

The Influence of Cereal Dextrin on the Conversion and Hydrate Volume Fraction of Methane Hydrate

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ABSTRACT – This study investigates the influence of cereal dextrin on two kinetic parameters of methane hydrate formation. Methane hydrate, solid structure formed by gas and water molecules, are gaining attention for its energy potential and climate regulation. Overcoming challenges like high-pressure requirements, slow formation rates, and economic viability is crucial. The study introduces cereal dextrin as a biodegradable kinetic promoter. In order to explore the influence of cereal dextrin on the formation of gas hydrate, a series of experiments were conducted using a stirred batch cell with a total volume of 169 cm³. The temperature of the cell was carefully controlled at 275.15 K, while the initial pressure was set at 7.5 MPa. Results show dextrin positively influences water to hydrate conversion (WHC) and hydrate volume fraction (HVF). After 100 minutes of hydrate growth, 1% dextrin increases WHC by 150.5% and HVF by 127.8%. The findings suggest dextrin, at 1 wt%, is an optimal concentration for enhancing the kinetics of methane hydrate formation, offering potential applications in energy and environmental fields.

KEYWORDS: Clathrate hydrates; Energy; Cereal Dextrin; Hydrate volume fraction.

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1. INTRODUCTION

Gas (clathrate) hydrates are solid formations resulting from the combination of suitably sized gas molecules and water molecules under relatively mild thermodynamic conditions. These nonstoichiometric ice-like compounds are made up of gas molecules encaged in a network of hydrogen bonded water molecules [1]. Methane, the primary constituent of natural gas, holds significant value as an energy resource. Estimates indicate that the global methane hydrate reserves could surpass conventional natural gas reservoirs. By increasing the global energy demand, gas hydrate exploration and exploitation offers a promising alternative to traditional fossil fuels [2-5]. Additionally, gas hydrates are significant in the global carbon cycle and contribute to climate regulation. Methane is sequestered in hydrate forms, preventing its release into the atmosphere. Comprehending the kinetics and thermodynamics of gas hydrates is fundamental to predict and mitigate the impacts of climate change.

Although gas hydrates have been recognized for decades, their importance is increasingly gaining attention due to their potential impact on energy resources, energy storage, climate change, air conditioning system, and geological processes [6-18]. However, there are several obstacles and challenges that impede the widespread adoption of this technology. It is crucial to understand and overcome these hurdles to unlocking the complete potential of gas hydrates in practical applications. Formation and stability of gas hydrates necessitate high pressure and low temperature. Achieving and maintaining these conditions in industrial settings can be energy-intensive and economically impractical [19-23]. However, the sluggish rate of gas hydrate formation and dissociation imposes constraints its responsiveness to changes in operating conditions. The sluggish rate at which gas hydrates form presents a challenge in customizing gas hydrate applications to meet operational needs. Adapting these applications to specific operational

requirements becomes challenging due to the delayed hydrate formation. The utilization of kinetic and thermodynamic additives (promoters) is one of the most common methods to address this problem. [19, 24-36]. Surfactants, which are an essential type of kinetic promoters, have been widely employed by many researchers in recent years [11, 37-45]. Surfactants are special compounds composed of hydrophilic and hydrophobic groups that can interact at interfaces. Surfactants are categorized as anionic, cationic, nonionic, and amphoteric based on their charges. Anionic surfactants such as sulfates and sulfonates bear a negative charge. Cationic surfactants, such as quaternary ammonium compounds, are positively charged. Nonionic surfactants, such as ethoxylated compounds, have no charge. Amphoteric surfactants have both positive and negative charges [46].

