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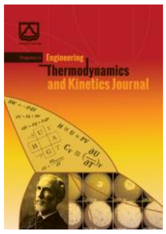

Research Article

The Influence of Ultrasonic Waves on Ice and THF Hydrate Formation

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ABSTRACT

In this work, the influence of ultrasonic waves was investigated on ice and THF/H_2O hydrate formation. The experiments were carried out under ambient pressure, with ultrasonic power ranging from 0 to 288W and irradiation temperature ranging from 6 to 12°C. The effect of the ultrasonic waves with a frequency of 25 kHz was analyzed on the induction time and freezing point. The results indicate that ultrasonic waves increase the nucleation temperature of THF/H_2O solution and decrease the induction time. Likewise, an optimal temperature was selected as irradiation temperature. It was observed that lower temperatures, or the closest temperature to equilibrium temperature of ice (0 ºC) and THF/H_2O hydrate (4.4°C), were considered the most suitable temperature for ultrasonic radiation. At lower power levels of ultrasonic waves, both ice and THF/H_2O hydrate formation were reduced due to prolonged irradiation and extra heat generation. Therefore, ultrasonic irradiation at 50% and 70% duty cycles was employed to mitigate heat generation. Subsequently, it was demonstrated that utilizing ultrasonic waves with a duty cycle of 70% promoted the process of hydrate formation.

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1. Introduction

The crystallization process is a phase change process from liquid or gas to solid. In other words, it considers the formation of solid crystal within a solution. The speed of crystallization is influenced by the saturation degree and density of solution. The parameters including size of nuclei, the crystal morphology, induction time, and initial nucleation temperature are affected by the degree of saturation and ambient conditions [1, 2]. The hydrate

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formation process is similar to the crystallization process. Hydrates are ice-like crystalline structures composed of small molecules (gas or liquid) trapped in an unstable network of water molecules, known as hydrate clathrates. Gases such as Methane, Ethane, Propane, and some refrigerant like Tetrahydrofuran (THF) and Cyclopentane (CP) can form clathrate hydrates. The most important properties of hydrates include high storage capacity, portability, and applications in water desalination [3-11]. Hydrates exhibit various structures, with most liquid hydrate formers such as THF that can adopt structure II. The hydrate formation process involves two steps: nucleation and growth. In the nucleation stage, initial nuclei are invisible with an unarmed eye. As temperature increases and more particles form, the clusters of nuclei become visible and grow. Some hydrate formers are considered as cold storage materials due to their proper phase change temperature, substantial fusion heat, and formation at ambient pressure. This matter makes 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 shown that ultrasonic waves can improve the crystallization process in hydrate formation and water freezing [17]. The use of ultrasonic waves affects the heat transfer coefficient, leading to an increase in the speed of freezing process [18]. During the crystallization process, the application of ultrasonic waves induced bubble formation, creating an acoustic flow in the solution. Cavitation and the collapse of bubbles play an effective role in 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. They reported that ultrasonic was effective on the rate of nucleation and crystal growth [22].

In ultrasonic-assisted crystallization, both irradiation and mass transfer coefficient increase, enhancing the degree saturation of solution [23]. The nucleation process is changed by using ultrasonic irradiation. Likewise, it significantly reduces the super-cooling degree at high intensity [24-26]. Baogou et al. studied the effect 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. When the samples were irradiated at a temperature close to nucleation temperature, ultrasonic waves were effective [28].

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Additionally, ultrasonic waves can enhance fluid collision, prevent crystals agglomeration [29], increase the formation rate, and change the byproducts elimination process in chemical process [30]. Park and Kim studied the influence of ultrasonic waves in the range of 100 to 200W on gas consumption during methane hydrate formation process. Furthermore, increasing hydrate formation and reducing the 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. Due to the application of ultrasonic, the efficiency of food and water freezing was improved. The results showed a linear relationship between 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 the 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 process of crystal formation and growth is the same between hydrate formation and freezing, it is expected that ultrasonic waves have a similar influence on hydrate formation.

Gas hydrate formation or decomposition processes are considered from two points of view, equilibrium thermodynamic and the kinetics of these processes. While some researchers have studied the process of hydrate thermodynamic, the study of the kinetics of hydrate formation and the parameters affecting this process is more considerable. Some liquid hydrate formers such as THF, TBAB (Tetra butyl ammonium bromide), and Cyclopentane can be good alternatives instead of gas hydrates, as they can form structures similar to gas hydrate. For example, nitrogen, as a natural gas hydrate former, can participate in 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.

