Inhibition and promotion effects of modified HECs and modified starches on the growth rate of hydrate in methane-propane-water system

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A B S T R A C T

This paper investigates the potential of modified hydroxyethyl celluloses (HECs) and modified starches as novel inhibitors and promoters in hydrate formation with methane-propane gas mixture. A series of modified HECs and modified starches were synthesized by graft copolymerization and functionalization techniques. The effects of the HEC, starch, and synthesized products in the concentration range of 0.10 to 0.50 wt% were examined on the growth rate of hydrate crystals. Native HEC, starch, and all grafted copolymers which were synthesized by ceric ammonium nitrate and ammonium persulfate (modified HECs 1 and 2 and modified starches 1 and 2) showed inhibition effects. Interestingly, the modified HEC and modified starch which were produced by graft copolymerization of acrylamide on HEC and starch in the presence of a mixture of ammonium persulfate and sodium bisulfite (modified HEC 3 and modified starch 3), and also the functionalized products (modified HEC 4 and modified starch 4) showed kinetic promoting behavior for methane-propane hydrate formation. In this regard, functionalized products were good promoters such that the hydrate growth rate could be enhanced, even to 3 times higher than pure water. In addition, surface tension and zeta potential measurements showed the more adsorption of modified structures on hydrate crystals can lead to better performance of some modified products. The experimental results also indicated that some products can be applied for the development of new promoters in gas hydrate applications.

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1. Introduction

Gas hydrates are non-stoichiometric crystalline compounds formed when gas molecules are trapped in a hydrogen-bonded framework of water molecules. The cage-like crystalline framework is usually stabilized in presence of small gas molecules (such light hydrocarbons) in low temperature and high pressure. These crystalline compounds are divided into three main types of crystallographic structures including structure I (sI), structure II (sII) and structure H (sH) [1]. Although hydrate formation can cause blockages in gas and petroleum pipelines [2,3] and must be inhibited, but some of its applications such as gas storage and transportation [4,5], air-conditioning and cooling system [6,7], separation of different gases [8,9], concentration of aqueous solution [10], water purification and desalination of seawater [11,12] have led to more studies on promotion of hydrate formation.

The inhibition and promotion of hydrate formation is of importance in the aforementioned fields. In this regard, kinetic additives can be used to decrease or increase of hydrate growth rate. PVP, PVCap, Gaffix VC-

713 and ionic liquids are the most common kinetic inhibitors to reduction of hydrate growth rate [13–17], while anionic surfactants (such as SDS) are well-known kinetic promoters [18,19]. Water soluble polymers are usually used as effective additives. However, application of some polymers is limited due to the poor biodegradability. Therefore, the use of additives with more environmentally friendly and biodegradable properties is of importance [13]. Antifreeze proteins (AFPs) and antifreeze glycoproteins (AFGPs) are a main group of biodegradable additive to slow down hydrate growth [20]. Also, the natural biodegradable polymers such as starch, cellulose derivatives, chitosan, and pectin can be used, although their effects are investigated only in a few literatures. For example, Fakharian et al. [21] studied the effects of potato starch on methane hydrate formation. They found that potato starch as a hydrate promoter can increase the hydrate formation rate in all tested concentrations. Jokandan et al. [22] investigated the synergistic effect of hydroxyethyl cellulose (HEC) when combines with a well-known kinetic inhibitors such as PVP. They observed that the addition of HEC to PVP solution can enhance inhibition efficiency. Xu et al. [23] tested the effects of pectin as inhibitor. They concluded that pectin can successfully inhibit methane hydrate formation. Xu et al. [24] introduced chitosan as green kinetic inhibitor. They investigated the

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inhibition effects of a number of chitosans on methane and methane/ethane hydrate formation. Their results indicated that chitosan was a good kinetic inhibitor.

Although natural biodegradable polymers can be applied for development of new additives, but some problems such as low solubility, high viscosity, and low efficiency can limit their application as additive for hydrate formation. However, chemical modification in natural polymers (such as HEC and soluble starches) can be a practical idea for improvement of their performance as inhibitor or promoter. In this regard, Talaghat [25] applied a modified starch as a kinetic inhibitor. His results showed that oxidized starch can decrease rate of hydrate formation in the presence of different gases such as methane, propane, iso-butane, and CO_2. Also Lee et al. [26] showed that cationic starches can be introduced as gas hydrate kinetic inhibitor. They examined the inhibitory properties of cationic starches in hydrate formation with methane and methane/ethane and methane/propane gas mixtures. They found that starches (except for tapioca starch) exhibit a very weak inhibition effect in hydrate formation with methane/propane gas mixtures. It should be demonstrated that although a number of starches (such as potato starch) was introduced as promoter [21], but with modification, they may show inhibition properties [25,26]. Therefore, with modification of natural biodegradable polymers (such as HEC and starch) the inhibition and promotion effects may be altered. The effects of modified starches are limited to the aforementioned literatures. Unfortunately no report has been dedicated to investigating the effects modified HECs on hydrate formation. Especially when HEC and starch are grafted and functionalized with acrylamide, their effects as promoter or inhibitor is not determined yet in literatures and experimental researches. Therefore, investigation of modified HECs and modified starches (grafted and functionalized with acrylamide) can be useful for development of new inhibitors and promoters.

In this work, the effects of HEC, modified HECs 1, 2, 3, and 4, starch, modified starches 1, 2, 3, and 4 on the growth rate of methane-propane hydrate were investigated. The potential of the tested additives as promoter and inhibitor was determined and ranked based on the rate of gas consumption during hydrate formation, and was evaluated numerically by the average growth rate of hydrate and the obtained kinetic parameter of the chemical affinity model. In addition, the surface tension and zeta potential measurements were performed to analyze of the results.

2. Experimental

2.1. Materials

Analytical grade methane (99.99%), and propane (99.995%) supplied by Technical Gas Services were used to prepare a gas mixture of methane and propane. Also, nitrogen (99.999%) was applied for synthesis. HEC, soluble starch, acrylamide (AM), ceric ammonium nitrate (CAN), ammonium persulfate (APS), sodium bisulfite (SB), and sodium hydroxide were supplied from Merck, Germany. Also, nitric acid, acetic acid, methanol, isopropanol, and acetone were purchased from Neutron Co. Tetrahydrofuran (THF) was also provided from Acros Co. Chemical formula and purity of the components are listed in Table 1.

2.2. Experimental apparatus

The schematic diagram of the apparatus for hydrate formation is shown in Fig. 1, which mainly contains a high-pressure stainless steel cell, a cooling thermostat (Lauda Alpha RA 8, Germany), a gas flowing system, and a data acquisition system. The jacketed cell was designed with the total volume of 650 mL, operated with a maximum working pressure of 60 bar, and equipped with mechanical stirrer. The stirring speed could be adjusted in the range 0 to 1500 rpm with the help of

Table 1
The chemicals used for presented experiments.