In 2004, Lin and coworkers demonstrated that 650 ppm SDS promotes the kinetics of methane hydrate formation significantly, leading to a noticeable increase in the amount gas storage capacity (SC) of up to 170 v/v [47]. Fazlali and colleagues (2013) investigated the impact of SDS, HTABr, Brij-58, and their combination on the kinetics of methane hydrate. Their study revealed that the optimal performance in enhancing kinetic parameters was achieved by utilizing 500 ppm of SDS [48]. Du and coworkers explored the influence of various ionic surfactants, including SDS, DAH, DTAC, and DN2Cl, all possessing identical carbon chain lengths, on the kinetics of formed methane hydrate. The study uncovered a hierarchy in surfactant effectiveness for reducing methane hydrate formation induction time: $\text{SDS} > \text{DAH} > \text{DN2Cl}$. Moreover, they showed that the influence of DTAC on the kinetics of formed hydrate was insignificant [49]. Researchers also employ various materials as kinetic additives, including carbon nanotubes [50], activated carbon [51], graphene [52-54], porous media [55], metal nanoparticles [33, 56], and etc.

Recently, the simultaneous effect of kinetic and thermodynamic additives on the kinetics of gas

hydrate formation have been studied by some researchers [57-60]. In 2022, Bozorgian and coworkers investigate the effect of various concentrations of alkyl polyglycoside (APG), aluminum oxide nanoparticles, and tetra-n-butyl ammonium chloride (TBAC) on the storage capacity of carbon dioxide hydrate formation. They found that all tested additives promote the kinetics of carbon dioxide hydrate formation, considerably [58].

The aim of this research is to examine the influence of a biodegradable compound, cereal dextrin, on two crucial kinetic parameters associated with growth of methane hydrate: the conversion percentage of water to hydrate (WHC) and the hydrate volume fraction (HVF).

2. EXPERIMENTAL

2.1. Materials

For the hydrate formation experiments, we utilized double-distilled water as the main solvent. The methane gas employed in these trials was obtained from Kavian Gas Company and had a purity level of 99.95%. The cereal dextrin, sourced from Sigma-Aldrich, was obtained with a purity of 97 wt%.

2.2. Apparatus and Procedure

A comprehensive description of the experimental apparatus can be found in our previously published papers [61, 62]. Figure 1 illustrates a photograph of the hydrate formation apparatus utilized in this research.

Figure 1

At the start of each kinetic hydrate formation experiment, the reactor undergoes a cleaning procedure using distilled water. Subsequently, the interior of the reactor is purged of air using a vacuum pump, and 25 cm³ of the solution is introduced into the cell. The reactor's temperature is precisely set to 275.15 Kelvin using a temperature bath. Methane, the hydrate-forming gas in this instance, is introduced into the cell until the desired pressure is achieved. Following this, the electromotor is activated and adjusted to a speed of 10 rpm. The quantification of gas uptake is achieved using the PR EOS [63]. Throughout the hydrate formation process, temperature-time and pressure-time data are digitally recorded using a computer.

3. RESULTS AND DISCUSSION

The quantity of WHC is defined as the percentage of injected water that transforms into hydrate. The following equation can be utilized to compute the amount of WHC:

$$\text{WHC} = \frac{\text{HN} \times \Delta n_{\text{g,uptake}}}{n_{\text{w,feed}}} \quad (1)$$

Where HN, $\Delta n_{\text{g,uptake}}$, and $n_{\text{w,feed}}$ denote the hydration number, the quantity of gas uptake, and the quantity of injected solution, respectively.

The hydration number of the formed hydrate with structure sI can be calculated as follows:

$$\text{HN} = \frac{46}{6\theta_{\text{Large}} + 2\theta_{\text{Small}}} \quad (2)$$

The quantity of gas consumed shows the amount of hydrated methane and the following equation can be utilized to compute the amount of consumed gas:

$$\Delta n_{g,\text{uptake}} = n_{g,0} - n_{g,t} \quad (3)$$

Where $n_{g,0}$, and $n_{g,t}$ represent the amount of methane inside the reactor at time $t=0$ and time t , respectively. The instantaneous mole number of gas phase is calculated as follows:

$$n_{g,t} = \frac{P_t V_t}{Z_t R T_t} \quad (4)$$

The difference in molar volumes between formed gas hydrate and liquid phase can alter the volume of gas within the cell. As a result, the volume of gas inside the cell at any given time, denoted as V_t , can be calculated using the following equation:

$$V_t = V_{\text{Reactor}} - V_{\text{Feed.Sol}} + V_{\text{React.Sol}_t} - V_{\text{Hyd}_t} \quad (5)$$

Figure 2 illustrates the influence of dextrin on the evolution of gas volume within the reactor over time during the methane hydrate formation process. As depicted in the figure, the gas volume within the reactor diminishes as the hydrate formation reaction advances. This phenomenon arises from the contrast in molar volumes between the generated hydrate and the aqueous solution. Forming the hydrate, possessing a greater molar volume than the reacted water, leads to a reduction in the total volume occupied by the gas phase.

