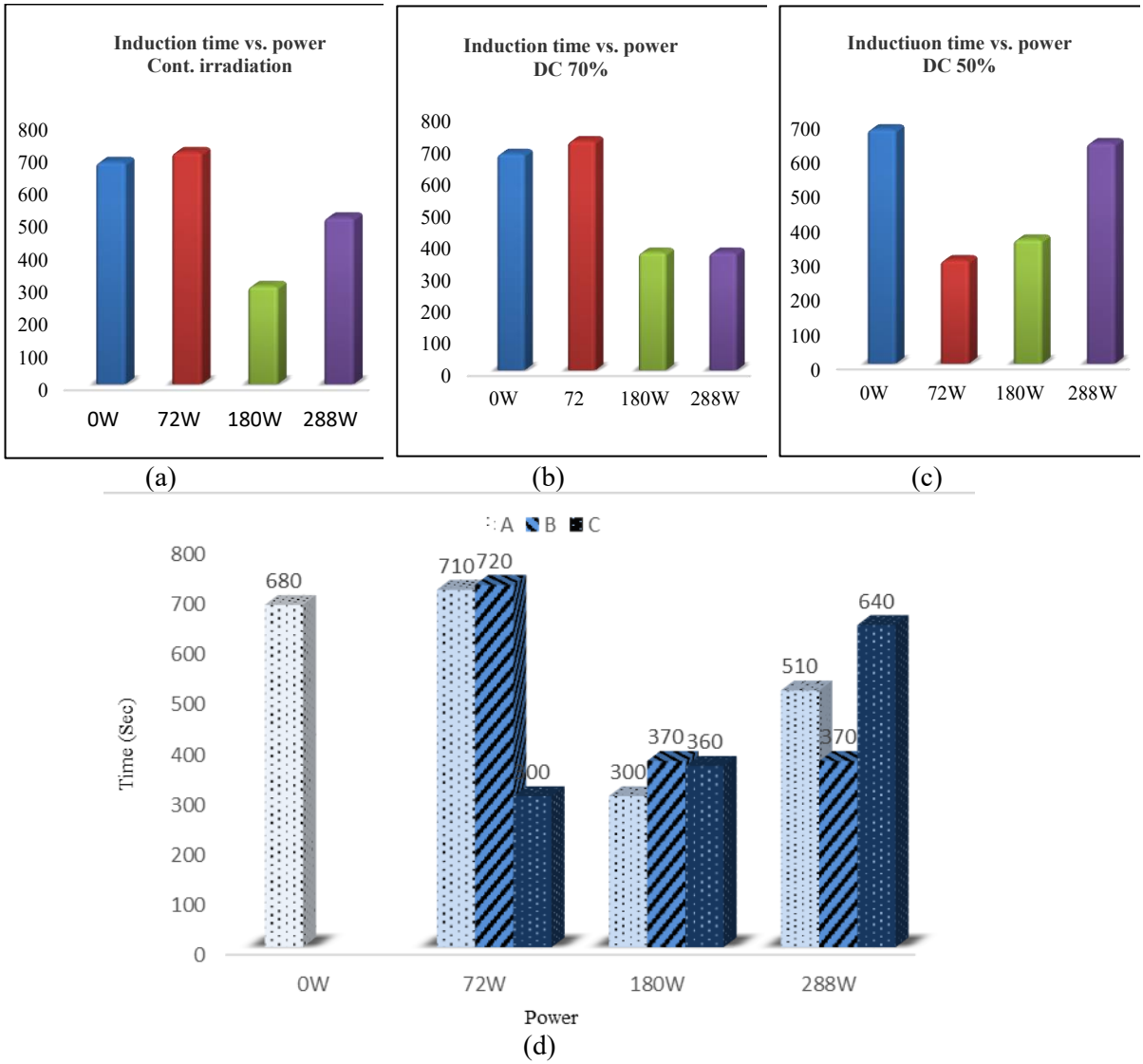


Figure 9. Induction time of THF hydrate formation at all power levels applied.

According to the results shown in Fig. 9, it has been observed that the optimal power was determined to be 180 W. At this ultrasonic power, wave irradiation acts as a promoter for the formation of initial nuclei and the subsequent growth of clusters. Additionally, operating at a DC 70% proved to be highly effective for enhancing the kinetics of hydrate formation. In Figs. 10, 11, and 12, the time and nucleation temperature are compared at power levels of 120W, 300W, and 480W, respectively.