In this study, the formation of ice and THF hydrate was checked out under atmospheric pressure using ultrasonic waves. 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 improve the nucleation and growth processes. Furthermore, the obtained results were compared with normal crystallization data, and the effect of different irradiation temperatures and powers on the formation process was investigated. Likewise, the optimal conditions

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were identified for both temperature and power of irradiation. 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 system, and a data acquisition system. The reactors are constructed from double-walled stainless-steel cells, each equipped with three piezoelectric transducers fixed at the bottom of each cell. These transducers are controlled by the ultrasonic wave generator. The generated waves are transmitted from the bottom of the cell into the solution. To control the solution temperature, a mixture of water and ethylene glycol (50% volumetric) circulates through a thermal jacket. Due to early nucleus formation and heat generation, the temperature of solution increases. Consequently, a cooling system is employed to prevent hydrate dissociation. Thus, two thermometers (K-type) are used to measure the solution temperature at different locations within each cell. The temperature changes over time are recorded every ten seconds by a data logger.

The volume of the cell is approximately 300 cm3. The solution consists of deionized water and THF (in a molar ratio of 1:17), which was used to investigate the impact of ultrasonic waves irradiation on the formation process. To achieve this aim, waves with a frequency of 25 kHz and the powers ranging from 0 to 240W were studied during both the freezing and the hydrate formation processes. To maintain consistent conditions, the operating parameters were kept constant throughout both processes. By circulation a mixture of water and ethylene glycol (-10 ˚C), the initial solution temperature (20˚C) was lowered. Subsequently, the induction time was recorded by applying the ultrasonic waves at desired temperatures (12, 10, 8, and 6 ˚C).

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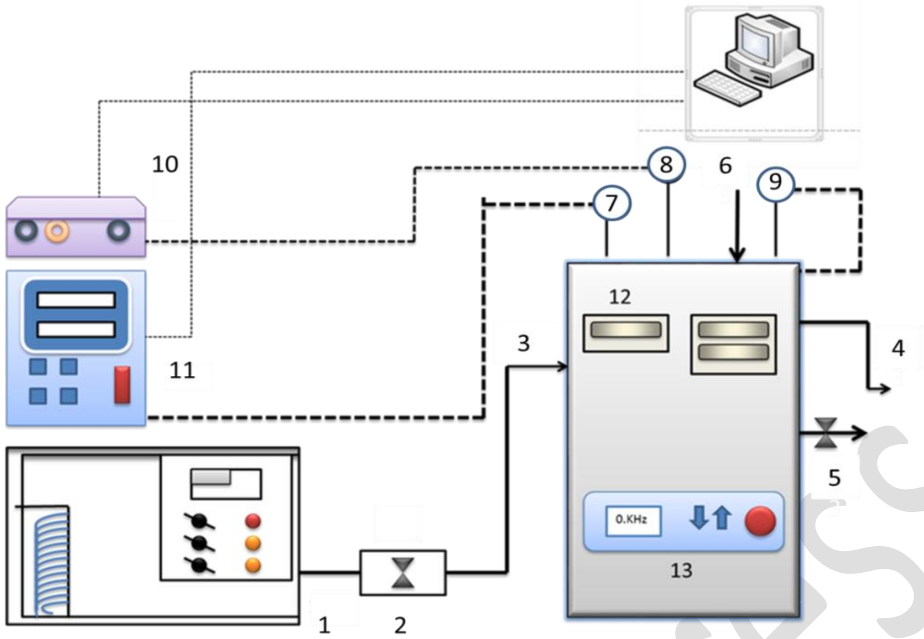

Figure 1. Schematic of experimental setup 1. Cooling system, 2, Coolant pump, 3. Coolant input, 4: Coolant output, 5. Vent, 6. Entrance, 7. Thermocouples, 8. Hydrophone, 9. Thermocouples 10. Oscilloscope, 11. Data logger, 12. Display temperature, 13. Display frequency and power.

2.2. Apparatus II

The setup was configured to enhance the uniformity of output power in the cell and investigate the effects of wave irradiation duration on nuclei temperature and induction time. The schematic of this configuration is shown in Fig 2. This device consists of three double-layer stainless steel cells, each with a volume of 100 cm3. At the bottom of each cell, a piezoelectric is mounted to generate ultrasonic waves. The power of the ultrasonic waves was adjustable by the generator within the range of 0 to 480 W. An electrical board was installed between the current electric generator and the piezoelectric transducer to control the duration of wave irradiation. The objective of this modified setup was to improve the repeatability and reproducibility of experimental results across the three reactors operating under the same conditions.