Figure 2

Upon examining the curves in this figure, it is evident that the use of dextrin results in a reduction in the gas volume within the reactor. This indicates that the application of this degradable additive positively influences the kinetics of the process.

Table 1 provides the WHC over time, both with and without the inclusion of dextrin, throughout the process. These data are graphically represented in Figure 3. As illustrated in Figure 3 and

detailed in Table 1, the incorporation of dextrin at concentrations of 0.5%, 1%, and 3% by weight leads to an elevation in the WHC compared to using pure water.

Table 1

Specifically, after 100 minutes of hydrate growth, the calculated WHC values for pure water, dextrin solution (0.5% wt), dextrin solution (1% wt), and dextrin solution (3% wt) are 28.3%, 35.6%, 70.9%, and 61%, respectively. This indicates that the utilization of 0.5%, 1%, and 3% by weight of dextrin increases the WHC by 25.8%, 150.5%, and 115.5%, respectively, in comparison to using pure water.

Figure 3

The data presented in Table 1 indicate that employing 0.5%, 1%, and 3% by weight of dextrin results in a respective WHC increase of 5.5%, 33.3%, and 11.7% compared to the use of pure water after 600 minutes of hydrate growth. The comparison of different dextrin concentrations on WHC reveals that the optimal concentration of dextrin is 1 wt%.

The hydrate volume fraction (HVF) serves as a kinetic parameter, indicating the proportion of hydrate formed in an aqueous solution. The calculation of HVF is performed using the following equation:

$$\text{HVF} = \frac{V_{\text{Hyd}_t}}{V_{\text{Hyd}_t} + V_{\text{Unreact.Sol}_t}} \quad (6)$$

Figure 4 depicts the impact of dextrin concentrations spanning from 0 to 3 wt% on the hydrate volume fraction (HVF) over time in the process. As illustrated in the figure, the HVF rises as the

hydrate formation reaction progresses. As the formation process advances, the volume of formed hydrate within the reactor increases, while the unreacted solution volume decreases, consequently causing an increase in the HVF.

Figure 4

Table 2 furnishes the hydrate volume fraction (HVF) at specific time points ($t=10, 25, 50, 100, 225, 440,$ and 600 min) during the hydrate growth process, both with and without the incorporation of dextrin. The data presented in Table 2 are visually depicted in Figure 5. As shown in the figure and outlined in Table 2, the introduction of dextrin at concentrations of 0.5%, 1%, and 3% by weight results in an increase in the hydrate volume fraction (HVF) compared to using pure water.

Table 2

After 100 minutes of hydrate growth, the computed hydrate volume fraction (HVF) values for pure water, dextrin solution (0.5% wt), dextrin solution (1% wt), and dextrin solution (3% wt) are 0.331, 0.410, 0.754, and 0.661, respectively. This indicates that the incorporation of 0.5%, 1%, and 3% by weight of dextrin results in an increase in HVF by 23.9%, 127.8%, and 99.7%, respectively, compared to the use of pure water.

Figure 5

4. CONCLUSIONS

In this study we investigated the influence of cereal dextrin on the kinetics of methane hydrate formation, shedding light on its potential applications in energy and environmental domains. The introduction of cereal dextrin as a biodegradable kinetic promoter reveals positive effects on two key kinetic parameters: WHC and HVF. Notably, at a concentration of 1 wt%, dextrin significantly

enhances WHC by 150.5% and HVF by 127.8% after 100 minutes of hydrate growth. These findings emphasize the potential of dextrin as a degradable additive for improving methane hydrate formation kinetics, offering promising avenues for advancements in energy and environmental sectors.