Component	Chemical formula	Purity	Supplier
Methane	CH_4	99.99%	Technical Gas Services
Propane	C_3H_8	99.995%	Technical Gas Services
Nitrogen	N_2	99.999%	Technical Gas Services
Starch	$(C_6H_{10}O_5)_n$	GR for analysis	Merck
HEC	–	GR for synthesis	Merck
Acrylamide	$CH_2CHCONH_2$	≥99%	Merck
CAN	$(NH_4)_2[Ce(NO_3)_6]$	≥99%	Merck
APS	$(NH_4)_2S_2O_8$	≥98%	Merck
SB	$NaHSO_3$	≥98%	Merck
Sodium hydroxide	$NaOH$	≥98%	Merck
Nitric acid	HNO_3	65%	Neutron
Acetic acid	CH_3CO_2H	≥99.8%	Neutron
Methanol	CH_3OH	99.9%	Neutron
Isopropanol	$(CH_3)_2CHOH$	99.5%	Neutron
Acetone	CH_3COCH_3	99.0%	Neutron
THF	C_4H_8O	≥99%	Acros
Water	H_2O	Deionized-distilled	Abtin

speed controller. The cell temperature was controlled with water jacket connected to an external cooling bath (Lauda Alpha RA 8 with a working temperature range of 248.15 to 358.15 K). The temperature was measured by a PT100 thermometer with a precision of ± 0.1 K. Also, the cell pressure was measured by a pressure transmitter (with an uncertainty of ± 0.1 bar). The temperatures and pressures were monitored and recorded with the help of a data acquisition system connected to a computer.

The setup for chemical modification of HEC and starch contained a three necked flask under a nitrogen atmosphere. The necked flask was equipped with magnetic stirring bar and immersed in a constant-temperature water bath. Also, a laboratory hot plate with magnetic stirrer was used for heating and stirring of the sample solution. The middle opening of the necked flask was connected to a condenser column. The second opening of three necked flask was connected to a nitrogen line and a vacuum pump. Also, a thermocouple was inserted into the other opening. In addition, a pH meter (with 0.01 pH unit precision) was used to control of pH during reaction and neutralization of products.

Surface tensions of aqueous solutions were measured at 2 °C using a Kruss K100 tensiometer (Kruss GmbH, Germany), which was equipped with a Wilhelmy plate. Also, the zeta potential measurements were performed on the samples using zeta potential analyzer (Zeta Compact CAD, France).

2.3. Experimental procedure for hydrate formation

In all the experiments, the hydrate formation cell was washed and rinsed with de-ionized water for three times and then evacuated by a vacuum pump. Subsequently, 300 mL of water or aqueous test solution was injected into the cell. The cooling bath was turned on, and the temperature was set at 275 K. The cell was pressurized to reach the desired pressure after temperature stabilization at 275 K. Stirring speed was also set to 400 rpm. When the cooled solution was saturated with gas mixtures of methane and propane, the cell pressure was suddenly decreased and a sudden increase in the temperature was observed due to hydrate formation. The pressure changes during hydrate formation were recorded and the moles of gas consumed were measured. Then, the performance of chemicals and synthesized polymers as inhibitor and promoter was evaluated based on the rate of gas consumption during hydrate formation. In addition, the average growth rate when 0.1 mol of gas was enclathrated in hydrate cages, and also kinetic parameter of the chemical affinity model ($-A_r/RT$) were calculated to investigate the effects of additives numerically. The values of $-A_r/RT$ were
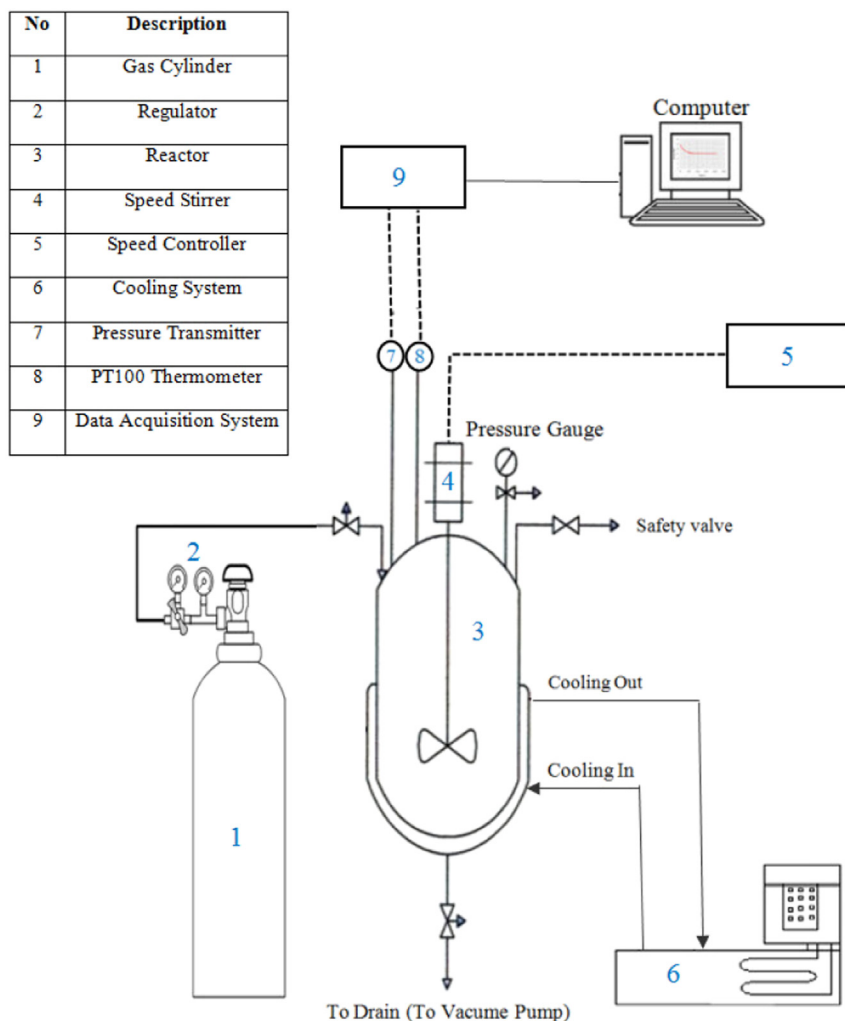
No	Description
1	Gas Cylinder
2	Regulator
3	Reactor
4	Speed Stirrer
5	Speed Controller
6	Cooling System
7	Pressure Transmitter
8	PT100 Thermometer
9	Data Acquisition System

Fig. 1. Schematic of the experimental apparatus for hydrate formation.

calculated based on the following equations and the presented algorithm in the previous work [27].

$$\frac{A_i}{RT} = -\ln \frac{n_{ci}}{n_{cf}} \qquad (1)$$

$$\frac{A_i}{RT} = -\frac{A_r}{RT}\left[-\ln\left(\frac{t_i}{t_k}\exp\left(1-\frac{t_i}{t_k}\right)\right)\right] \qquad (2)$$

$$\frac{n_{ci}}{n_{cf}} = \left[\left(\frac{t_i}{t_k}\exp\left(1-\frac{t_i}{t_k}\right)\right)\right]^{\frac{-A_r}{RT}} \qquad (3)$$

In Eqs. 1–3, n_{ci}, n_{cf}, t_i, t_k, R, T, A_i, and A_r are moles of gas consumed up to time t_i, total moles of consumed gas, time required to reach state i, time required to reach equilibrium conditions, universal gas constant, temperature, the chemical affinity at state i, and kinetic parameter of the chemical affinity model, respectively.