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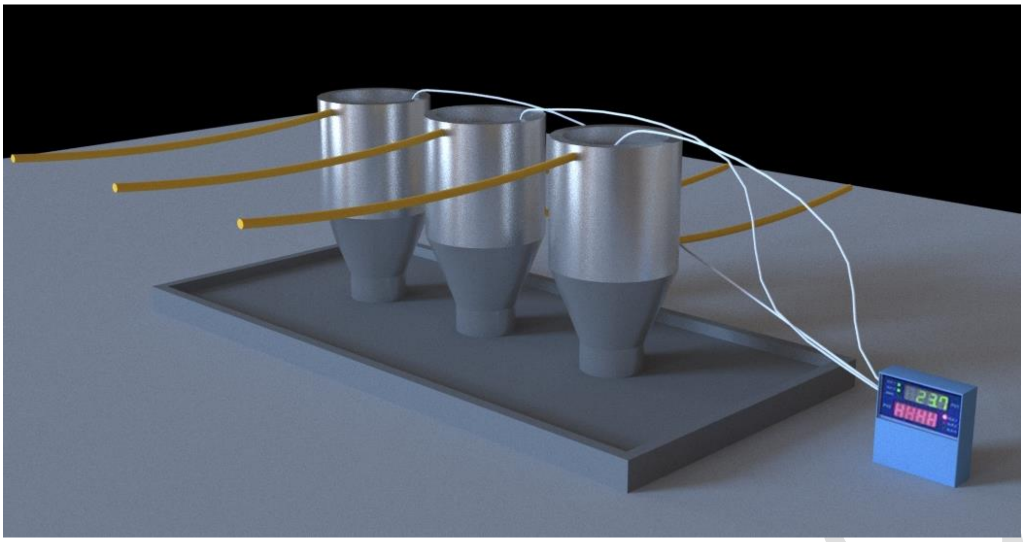

Figure 2. Schematic of ultrasonic setup II, 1. Coolant input, 2. Coolant output, 3. Double layer cells, 4. Piezoelectric, 5. data logger

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. Assisted UL, b. Without UL

The experiments were performed using two different devices to examine the effect of ultrasonic waves on the freezing 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 ultrasonic system at constant power (240W)

Temperature of irradiation (℃)	$T_{induction}$ (℃) HF	$T_{induction}$ (℃) F	T_{max} (℃) HF	T_{max} (℃) F	Time of irradiation(Sec.) HF	Time of irradiation (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 trend of water freezing and hydrate formation at the power of 240W are illustrated in Figs. 4 and 5, respectively. In Figs. 4 and 5, it can be observed that the temperature of the solution increases with the formation of nuclei. This sudden temperature rise is considered as nucleation point. The results indicate that the duration of nucleation varies at different temperatures, with shorter nucleation periods at lower temperatures (6 and 8 ºC). Furthermore, ultrasonic irradiation is observed to enhance both water freezing and hydrate formation.

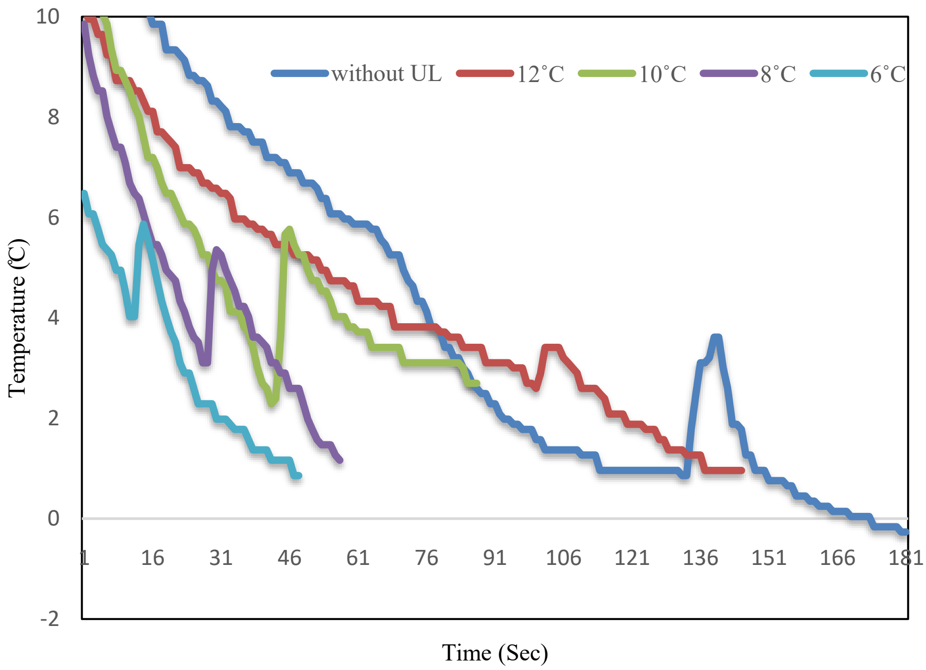

Figure 4. The temperature trend of water freezing (240W)

