



Evaluation of Empirical Correlations for Predicting Gas Hydrate Formation Temperature

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Abstract: One of the important, practical and simple methods for hydrate formation condition is empirical equations, and so far many empirical equations have been presented to predict the temperature and pressure of hydrate formation. In this study, the methods and empirical correlations have been reviewed and their predictive capabilities have been evaluated with the use of more than 2000 experimental data collected from literature. These data have been separated in three groups: (1) simple natural gas components included methane, ethane, propane, isobutane, carbon dioxide, nitrogen, and hydrogen sulfide (2) binary gas mixtures and (3) gas mixture similar to natural gas. In this paper, after expressing the restrictions of some empirical correlations have been proposed by scientists before and proposed empirical correlation in the present study, the results of evaluating have been presented in several tables and curves. The proposed empirical correlation in the present study has shown reliable performance for both simple natural gas components and mixtures. Despite the existence three adjustable parameters, the accuracy of this equation shows the ranking 1 to 3 compare to the rest of the equations.

keywords: Empirical Correlations, Gas Hydrate Formation Condition, Natural Gas Mixtures, Hydrate Formation Predicting, Hydrate Formation Temperature

1. Introduction

Natural gas (NG) is a gas consisting primarily of methane, which forms naturally in the underground floors (Sahabi, 1996). Raw natural gas comes from three types of wells: oil wells, gas wells, and condensate wells. Whatever the source of the natural gas, once separated from crude oil (if present), it commonly exists in mixtures with other hydrocarbons, principally ethane, propane, butane, and pentanes. Associated hydrocarbons, known as "natural gas liquids" (NGL), are used as raw materials for oil refineries or petrochemical plants and as sources of energy (Devold, 2013). These liquids present about 0.07 per thousand of natural gas (Sahabi, 1996).

In addition to natural gas liquids, there are other impurities in natural gas, such as N₂,

CO₂, water vapor, H₂S. Water vapor is the most common undesirable impurity found in natural gas. By virtue of its source, natural gas is almost always associated with water usually in the range of 400-500 lb water vapor/MMscf gas (Kumar, 1987).

Liquid water with natural gas lead to some problems which one of the most important is gas hydrate formation. Gas hydrates, which are ice-like structures of water and gas considered as the unconventional gas sources (Mokhatab, Poe, & Speight, 2006). Gas hydrates may lead to several industrial problems, such as erosion and/or corrosion in pipelines, the blockage of transfer lines, compressor damage, etc., which cost millions of dollars in production facilities and transmission pipelines every year (Safamirzaei & Modarress, 2011). On the other hand, due to the presence of large amounts of hydrocarbons,

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the formation of hydrates can lead to fire in the equipment. For example, the explosion and fire incident occurred in the refrigeration towers of Bandar Imam Petrochemical Company in 2011, which was due to the formation of propane gas hydrate in the absorbent beds of the tower (Kazempour, 2011).

Clathrate hydrates have been a source of problems in the energy industry because the conditions at which oil and gas are produced, transported, and processed are frequently suitable for clathrate hydrate formation (Englezos, 1993). In order to prevent the formation of hydrate; gas stream is dehydrated in different stages of refining and transfer.

Since 1934, the time of discovery of hydrates in pipelines by Hummer schmidt (Hammerschmidt, 1934), many investigations have been done about natural gas hydrates and avoiding hydrate formation and several correlations have been presented to facilitate hydrate formation prediction and interpretation.

In this study, the methods and empirical correlations for predicting gas hydrate formation temperature have been reviewed and their applications have been evaluated. The empirical correlations include Motiee (Motiee, 1991), Tolwer and Mokhatab (Towler & Mokhatab, 2005), Hammer schmidt (Hammerschmidt, 1934), Safamirzaei (Safamirzaei M. , 2015), Bahadori (Bahadori, 2009) , Berge (Berge, 1986) and proposed empirical correlation in the present study. The results of evaluating have been presented in several tables and curves and finally it has been determined that which empirical correlation spresent the perfect results for each group of compounds.