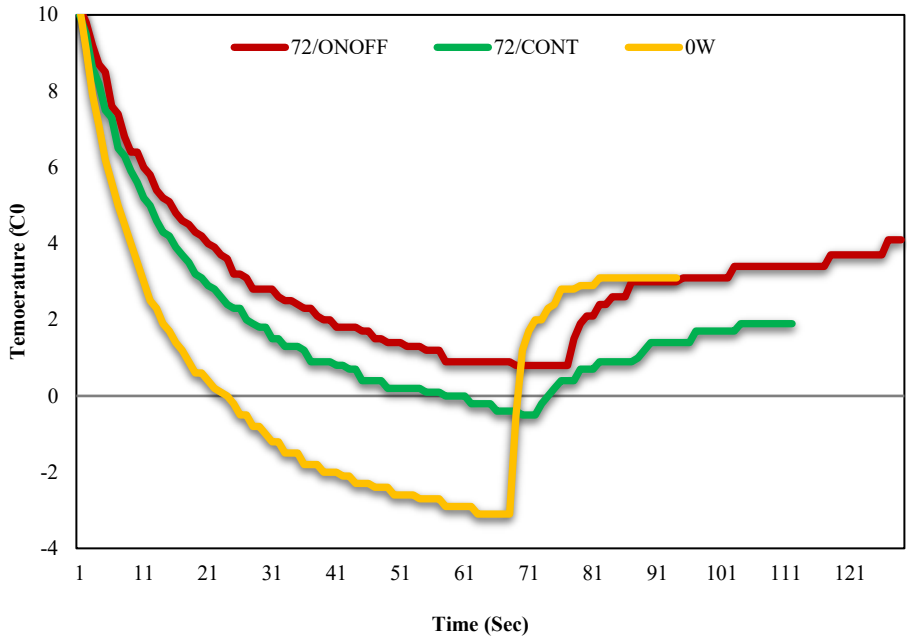


Figure 10. Nucleation temperature of THF hydrate formation at the power of 120W.

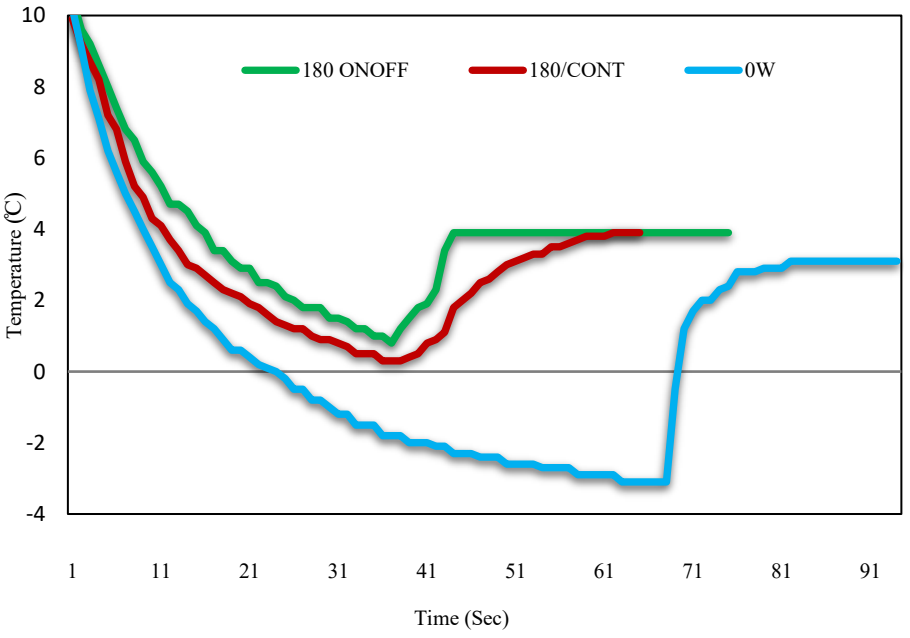


Figure 11. Nucleation temperature of THF hydrate formation at the power of 300W.