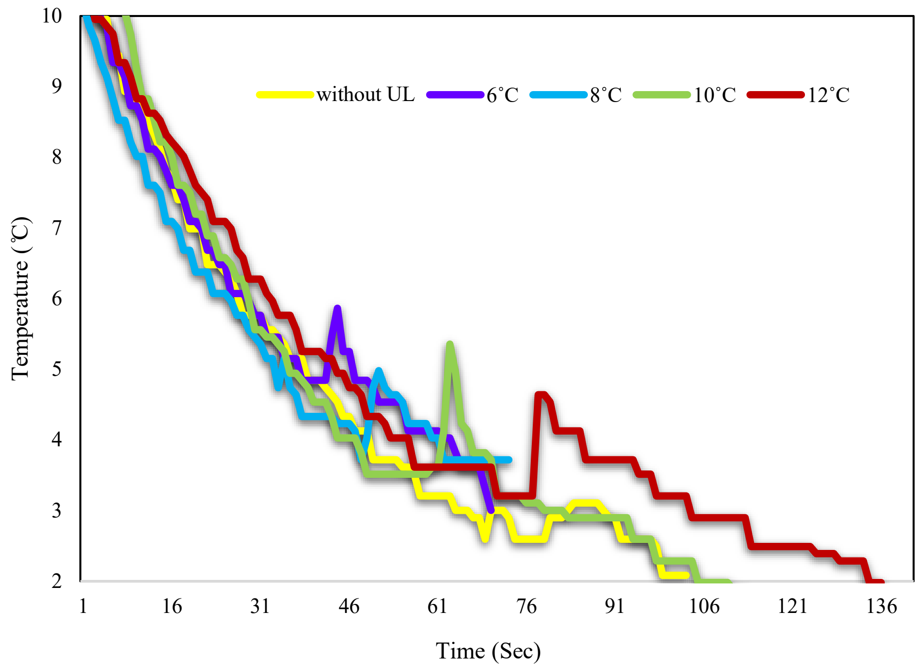

Figure 5. The temperature trend of hydrate formation (240W)

Since the volume of cell is large in the first apparatus, it is not easy to control the temperature uniformity. However, employing different powers of ultrasonic waves and periodic radiation assists in achieving greater temperature uniformity within the solution. As depicted in Fig. 2, three stainless steel cells with transducers located at their bottom part were selected to study the effect of periodic irradiation and transducer power. Additionally, it was shown that the roughness of the cell wall significantly influenced nuclei temperature and formation rate. The freezing behavior and the formation of nucleation differ with the assistance of ultrasonic waves compared to without it. Moreover, adjusting the recycle valve of the refrigerator under optimal conditions can improve the formation process and temperature uniformity. 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 determine of the optimal temperature value. The results and trends depicted in these figures indicate that lower temperature or closest to the equilibrium temperature of ice (0 ºC) and THF (4.4°C), are considered as the optimal temperature when applying ultrasonic waves.

In the second part of the experiments, following the achievement of optimal temperature, the effect of varying power intensities of piezoelectric (continuous intensity) was studied. In Fig. 6, the temperature trend of THF/H2O solution is illustrated at different powers of ultrasonic (including 72W, 180W, and 288W) under continuous irradiation. It was found that the delay between ultrasonic irradiation and the appearance of first nuclei is influenced by the ultrasonic power, while there is no clear correlation between power and delay or nuclei temperature. As seen in Fig. 6, the nucleation temperature during irradiation with a power of 288W is higher than under other conditions, while a power of 180W improves the freezing process and decreases the induction time in hydrate formation. It should be noted that the application of ultrasonic irradiation has improved the hydrate formation process across all power levels.

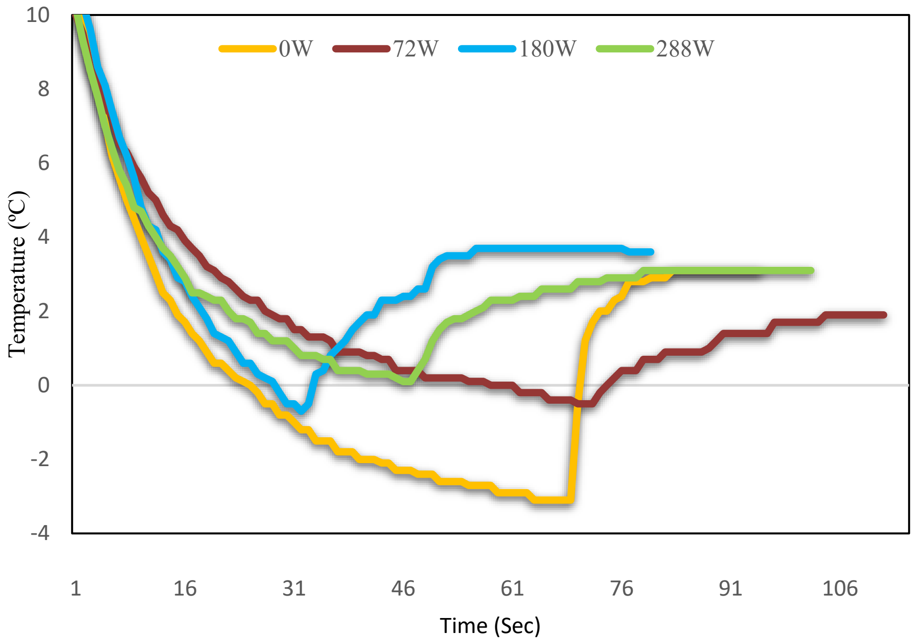

Figure 6. Temperature trend of solution at different powers (Continues irradiation)