2.4. Synthesis of modified HECs and modified starches

In this work, HEC and starch were modified with acrylamide. Grafting copolymerization of acrylamide (AM) onto HEC and starch was conducted. The reactions were carried out in three different initiator systems, including ceric ammonium nitrate (CAN), ammonium persulfate (APS) and mixture of ammonium persulfate (APS) and sodium bisulfite (SB). Also, HEC and starch were functionalized with acrylamide.

The graft copolymers of polyacrylamide on natural polymers (HEC and starch) were prepared as follows: first, the reaction flask was evacuated and then charged with nitrogen atmosphere. Afterwards, 1.0 g of natural polymers was added to the three necked flask including 30 mL de-ionized water. The flask was immersed in water bath. The magnetic stirrer was turned on and temperature was adjusted at 70 °C and 90 °C for HEC and starch solubilization, respectively. When a homogeneous solution was achieved, a definite amount of initiator was added to homogeneous solutions. In presence of ceric ammonium nitrate as initiator, HEC and starch solutions were first cooled and then 1 mL of a 0.1 M solution of CAN was dissolved in 1 M nitric acid and subsequently was added to homogeneous solutions. Also, the temperature of reaction was maintained at 25 °C, while in presence of ammonium persulfate and mixture of ammonium persulfate and sodium bisulfite, the temperature was adjusted at 70 °C. After adding initiator, 1.0 g acrylamide was added to the solutions, and the reaction was continued with stirring for 120 min. Then reaction product was allowed to cool to room temperature and 200 mL of acetone or methanol were used to precipitate the copolymer. The obtained products were washed 10 times with acetone-water mixture (70:30, v/v) to remove homopolymer. Finally, the pure graft copolymer was washed with pure acetone and dried at 60 °C in an oven.

On the other hand, HEC and starch were also functionalized with acrylamide according to following method. First, 1.0 g HEC was dissolved
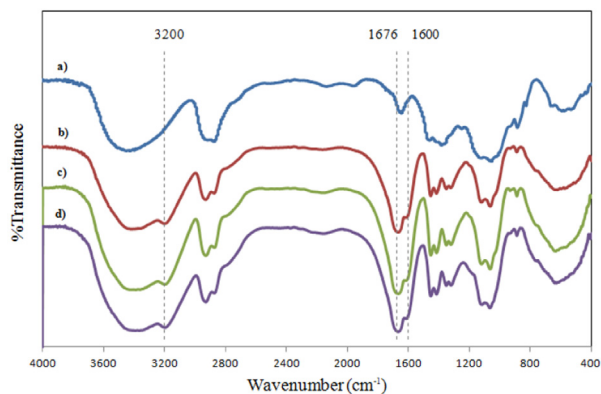
Fig. 2. (a) FTIR spectra of native HEC, (b) HEC-g-AM by CAN, (c) HEC-g-AM with the help of AP, (d) HEC-g-AM with the mixture of APS and SB.

Fig. 4. Gas consumption versus time during the hydrate formation in the presence of HEC.

in 30 mL water. It must be demonstrated that for starch modification, the reaction was performed in water-isopropanol medium (2:3 v/v). The solutions were heated to 75 °C. Then an aqueous solution of sodium hydroxide was added to the HEC and starch solutions. Subsequently, 2.0 g acrylamide was added to the flask, and the reaction was continued under stirring for 2 h. Afterwards, the reaction mixtures were neutralized by addition of diluted alcoholic acetic acid solution. The neutralization was controlled by a pH meter. Finally, the reaction mixture was precipitated in acetone, filtered and dried in an oven at 50 °C.

3. Results and discussion

3.1. Molecular structures of modified HECs and modified starches

FTIR technique was used for investigation of molecular structures of modified HECs and modified starches. Fig. 2 shows the FTIR spectrum of HEC, produced HEC-g-AM by CAN, obtained HEC-g-AM with the help of AP, and produced HEC-g-AM with the mixture of APS and SB. The FTIR results for HEC show a strong absorption between 3000 and 3800 cm^{-1} due to hydroxyl stretching vibration, while the FTIR results of grafted copolymers show a new peak in this range (3200 cm^{-1}) that corresponds to association of —NH$_2$ and —OH groups. In fact, this peak confirms the existence of the grafted copolymer. On the other hand, comparing the FTIR spectra of HEC with graft copolymers also shows other major changes. Two new peaks are observed at 1676 and 1600 cm^{-1}, which according to the reports of other researchers are evidences for the presence of acrylamide on cellulose derivatives such as HEC. Similarly, Fig. 3 shows three major peaks (3200, 1676, and
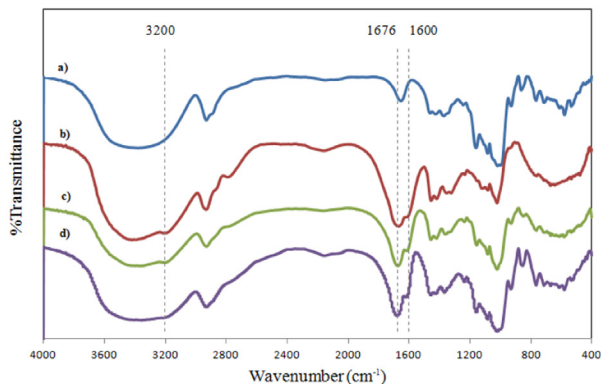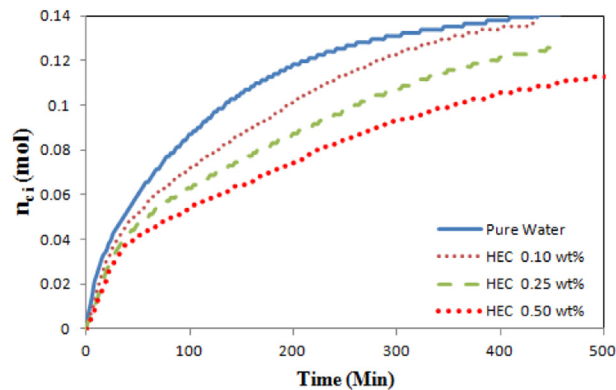
1600 cm^{-1}) in modified starch which confirms the grafting of polyacrylamide onto the soluble starch. Also, the results of FTIR show that when starch and HEC were functionalized with acrylamide, two new peaks at 1676, and 1600 cm^{-1} are observed.

3.2. The effects of HEC and starch on growth rate of gas hydrate in methane-propane-water system

In this work, a gas mixture containing 85 mol% methane and 15 mol% propane was used for hydrate formation. First, the effects of HEC on the growth rate of hydrate were investigated in concentrations of 0.10, 0.25, and 0.50 wt%. Fig. 4 shows that the rate of gas consumption during hydrate formation in the presence of HEC is decreased in comparison to pure water. In the other words, HEC has showed an inhibition effect. Also, it is observed that with the increase of concentration, the inhibition effect is enhanced. For better investigation of the effects of additives, the average rate of hydrate growth and kinetic parameter of the chemical affinity model ($-A_r/RT$) were calculated. Table 2 shows that when the concentration is increased from 0.10 to 0.50 wt%, the growth rate of hydrate is decreased from 0.52 to 0.28 (mmol/min). Also, the value of $-A_r/RT$ is reduced from 0.659 to 0.608 and confirms the reduction in the growth rate during the total time of hydrate formation. The experiments were repeated with starch. The results in Fig. 5 and Table 2 indicate that starch has a weak inhibition effect on the rate of gas hydrate formation. While in the literatures potato starch was as a good promoter and cationic starches were introduced as inhibitors. This notes that the modified starch may be more effective on hydrate formation. In addition, Table 2 shows that the inhibition effect of HEC is very significant in comparison to starch. Unfortunately, the effect of HEC on the growth rate of gas hydrates is not yet reported in literatures, and only its effect as synergist for the well-known inhibitors was tested. Therefore, more investigation on the effects of modified HECs may lead to interesting and new findings.