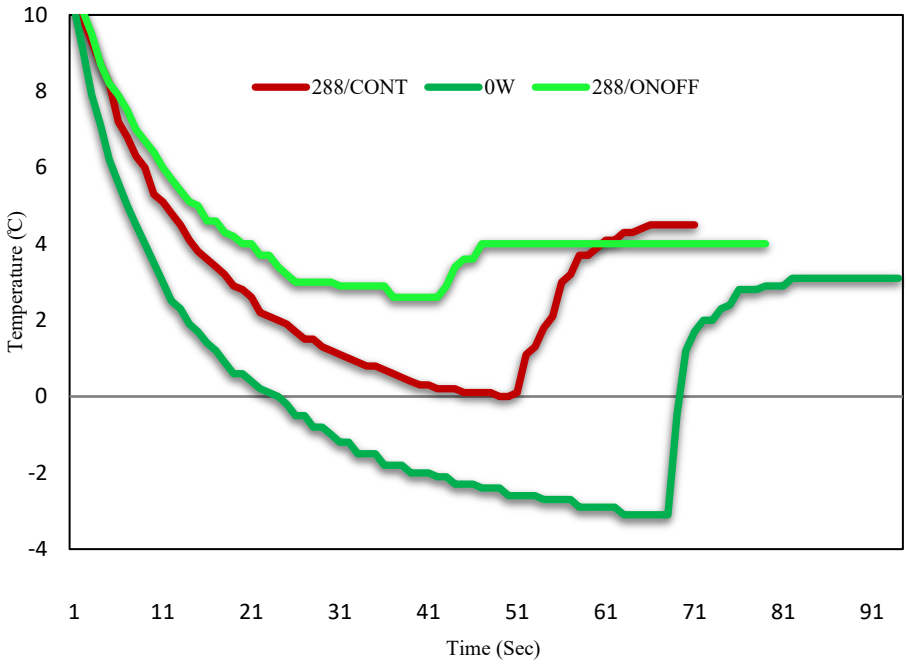
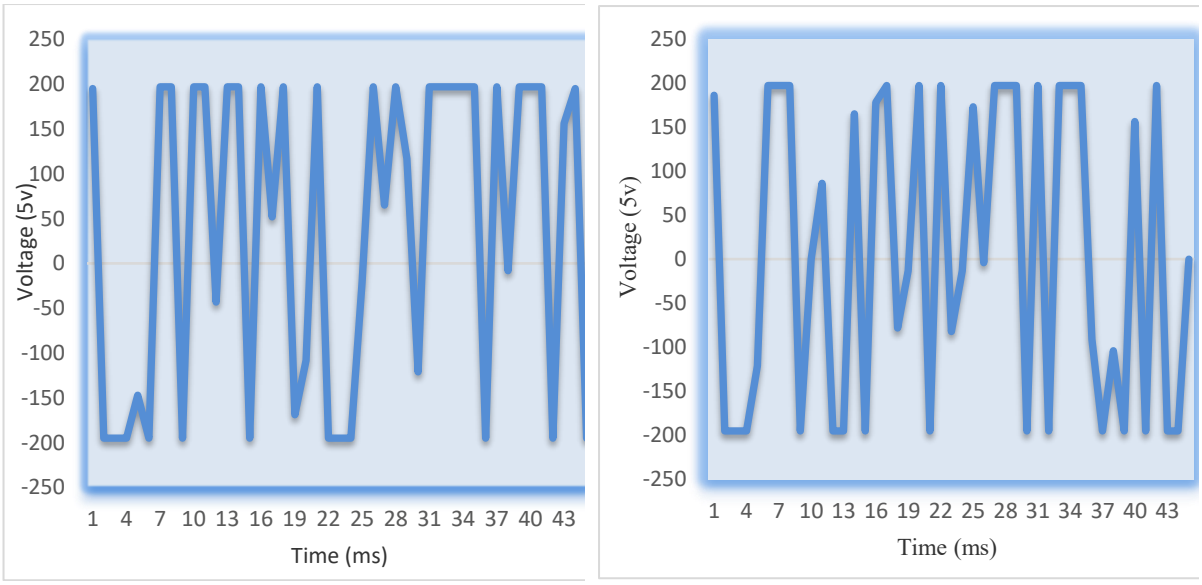


Figure 12. Nucleation temperature of THF hydrate formation at the power of 480W.

Oscilloscope monitoring revealed distinct alterations in the waveform characteristics during the crystallization process. These changes are illustrated in Fig. 13, which shows that the voltage amplitude remains stable before the formation of hydrate and solid phases (Fig. 13a), while attenuated waveforms are evident in figure 13b post-nucleation.



(a) (b)

Figure 13. The waves received by the oscilloscope.

4. Conclusions

In this research, the effect of ultrasonic waves on water freezing and THF hydrate formation was investigated. The effective parameters influencing the hydrate formation include the solution temperature, irradiation time, and ultrasonic power. The experiments were conducted in two parts. Initially, the optimal solution temperature was determined within the temperature range of 6-12℃ under ultrasonic irradiation. The results demonstrated that both freezing and hydrate formation processes were significantly enhanced by the application of ultrasonic waves compared with the conventional method. Consequently, the nucleation temperature for both freezing and hydrate formation increased, while the induction time decreased. When the irradiation temperature was close to the equilibrium temperature of the solution (water or THF), nucleation was initiated. The ultrasonic waves were applied in the power range of 0 to 288W, with the power setting at 180W demonstrating the lowest induction time among other power levels. The use of ultrasonic irradiation during crystallization generates excess heat. To control this additional heat, different duty cycles (50% and 70%) of ultrasonic waves were employed. Irradiation for an appropriate duration at the optimum solution temperature successfully initiated hydrate nucleation. The most effective heat removal was achieved with a duty cycle of 70%.

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