It should be mentioned that the continuous flow of ultrasonic waves leads to decomposition and dissociation of hydrate and ice. The application of ultrasonic waves induces an exothermic reaction during the crystallization, resulting in the generation of heat within the solution. Under special conditions, this heat affects the nucleation process and hydrate formation, 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 trends of THF/H2O solution at duty cycles (DC) of 70% and 50% are indicated in Figs. 7 and 8, respectively. In fig. 7, it can be observed that the effect of power on hydrate formation is more pronounced at high power (288W) than at low power (72W) with a duty cycle 70%. Furthermore, the utilizing ultrasonic waves with a DC of 70% can eliminate extra heat, although it may be affected by a cavitation mechanism during this process. Besides, the effect of duty cycle of 50% on the formation of ice and hydrate was studied. As shown in Fig. 8, the temperature trend is significantly different, with powers of 72W and 180W demonstrating a notable effect on reducing nucleation time, while the power of 288W remains unchanged.

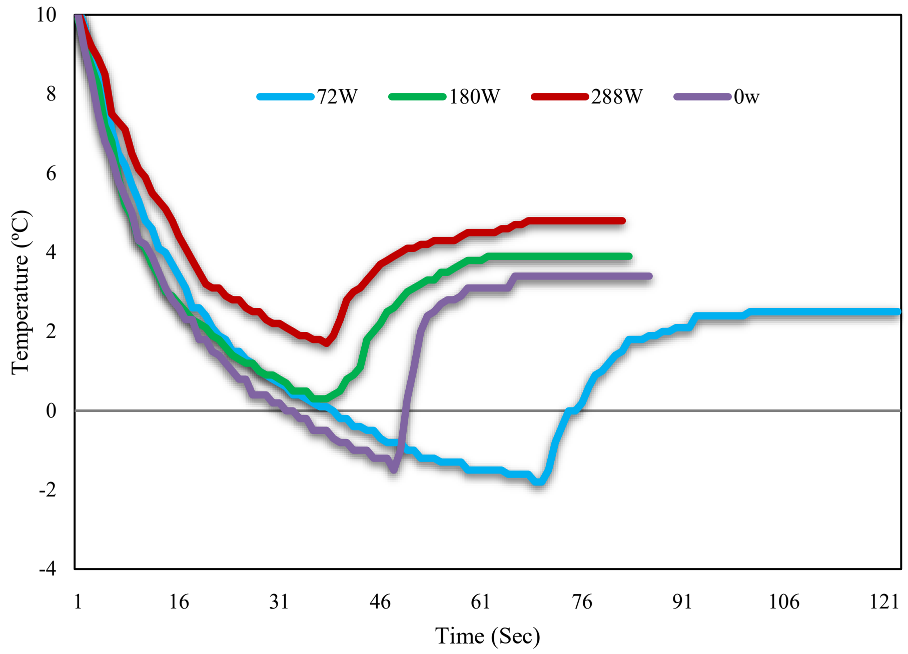

Figure 7. Temperature trend of THF hydrate formation vs. time at DC 70%

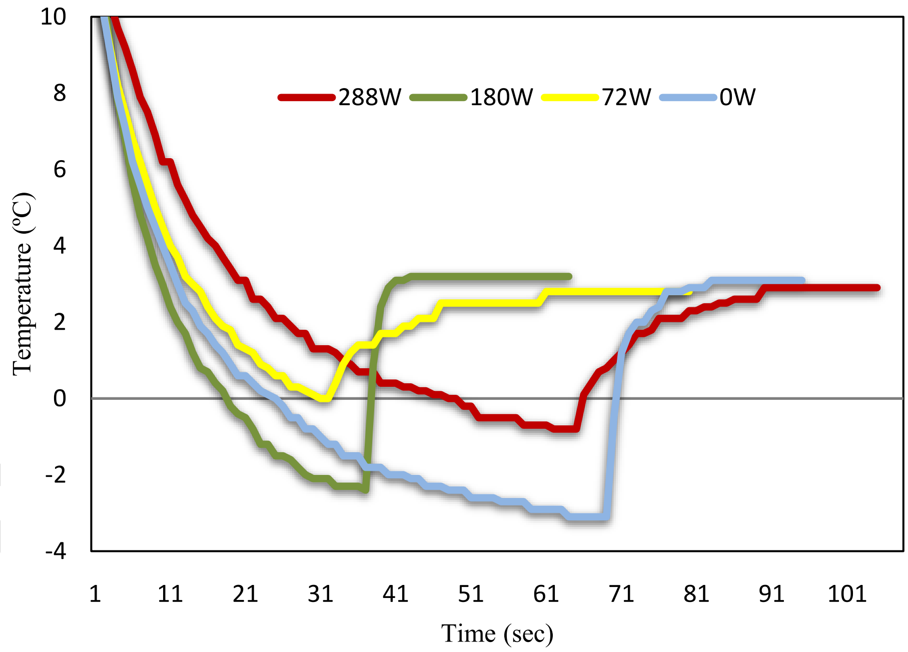

Figure 8. Temperature trend of THF hydrate formation vs. time at DC 50%.