Fig. 3. (a) FTIR spectra of native starch, (b) starch-g-AM by CAN, (c) starch-g-AM with the help of AP, (d) starch-g-AM with the mixture of APS and SB.

Table 2
The obtained kinetic parameters for investigation of hydrate growth rate in the presences of HEC and starch.

Additives	Concentration (wt%)	Average growth rate (mmol/min)	$-A_r/RT$
Pure	–	0.75	0.697
HEC	0.10	0.52	0.659
HEC	0.25	0.38	0.620
HEC	0.50	0.28	0.608
Starch	0.10	0.74	0.693
Starch	0.25	0.70	0.687
Starch	0.50	0.66	0.664
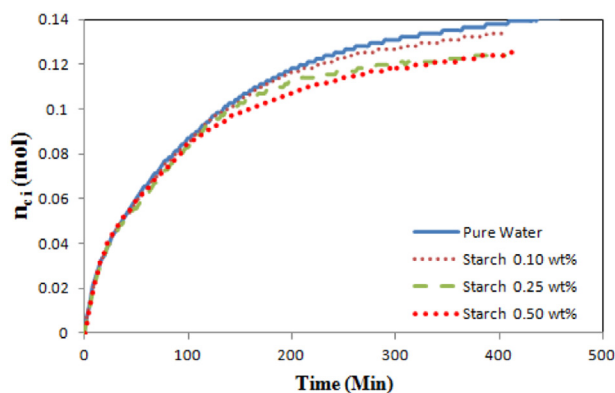
Fig. 5. Gas consumption versus time during the hydrate formation in the presence of starch.

Table 3
The calculated kinetic parameters for investigation of hydrate growth rate in the presences of modified HECs.

Additives	Concentration (wt%)	Average growth rate $-A_r/RT$ (mmol/min)	
Modified HEC 1	0.10	0.60	0.666
Modified HEC 1	0.25	0.54	0.654
Modified HEC 1	0.50	0.44	0.651
Modified HEC 2	0.10	0.58	0.664
Modified HEC 2	0.25	0.48	0.635
Modified HEC 2	0.50	0.40	0.609
Modified HEC 3	0.10	1.16	0.756
Modified HEC 3	0.25	1.31	0.787
Modified HEC 3	0.50	1.35	0.812
Modified HEC 4	0.10	1.25	0.786
Modified HEC 4	0.25	1.39	0.827
Modified HEC 4	0.50	2.27	1.308

3.3. The effects of modified HECs on the growth rate of gas hydrate in methane-propane-water system

First, the effects of modified HECs (modified by graft copolymerization) on the growth rate of methane-propane hydrate were investigated. Fig. 6 displays the effects of three types of modified HECs, including modified HEC 1 (modified with acrylamide and CAN), modified HEC 2 (modified with the help of acrylamide and APS), and modified HEC 3 (modified by acrylamide, APS and SB) on the gas consumption rate during hydrate formation. It is observed that (Fig. 6(a)) the growth rate of hydrate is decreased in the presences of 0.10 wt% modified HEC 1 and modified HEC 2. However, a slower hydrate growth rate was obtained with modified HEC 2 in comparison to modified HEC 1, although the difference is not significant. On the other hand, an interesting finding was obtained in the hydrate formation with modified HEC 3. While modified HEC 1 and modified HEC 2 show inhibition effects, the modified HEC 3 acts as promoter. The values of Table 3 indicate that the average rate of hydrate formation in the presence of 0.10 wt% modified HEC 3 is about 1.55 times higher in comparison to pure water. Also, the increase

in the value of $-A_r/RT$ confirms the higher rate of hydrate formation in the presence of modified HEC 3. The experiments were also conducted at concentrations of 0.25 and 0.50 wt%. Fig. 6(b) and (c) shows that the modified HEC 2 is the most effective additive to decrease hydrate formation rate. While modified HEC 1 has less inhibition effect in these concentrations. On the other hand, modified HEC 3 shows remarkable effects on growth rate of hydrate when the concentrations are increased to 0.25 and 0.50 wt%. The results of Table 3 also confirm that when aqueous solutions of modified HEC 3 (in the concentrations of 0.25 and 0.50 wt%) are used instead of pure water for hydrate formation, the average growth rates become higher (about 1.75 and 1.80 times, respectively). Also the value of $-A_r/RT$ are increased significantly in these concentrations. Fig. 6(d) also confirms that modified HEC 1 and modified HEC 2 can be introduced as inhibitor and modified HEC 3 can be applied as a good promoter of hydrate growth in the tested concentrations.

HEC was also functionalized with acrylamide (modified HEC 4) and its effect on the kinetics of methane-propane hydrate was tested. Fig. 7 exhibits the gas consumption during hydrate formation with aqueous
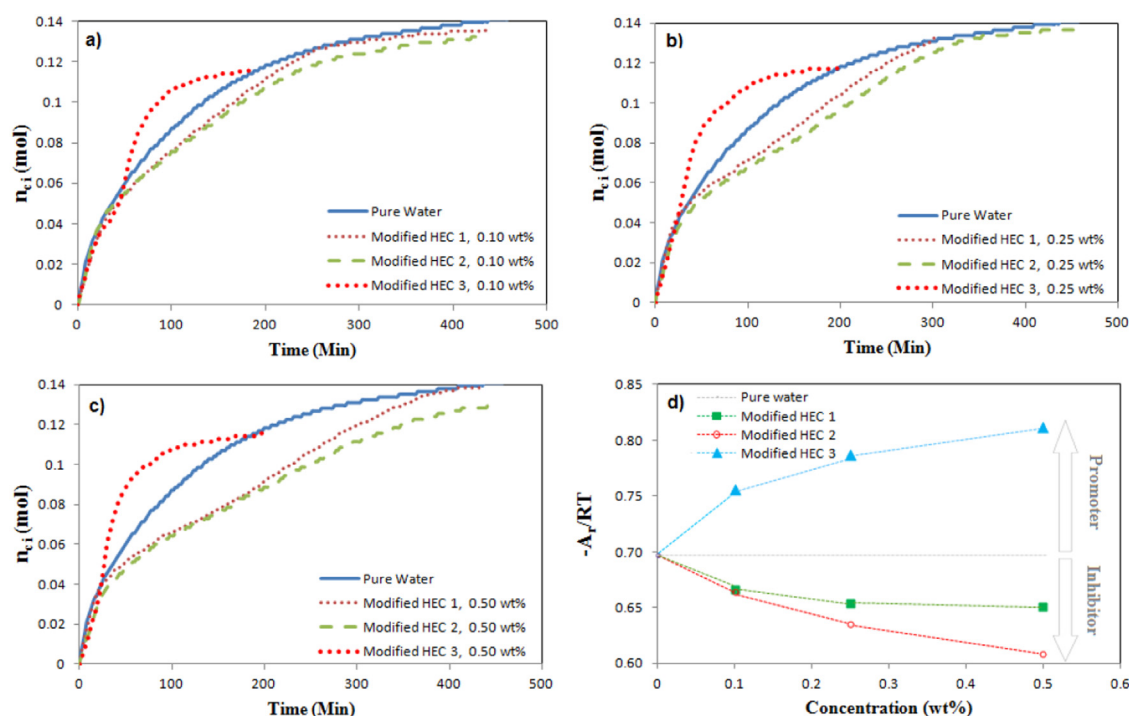