NOMENCLATURE LIST

SYMBOLS

WHC	Water to hydrate conversion
$\Delta n_{g,\text{uptake}}$	Quantity of gas uptake
$n_{w,\text{feed}}$	Quantity of injected solution
HN	Hydration number
P	Pressure
R	Universal gas constant
T	Temperature
V	Volume of the gas phase
Z	Compressibility factor
HVF	Hydrate volume fraction

Greek letters

θ	Fractional occupancy of cavities
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Subscripts

0	Conditions of the cell at time $t=0$
Hyd	Hydrate
Larg	Large cavities
React.Sol	Water reacted
Small	Small cavities
Feed.Sol	The initial condition of the aqueous solution
t	Time t

TABLES

Table 1: The impact of dextrin on the amount of water to hydrate conversion^a over time during the process of methane hydrate formation

System	Conversion at t=10 min	Conversion at t=25 min	Conversion at t=50 min	Conversion at t=100 min	Conversion at t=225 min	Conversion at t=400 min	Conversion at t=600 min
Pure water	1.1	2.7	8.2	28.3	58.9	61.3	61.6
Dextrin 0.5 wt%	2.0	8.7	20.5	35.6	61.2	64.3	64.7
Dextrin 1 wt%	17.3	41.2	66.2	70.9	72.9	82.9	86.4
Dextrin 3 wt%	11.3	14.9	36.3	61.0	65.7	68.6	69.8

^aThe maximum uncertainty in the measured water to hydrate conversion data is expected to be 2.4%.

Table 2: The impact of dextrin on the amount of hydrate volume fraction over time during the process of methane hydrate formation

System	HVF at t=10 min	HVF at t=25 min	HVF at t=50 min	HVF at t=100 min	HVF at t=225 min	HVF at t=400 min	HVF at t=600 min
Pure water	0.012	0.034	0.101	0.331	0.643	0.661	0.667
Dextrin 0.5 wt%	0.023	0.106	0.244	0.410	0.665	0.693	0.697
Dextrin 1 wt%	0.211	0.469	0.711	0.754	0.818	0.859	0.889
Dextrin 3 wt%	0.137	0.181	0.417	0.661	0.707	0.733	0.745

^aThe maximum uncertainty in the measured hydrate volume fraction is expected to be 0.016.

FIGURES

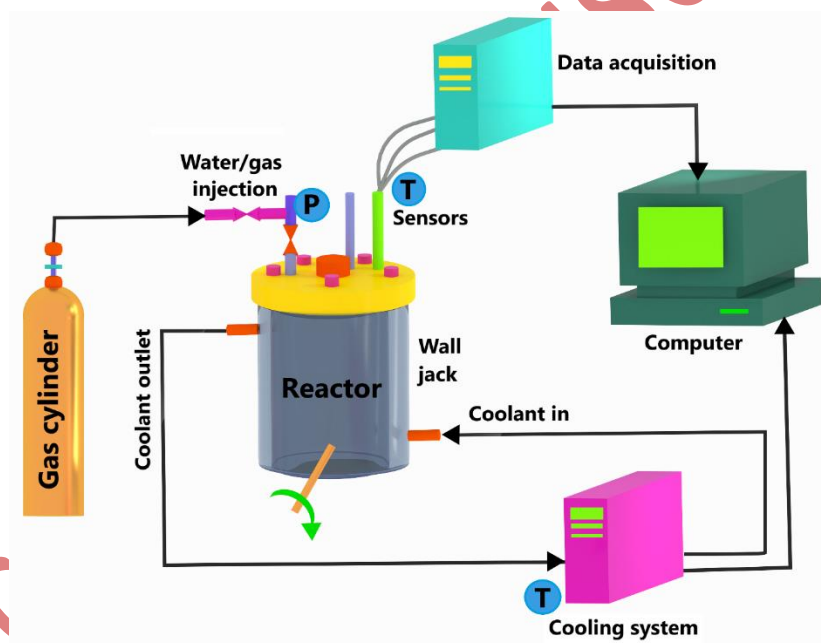


Figure 1: Visual representation of the experimental apparatus [62].