The induction times associated with the continuous ultrasonic irradiation, with duty cycles 70% and 50% for hydrate formation, are reported in Figs. 9 (a-c), respectively. For better comparison, the relationship between induction time and power is illustrated at various states in Fig. 9d.

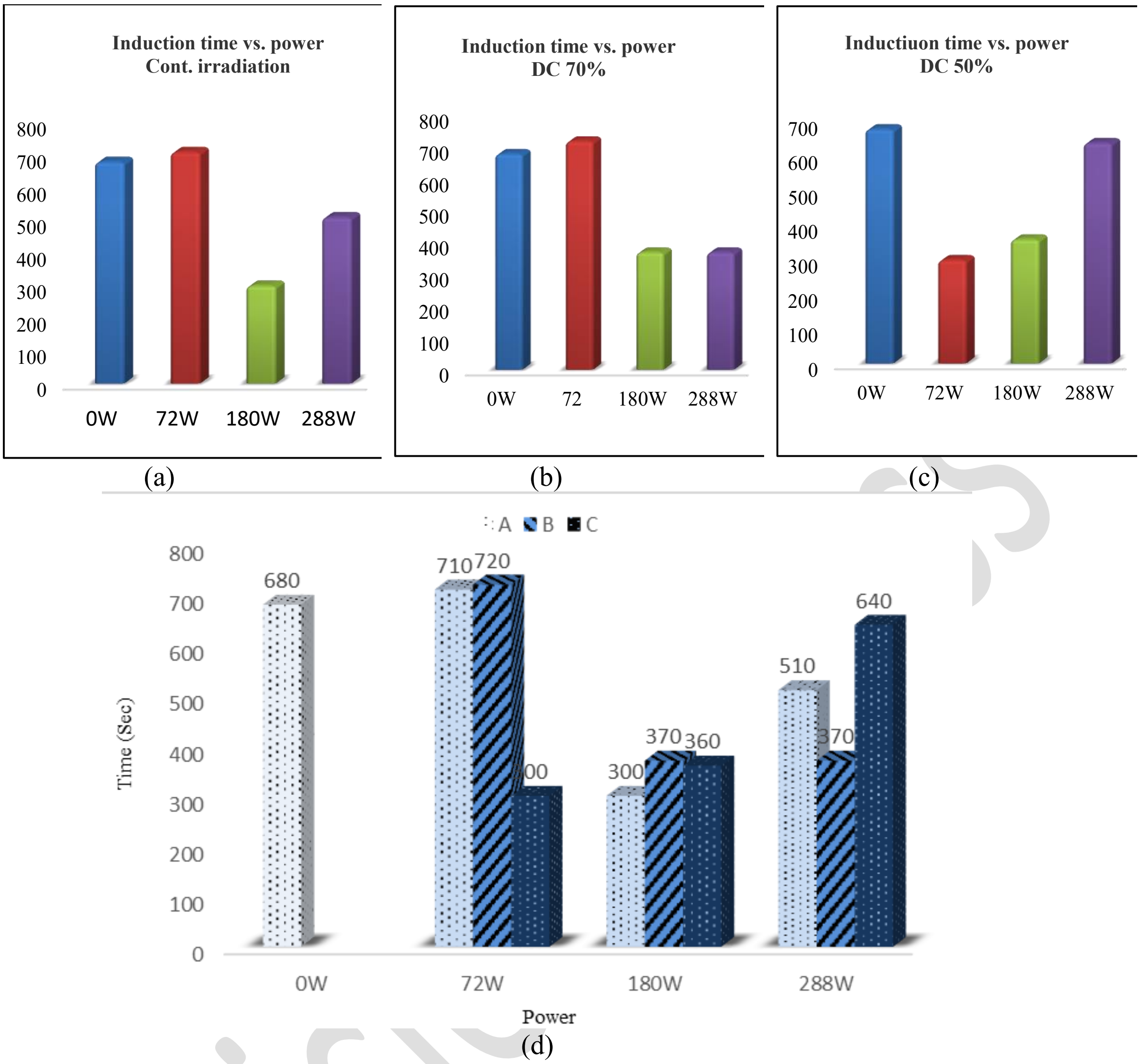

Figure 9. Induction time of THF hydrate formation at all power applied

According to the results shown in Fig. 9, it has been observed that the optimal power is 180 W. At this ultrasonic power, wave irradiation acts as a nucleation promoter at the formation of initial nucleation and growth of clusters. Additionally, utilizing ultrasonic with a DC 70% proved to be an effective choice for improving the kinetics of hydrate formation. In Figs. 10 to 12, time and nucleation temperature have been compared for the powers of 120W, 300W and 480W, respectively.