Fig. 6. The inhibition and promotion effects of modified HECs on hydrate formation in methane-propane-water system.
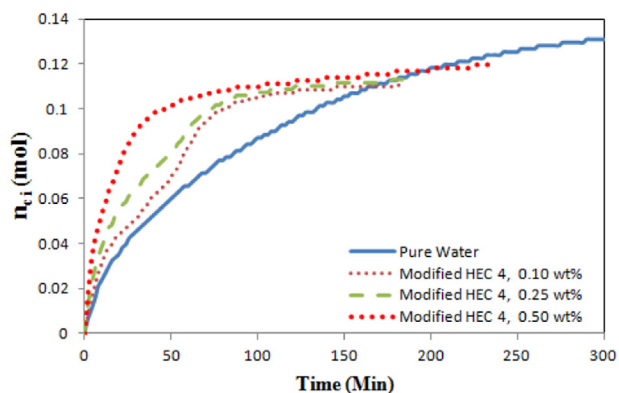
Fig. 7. The effect of modified HEC 4 as promoter on hydrate growth rate.

Table 4
The obtained kinetic parameters for investigation of hydrate growth rate in the presences of modified starches.

Additives	Concentration (wt%)	Average growth rate (mmol/min)	$-A_r/RT$
Modified starch 1	0.25	0.73	0.677
Modified starch 1	0.50	0.69	0.658
Modified starch 2	0.25	0.70	0.674
Modified starch 2	0.50	0.63	0.658
Modified starch 3	0.25	0.86	0.729
Modified starch 3	0.50	0.96	0.745
Modified starch 4	0.10	1.02	0.766
Modified starch 4	0.25	1.39	0.779
Modified starch 4	0.50	1.61	0.897

solution of modified HEC 4 in the concentration range of 0.10 to 0.50 wt%. The results show that the rate of hydrate formation can be significantly increased in the presence of modified HEC 4. Also, its performance as promoter is improved with increase of concentration, such that when the hydrate is formed in the presence of 0.50 wt% modified HEC 4, the growth rate becomes even 3 times higher than pure water. In addition, the value of $-A_r/RT$ at this concentration show the high potential of modified HEC 4 as a promoter. The values of the average growth rate of hydrate and $-A_r/RT$ also show that modified HEC 4 is a better promoter than modified HEC 3.

The experimental results show that the ranking of modified HECs (to increase the hydrate growth rate of hydrate in comparison to pure water) is as follows: modified HEC 4 > modified HEC 3 > pure water > modified HEC 1 > modified HEC 2. In the other words, modified HEC 1 and modified HEC 2 can be applied as new inhibitors with higher solubility than native HEC and also modified HEC 3 and modified HEC 4 can be used for development of new promoters.

3.4. The effects of modified starches on the growth rate of gas hydrate in methane-propane-water system

Similarly, starch was modified with acrylamide in the presence of three initiators. Fig. 8 shows the effects of modified starch 1 (modified with acrylamide and CAN), modified starch 2 (modified with the help of acrylamide and APS), and modified starch 3 (modified by acrylamide, APS and SB), on the kinetics of methane-propane hydrate formation. It considers that the growth rate of hydrate in the presences of 0.25 wt% of modified starch 1 and modified starch 2 has not significant change in comparison to pure water (Fig. 8(a)). Although a weak inhibition effect after 200 min can be observed. But when the hydrate was formed in the presence of 0.25 wt% of modified starch 3, a weak promotion effect was obtained. The values of $-A_r/RT$ (Table 4) also confirm that this modified structures are almost ineffective at the concentration of 0.25 wt%. Further experiments were carried out at concentration of

0.50 wt%. The results exhibit that modified starches are more effective on the hydrate growth at this concentration. According to Fig. 8(b), modified starch 1 decreased the rate of hydrate formation, but its inhibition effect was less than modified starch 2. This is also confirmed based on the obtained values of $-A_r/RT$ in Table 4. On the other hand, modified starch 3 could help promote hydrate growth, while at this concentration a faster rate of hydrate growth was achieved in comparison to the concentration of 0.25 wt%. The results of Table 4 also present that the promotion effects are more significant than inhibition effects. In addition, these values also confirm that the modification of HEC leads to better additives (as promoter or inhibitor) in comparison to modified starches. Table 3 shows that the values of $-A_r/RT$ for modified HECs is varied in the range of 0.609 to 0.666 when they act as inhibitors. Nevertheless, these values are in the range of 0.658 to 0.677 in the presences of modified starches. This confirms that modified HECs as inhibitors are more effective than modified starches. In addition, the values of $-A_r/RT$ indicate that they are also better promoter when the modification is based on a grafting reaction.

Starch was also functionalized with acrylamide (modified starch 4) and aqueous solutions of it were prepared for methane-propane hydrate formation. Interestingly, a strong effect of this modified starch was recorded. As it shown in Fig. 9, gas consumption rate is enhanced significantly by employing modified starch 4. The increase of concentration in the range of 0.10 to 0.50 wt% also improves the potential of this modified starch as promoter. The calculated values in Table 4 also represent that this modified starch (functionalized with acrylamide) as promoter has better performance than modified starch 3 (grafted with acrylamide). On the other hand, the results display that the promotion effects of modified HECs are more significant than modified starches when they are functionalized with acrylamide. For example, in concentration of 0.50 wt% the hydrate growth rate in the presence of modified HEC 4 is about 1.4 times higher in comparison to modified starch 4. According to the obtained results, it can be said that when HECs and starches are modified by grafting copolymerization reaction, two different behaviors can be observed. If the reaction was carried out with APS
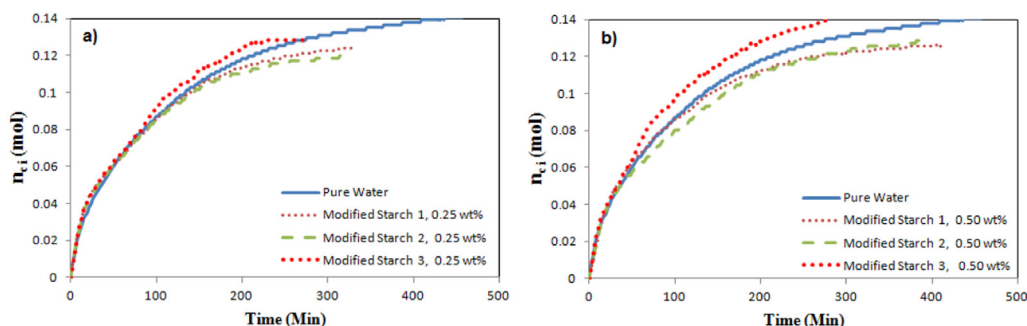