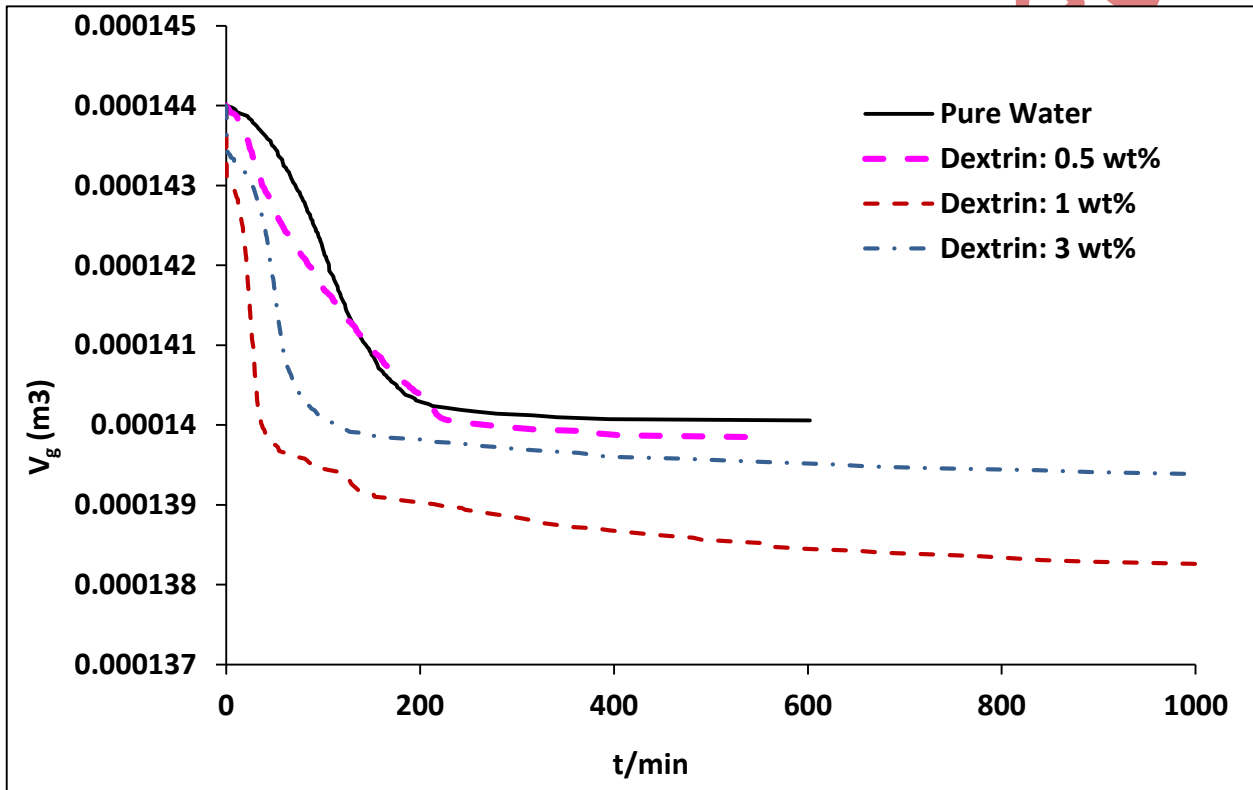


Figure 2: The volume of gas inside the reactor versus time in methane hydrate formation process.