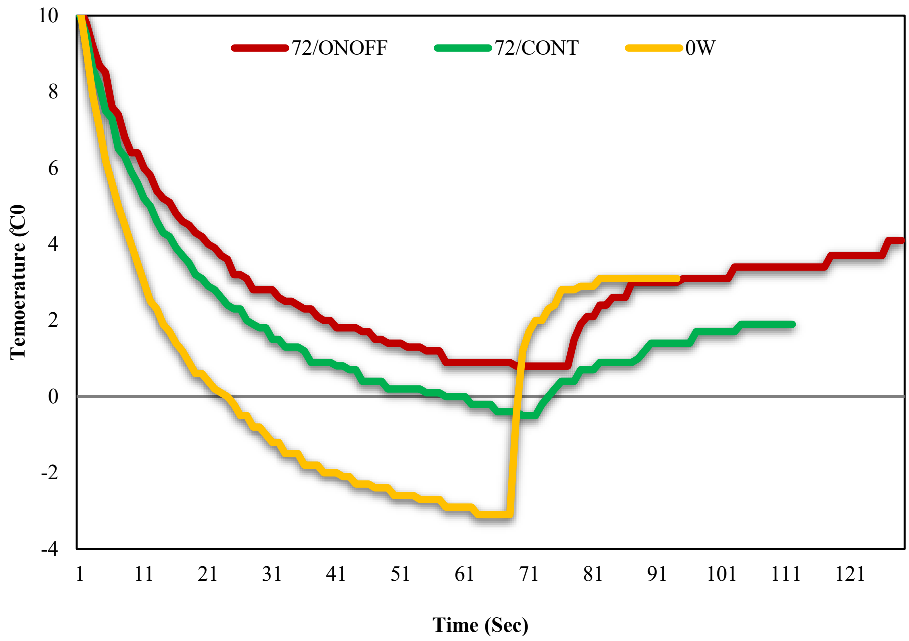

Figure 10. Nucleation temperature of THF hydrate formation at the power of 120W.

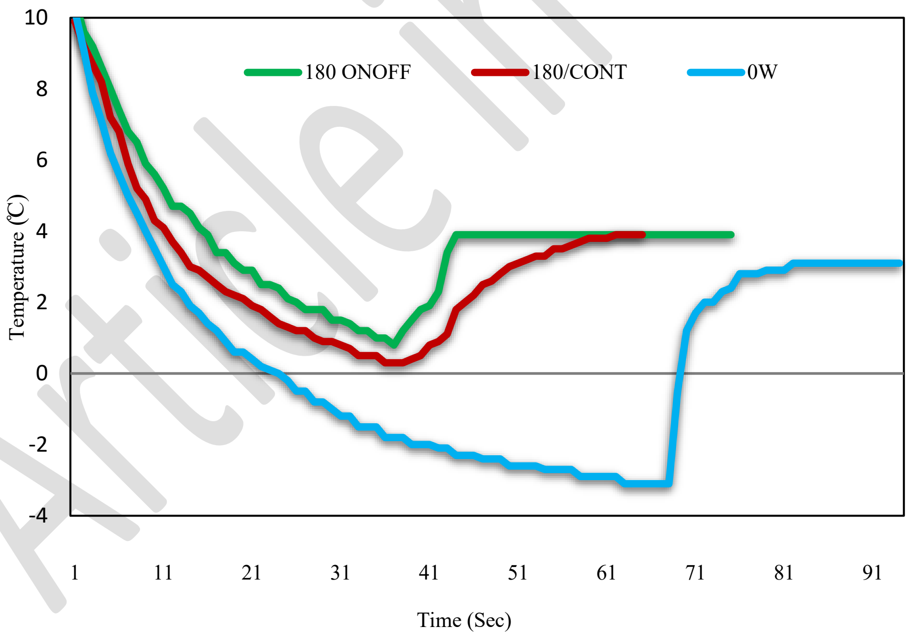

Figure 11. Nucleation temperature of THF hydrate formation at the power of 300W.