Fig. 8. Gas consumption versus time during the hydrate formation in the presence of modified starches.
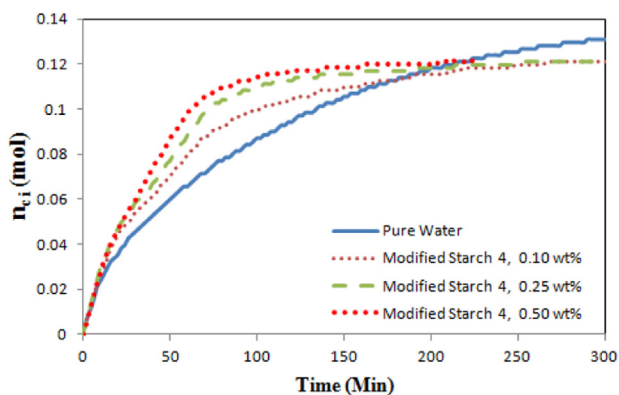
Fig. 9. The effect of modified starch 4 as promoter on hydrate growth rate.

or CAN, the final products acted as kinetic hydrate inhibitors, while if a mixture of APS and SB was used for grafting of acrylamide onto HEC and starch, the modified products could behave as promoters of hydrate growth. On the other hand, if they were functionalized with acrylamide, better promoters could be even obtained. It considers that various types of modified HECs and modified starches may have different influences on physical properties of water and hydrate crystals and subsequently affect the hydrate growth rate. Therefore, more investigation on the modified structures and their effects on the system may reveal some possible reasons for these interesting findings.

3.5. Analysis of the obtained results

The experimental results showed that some modified products have inhibitory effects and some exhibit promotion effects. One of the possible reasons may be the difference in surface tension between aqueous solutions of modified products. Some of literatures have noted that when the surface tension of aqueous solutions is reduced, the
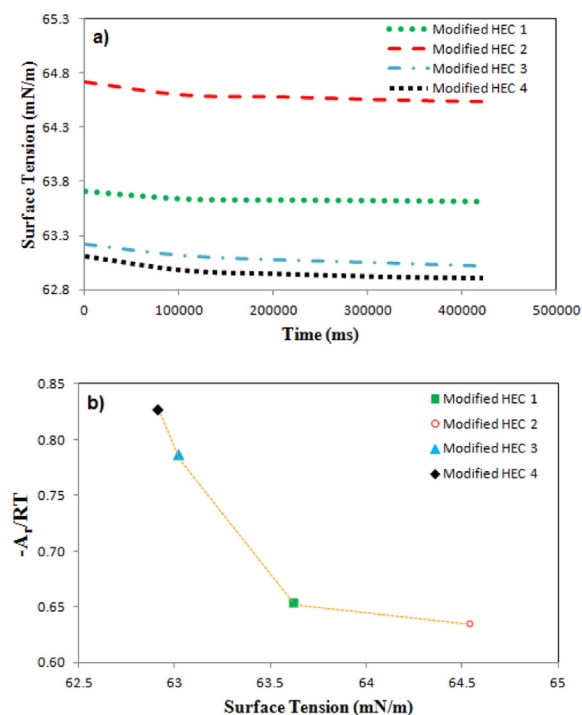
interaction among interfacial water molecules is weakened and gas molecules can be taken into the aqueous phase more easily and subsequently the hydrate growth rate can become faster [28–32]. Therefore, in this work surface tension for aqueous solutions of modified HECs was measured at 275 K. Fig. 10(a) shows the surface tension of aqueous solutions of modified HECs. In first view it seems that when surface tension of aqueous solutions of modified HECs is decreased, the hydrate growth rate is increased. Fig. 10(b) also confirms that with decrease of surface tension the value of $-A_r/RT$ is increased, which corresponds to higher rate of hydrate formation. However, in this respect, two points must be considered. First, it was expected that modified HECs 1 and 2 with less surface tension than pure water can be acted as promoter, but they show inhibition effects. Second, the difference in surface tensions is low, such that this difference for modified HEC 2 (as inhibitor) and modified HEC 4 (as a good promoter) is only 1.62 (mN/m). Also the surface tension for aqueous solution of modified HEC 4 in comparison to well-known promoters is very high. Therefore, it considers that although the surface tension of aqueous solution of modified HECs may be effective on the hydrate growth rate, but certainly it is not the main reason of the differences in the results. In this regard, Lo et al. [33] and Salako et al. [34] demonstrated that the adsorption of additives on hydrate surface is the most possible reason for changes in the growth rate of hydrate. On the other hand, it should be noted that the idea of modification of HEC and starch with acrylamide was due to the ability

Fig. 10. (a) The surface tension of modified HECs at 275 K, (b) the effect of surface tension on the value of $-A_r/RT$.
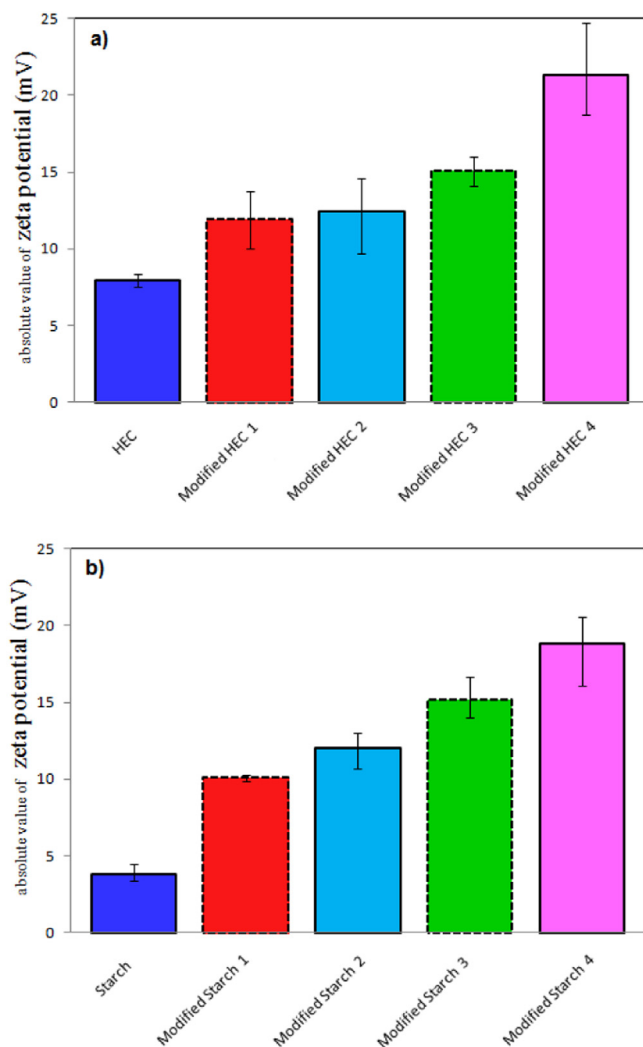
Fig. 11. Zeta potential measurements at the THF hydrate-liquid interface, (a) in the presences of modified HECs, (b) in the presences of modified starches.