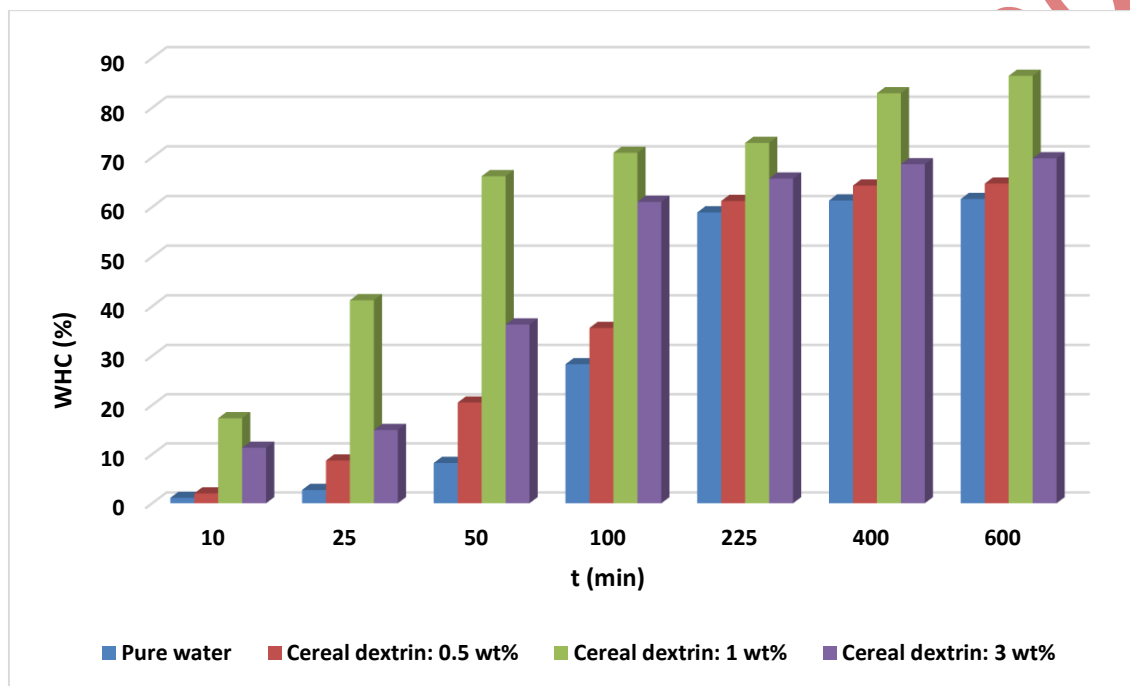


Figure 3: The impact of dextrin on the amount of water to hydrate conversion (WHC) over time during the process of methane hydrate formation