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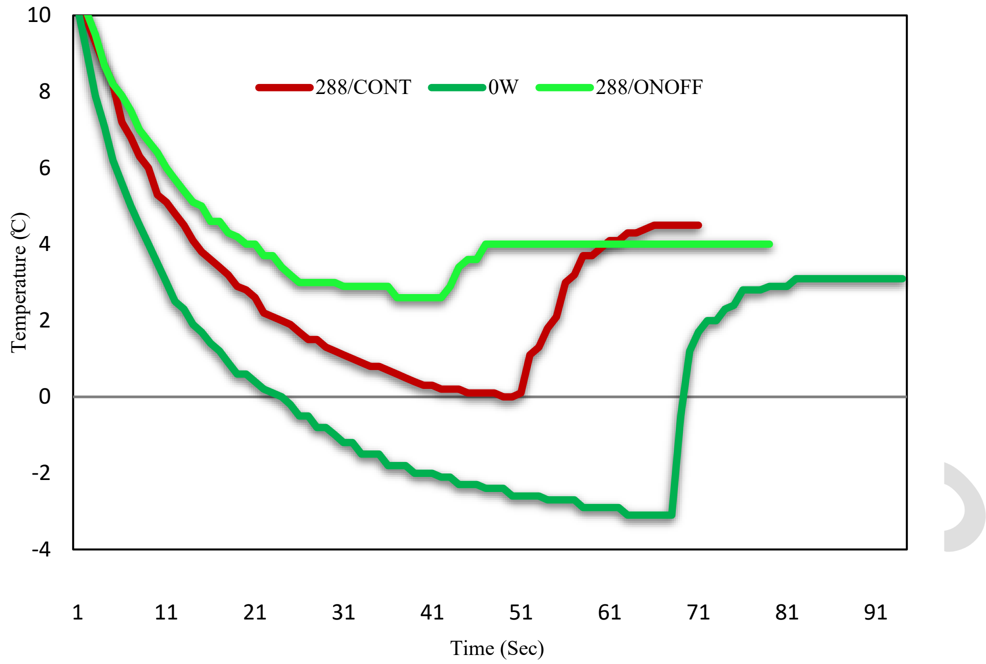

Figure 12. Nucleation temperature of THF hydrate formation at the power of 480W.

When the oscilloscope received the waves, it was observed that their appearance changed during crystallization. These changes have been illustrated in Fig. 13. In Fig. 13a, voltage changes remain uniform until hydrate and solid phases are formed, while shorter waves can be observed in Fig. 13b.

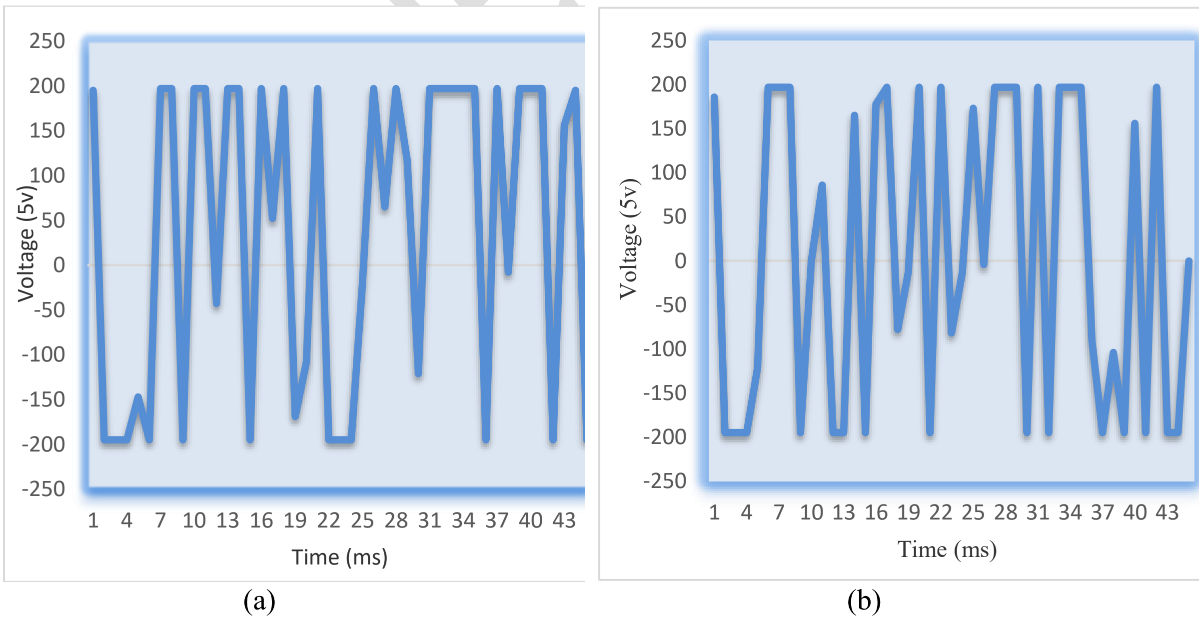

Figure 13. The waves received by oscilloscope.

5. 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 ℃ when applying the ultrasonic waves. Results were demonstrated that the freezing and hydrate formation processes were enhanced significantly with the use of ultrasonic waves compared to the non-ultrasonic method. As a result, the nucleation temperature for both freezing and hydrate formation were increased, while the induction time was decreased. When irradiation temperature is close to the equilibrium temperature of the solution (water or THF), nucleation initiation was occurred. 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 considered. Selecting an appropriate period of time at an optimum solution temperature was initiated hydrate nucleation. The most effective heat removal was achieved with a duty cycle of 70%.

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