of the amide group of acrylamide for strong hydrogen bond formation with water molecules of crystal surface. So, it was expected that the adsorption of modified HECs and modified starches on crystal surface may be more due to the presence of acrylamide in their structures. Therefore, the zeta potential measurements were performed to prove this claim. For this purpose, hydrate was formed with the help of THF, which could form structure II hydrate [35,36]. Then the zeta potential was measured at the THF hydrate-liquid interface. The liquid phase contains aqueous solutions of HEC, starch or their modified structures. The obtained results show negative charges on hydrate surface, such that in the presences of HEC and modified HECs the zeta potential is varied in the range of −7.98 to −21.33 (mV) and in the presences of starch and modified starches these values are in the range of −3.82 to −18.87 (mV). Fig. 11 shows that the absolute value of zeta potential for modified HECs and modified starches are higher in comparison to native HEC and starch. This corresponds to higher adsorption of these modified products on surface of crystals. It can be seen that among the modified structures with inhibition effects, modified HEC 2 has higher value of zeta potential than modified HEC 1 and subsequently its adsorption on crystal surface is more and therefore can be more effective to decrease the rate of hydrate formation. Also, the results indicated that the adsorption of modified starch 2 on hydrate surface is more than modified starch 1 and has higher inhibition effects. Similarly, among promoters, modified HEC 4 has the most ability for adsorption on hydrate crystals and also exhibits the best performance. Also the modified starch 4 is more adsorbed on hydrate surface (in comparison to modified starch 3) and therefore its effect is higher to promote the growth rate of hydrate. At the end, it should also be mentioned that in this work, some modified products showed inhibition effects and some acted as promoter for the growth of methane-propane hydrate.

It considers that the molecular structures of modified HECs and modified starches play main role in the growth of hydrate. According to some literatures [37–39], in synthesis of modified HECs 3 and 4 and modified starches 3 and 4, sodium can be participated in molecular structure, which can be a possible reason of promotion effects of the aforementioned modified structures.

It should be demonstrated that the applied materials to produce modified HECs and starches may also influence on the surface tension, adsorption, and the structures of the modified products and subsequently lead to different effects on growth rate of hydrate. Therefore, it is necessary to check the materials, which are present in the modified products. In this respect, all reactions for synthesis of modified HECs and starches should be investigated. Tables 5 and 6 present the main reactions for production of modified HECs and starches 1, 2, 3, and 4, respectively. In these reactions, CAN, APS, the mixture of APS and SB (as initiators), acrylamide, NaOH, NH_3 and CH_2CH_2COONa (produced from reactions 13 and 23) were separated from the final modified products by precipitation with acetone. Also, native HEC, starch and the homopolymer of acrylamide (the obtained product from reactions 5, 7, 9, 15, 17 and 19) were separated by fractional precipitation. Therefore, the final products (as modified HECs and starches) are including the obtained materials from other presented reactions. These materials can influence on the surface tension and adsorption of modified HECs and starches. Also, the obtained molecular structures may play roles in the organization of water molecules when hydrate is formed. At first, the effects of the materials on the surface tension and adsorption are discussed. As was shown in Fig. 10(a), the surface tension of water in the presences of modified HECs 3 and 4 was less in comparison to modified HECs 1 and 2. It considers that the presence of sodium in the structure of modified products leads to a decrease in surface tension and

Table 5
The main reactions for production of modified HECs [37–41].

Proposed reactions	Eq.
The possible reactions for synthesis of modified HEC 1	

$$\text{Cell-OR} + CH_2=CHCONH_2 \xrightarrow{\text{CAN (Ce}^{+4})} \text{Cell-O-}[CH_2\text{-CH-}]_a \quad \text{or} \quad \text{Cell-OR}^\circ\text{-}[CH_2\text{-CH-}]_a$$
$$|\quad\quad\quad\quad\quad |$$
$$CONH_2 \quad\quad\quad CONH_2 \quad (4)$$

$$CH_2=CHCONH_2 \xrightarrow{\text{CAN (Ce}^{+4})} [CH_2\text{-CH-}]_a$$
$$|$$
$$CONH_2 \quad (5)$$

| The possible reactions for synthesis of modified HEC 2 | |

$$\text{Cell-OR} + CH_2=CHCONH_2 \xrightarrow[\text{Heat}]{\text{APS}} \text{Cell-O-}[CH_2\text{-CH-}]_m \quad \text{or} \quad \text{Cell-OR}^\circ\text{-}[CH_2\text{-CH-}]_m$$
$$|\quad\quad\quad\quad\quad |$$
$$CONH_2 \quad\quad\quad CONH_2 \quad (6)$$

$$CH_2=CHCONH_2 \xrightarrow[\text{Heat}]{\text{APS}} [CH_2\text{-CH-}]_m$$
$$|$$
$$CONH_2 \quad (7)$$

| The possible reactions for synthesis of modified HEC 3 | |

$$\text{Cell-OR} + CH_2=CHCONH_2 \xrightarrow[\text{Heat}]{\text{APS/SB}} \text{Cell-O-}[CH_2\text{-CH-}]_m \quad \text{or} \quad \text{Cell-OR}^\circ\text{-}[CH_2\text{-CH-}]_m$$
$$|\quad\quad\quad\quad\quad |$$
$$CONH_2 \quad\quad\quad CONH_2 \quad (8)$$

$$CH_2=CHCONH_2 \xrightarrow[\text{Heat}]{\text{APS/SB}} [CH_2\text{-CH-}]_m$$
$$|$$
$$CONH_2 \quad (9)$$

$$\text{Cell-OR} \xrightarrow{\text{SB}} \text{Sodium-hydroxyethylcellulose complex} \quad (10)$$

| The possible reactions for synthesis of modified HEC 4 | |

$$\text{Cell-OR} + CH_2=CHCONH_2 \xrightarrow[\text{Heat}]{\text{NaOH}} \text{Cell-O-} CH_2\text{-}CH_2\text{-}CONH_2 \quad \text{or} \quad \text{Cell-OR}^\circ\text{-} CH_2\text{-}CH_2\text{-}CONH_2 \quad (11)$$

$$\text{Cell-O-} CH_2\text{-}CH_2\text{-}CONH_2 \xrightarrow[\text{Heat}]{\text{NaOH}} \text{Cell-O-}CH_2\text{-}CH_2\text{-}COONa + NH_3 \quad (12)$$

$$CH_2=CH_2CONH_2 \xrightarrow[\text{Heat}]{\text{NaOH}} CH_2=CH_2COONa + NH_3 \quad (13)$$

R noted to H or CH_2CH_2OH.
R° noted to CH_2CH_2O.

Table 6
The main reactions for production of modified starches [37–41].