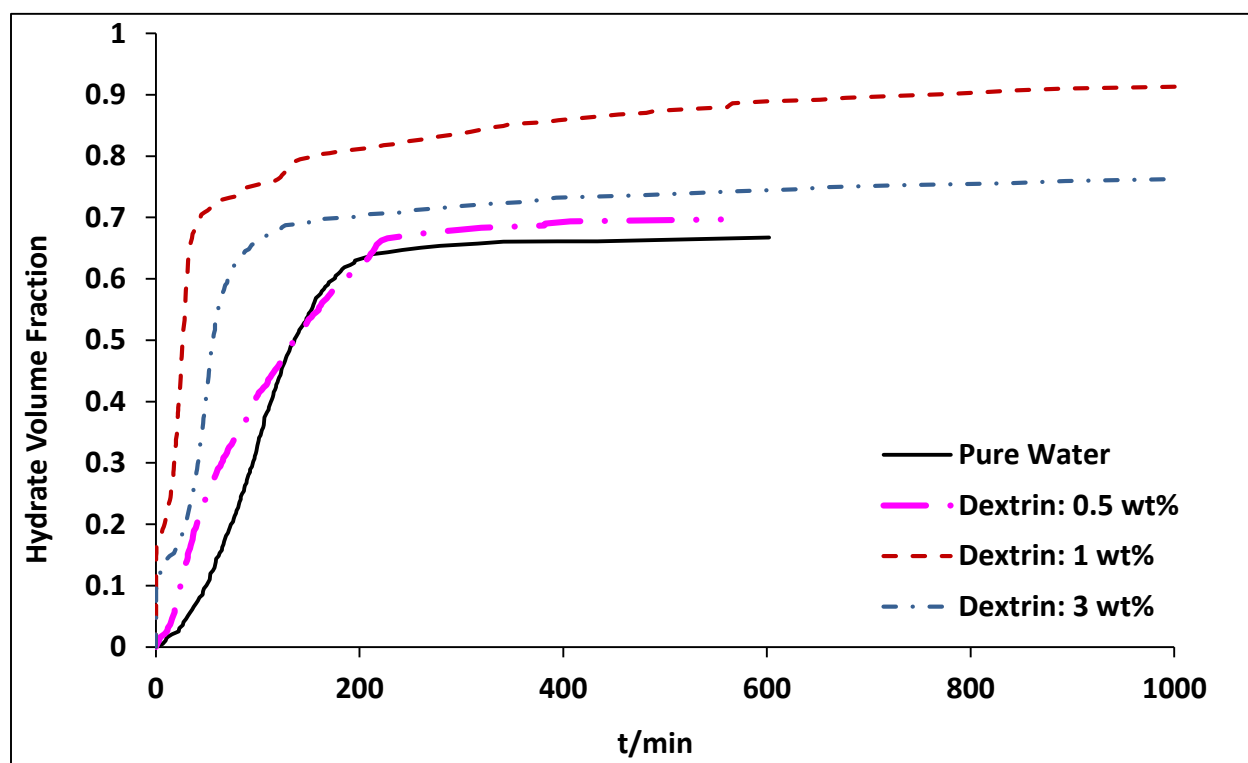


Figure 4: The evolution of the volume fraction of formed hydrates over time during the process of methane hydrate formation

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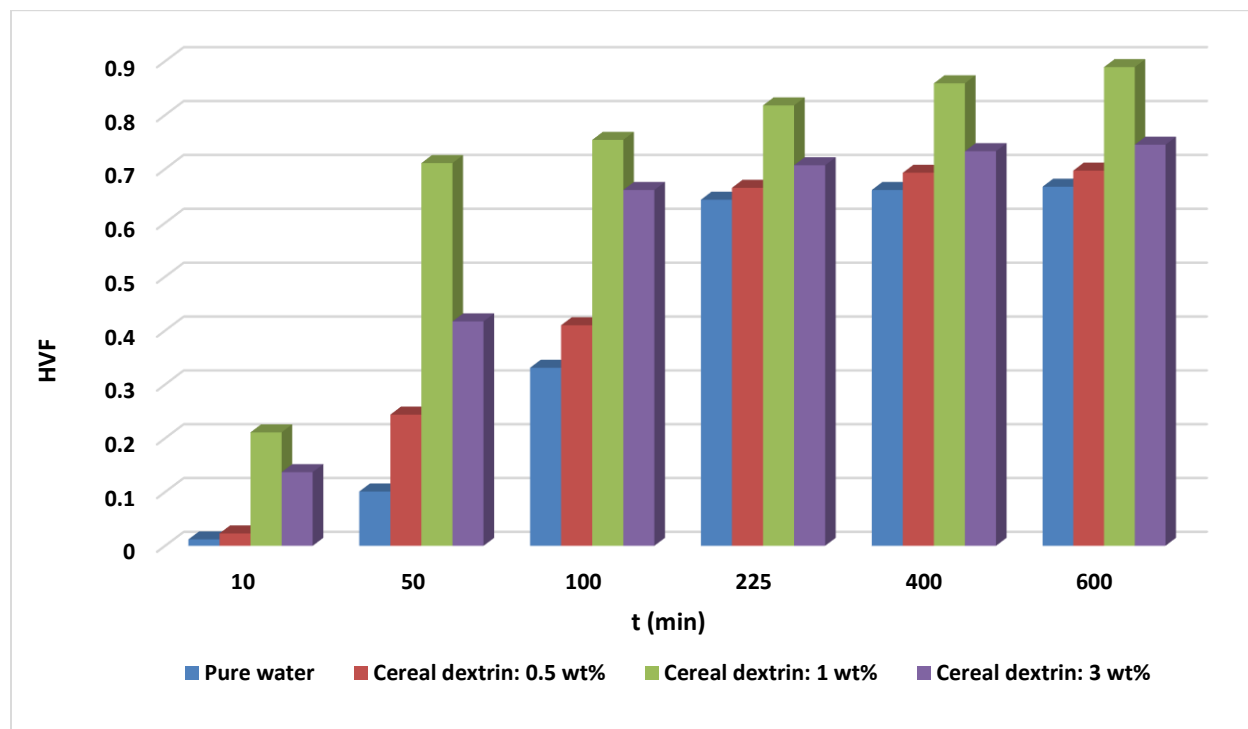


Figure 5: The impact of dextrin on the amount of hydrate volume fraction over time during the process of methane hydrate formation

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