Proposed reactions	Eq.
The possible reactions for synthesis of modified starch 1	

$$St\text{-}OH + CH_2\text{=}CHCONH_2 \xrightarrow{CAN\ (Ce^{+4})} St\text{-}O\text{-}[CH_2\text{-}CH\text{-}]_n$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CONH_2$$
(14)

$$CH_2\text{=}CHCONH_2 \xrightarrow{CAN\ (Ce^{+4})} [CH_2\text{-}CH\text{-}]_n$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad CONH_2$$
(15)

The possible reactions for synthesis of modified starch 2

$$St\text{-}OH + CH_2\text{=}CHCONH_2 \xrightarrow[Heat]{APS} St\text{-}O\text{-}[CH_2\text{-}CH\text{-}]_m$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CONH_2$$
(16)

$$CH_2\text{=}CHCONH_2 \xrightarrow[Heat]{APS} [CH_2\text{-}CH\text{-}]_m$$
$$\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad CONH_2$$
(17)

The possible reactions for synthesis of modified starch 3

$$St\text{-}OH + CH_2\text{=}CHCONH_2 \xrightarrow[Heat]{APS/SB} St\text{-}O\text{-}[CH_2\text{-}CH\text{-}]_m$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CONH_2$$
(18)

$$CH_2\text{=}CHCONH_2 \xrightarrow[Heat]{APS/SB} [CH_2\text{-}CH\text{-}]_m$$
$$\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad CONH_2$$
(19)

$$St\text{-}OH \xrightarrow{SB} Sodium\text{-}starch\ complex$$
(20)

The possible reactions for synthesis of modified starch 4

$$St\text{-}OH + CH_2\text{=}CHCONH_2 \xrightarrow[Heat]{NaOH} St\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CONH_2$$
(21)

$$St\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CONH_2 \xrightarrow[Heat]{NaOH} St\text{-}O\text{-}CH_2\text{-}CH_2\text{-}COONa + NH_3$$
(22)

$$CH_2\text{=}CH_2CONH_2 \xrightarrow[Heat]{NaOH} CH_2\text{=}CH_2COONa + NH_3$$
(23)

subsequently may result to an increase in growth rate of hydrate. In fact, according to some studies [42,43], sodium can decrease the surface tension of water.

The adsorption of modified HECs and starches on the THF hydrate surface can also be investigated based on the produced products. The results showed that modified HEC 4 has the highest adsorption on hydrate surface (Fig. 11(a)). It may be due to the presence of Cell-O-CH$_2$-CH$_2$-COONa in the produced modified HEC 4 (produced from reaction 12). The role of this component seems to be similar to the role of SDS (as a strong promoter), which was described in the work of Lo et al. [44] by a probable mechanism. Similarly, in this study, Cell-O-CH$_2$-CH$_2$-COONa can be ionized in water solution and then be adsorbed on hydrate surface. As shown in Fig. 12, the adsorbed molecules (Cell-O-CH$_2$-CH$_2$-COO$^-$) can provide nucleation sites for a favorable enclathration of hydrophobic gas molecules in the cages of hydrate. In fact, the ionic structure of modified HEC 4 leads to more adsorption on hydrate surface (Fig. 11(a) also evidences that modified HEC 4 has the highest value of adsorption) and therefore can provide more nucleation sites for promotion of hydrate growth. Similarly, modified HEC 3 can promote hydrate formation, although the growth rate is slower in comparison to modified HEC 4 (due to less adsorption). Also, modified starch 3 and 4 can behave similar to modified HEC 3 and 4 and increase the growth rate of hydrate.

Ultimately, it should be noted that the high potential of modified HEC 4 and modified starch 4 (to promote hydrate formation), may refer to their effects on organization of water molecules. In graft copolymers (especially modified HEC 1 and 2 and modified starch 1 and 2) the large size of acrylamide polymer (the grafted chain to HEC and starch) may disturb the organization of water molecules and subsequently decrease hydrate formation rate in comparison to modified HEC 4 and modified starch 4. In addition, Lo et al. [44] noted that when the net charge of hydrate surface is increased, the water hydrogen-bonding structure becomes stronger and can cause a favorable enclathration. According this hypothesis, the modified HEC 4 and modified starch 4, which have the highest value of net surface charge on the THF hydrate surface, show the best performance as promoter.

4. Conclusions

The results of experiments showed that HEC has a significant effect and starch has little effect to slow down the growth rate of hydrate in the methane-propane-water system. Functionalization and graft copolymerization of HEC and starch with acrylamide were subsequently performed and led to the production of four new promoters. The hydrate growth rate in the presences of modified HECs 3 and 4 and modified starches 3 and 4 could be enhanced to 1.8, 3, 1.28, and 2.14 times higher in comparison to pure water, respectively. The produced additives based on functionalization, were better promoters in comparison to the synthesized products by grafting. Also, modified HECs 1 and 2 and modified starches 1 and 2 showed inhibition effects and their ranking to decrease the hydrate growth rate was as follows: modified HEC 2 > modified HEC 1 > modified starch 2 > modified starch 1. In addition, zeta potential measurements indicated that some modified HECs and starches can be more adsorbed on hydrate surface and therefore can show better performance as promoter or inhibitor.
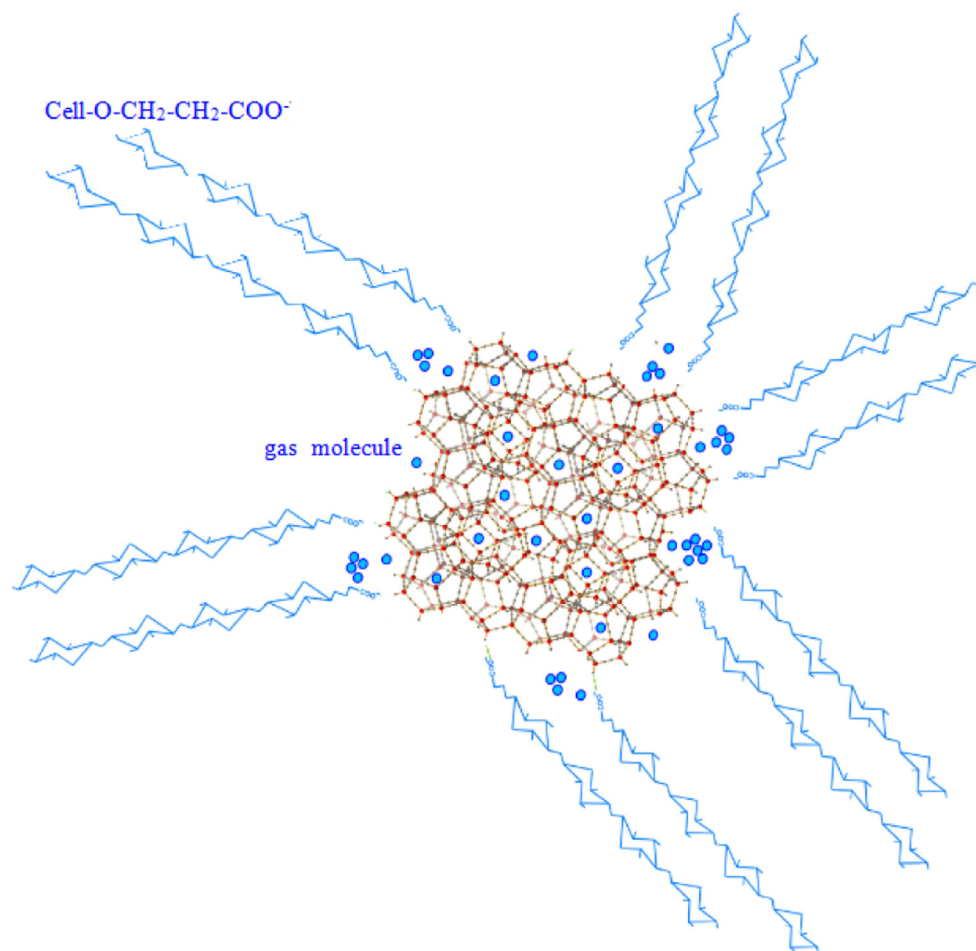
Fig. 12. Adsorption of Cell-O-CH$_2$-CH$_2$-COO$^-$ on the hydrate surface and the enclathration of gas molecules.

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