2. Theory

2.1 . Gas Hydrates

Natural gas hydrates are solid crystalline compounds, resembling ice or wet snow in appearance, but much less dense than ice. Natural gas hydrates are formed when natural gas component, notably methane, ethane, propane, isobutene, hydrogen sulfide, carbon dioxide and nitrogen enter the water lattice (which is looser than the ice lattice) and occupy the vacant lattice positions, causing the water to solidify at temperatures considerably higher than the freezing point of water. Enough gaseous molecules must enter the lattice and occupy the void to stabilize the lattice crystal (Kumar, 1987).

Four conditions are required to form hydrates (Sloan, Introductory overview: Hydrate knowledge development, 2004):

- 1- Low temperature (commonly less than 300 K)
- 2- High pressure (greater than 38 bar hydrostatic pressure at 277 K)
- 3- A non-polar guest molecule smaller than 0.9 nm, such as methane
- 4- Water.

Hydrates are classified by the arrangement of the water molecules in the crystal, and hence the crystal structure. Two types of hydrates are commonly encountered in the petroleum business: Type I and Type II, sometimes referred to as Structure I and II. A third type of hydrate that also may be encountered is Type H (also known as Structure H), but it is much less common (Carroll, 2009).

Some of the common Type I hydrate formers include methane, ethane, carbon dioxide, and hydrogen sulfide. Among the common Type II formers in natural gas are nitrogen, propane, and isobutene.

2.2 . The Methods for Predicting Gas Hydrate Formation

The first problem when designing processes involving hydrates is to predict the conditions of pressure and temperature at which hydrates will form (Carroll, 2009).

The best method for determining conditions of hydrate formation is to experimentally measure the formation at the temperature, pressure and composition of interest. Because it is impossible to satisfy the infinite number of conditions for which measurements are needed, hydrate formation prediction methods are needed to interpolate between measurements (Heydari, Shayesteh, & Kamalzadeh, 2006).

Methods to Predict Hydrate Formation include graphical calculations, empirical correlations, thermodynamic models and software packages. In this study the empirical correlations have been reviewed.

2.3 . Empirical Correlations

In 1934, Hammerschmidt proposed a correlation for gas hydrate formation, shown in Eq. 1(Hammerschmidt, 1934).

$$T_{(°F)} = 8.9P_{(psi)}^{0.285} \quad (1)$$

Where P is in PSI, T is in Fahrenheit. This equation is simple and does not take into account the effect of gas specific gravity.

In 1986, Berg proposed two T-explicit correlations (Berge, 1986). For $0.55 \leq \gamma < 0.58$:

$$T = -96.03 + 25.37 \times \ln P - 0.64 \times (\ln P)^2 \quad (2)$$

$$+ \frac{0.025 \times \left[\frac{80.61 \times P + 1.16 \times \frac{10^4}{P+596.16} - (-96.03 + 25.37 \times \ln P - 0.64 \times (\ln P)^2)}{\gamma_g - 0.555} \right]}{0.025 \times \left[\frac{80.61 \times P + 1.16 \times \frac{10^4}{P+596.16} - (-96.03 + 25.37 \times \ln P - 0.64 \times (\ln P)^2)}{\gamma_g - 0.555} \right]}$$

And for $0.58 \leq \gamma \leq 1$:

$$T = \left\{ 80.61 \times P - 2.1 \times 10^4 - \frac{1.22 \times 10^3}{\gamma_g - 0.535} \right. \quad (3)$$

$$\left. - \left[1.23 \times 10^4 + \frac{1.71 \times 10^3}{\gamma_g - 0.509} \right] \right\}$$

$$/ \left[P - \left(-260.42 - \frac{15.18}{\gamma_g - 0.535} \right) \right]$$

For equation (2), P is in PSI, T is in Fahrenheit but for equation (3), P is in kPa, T is in Fahrenheit.

It should be noted that Berg notified PSI and Fahrenheit as the units of equation (2) in his article, but since the use of these units showed Unreasonable results, different units have been tested and Considering to the units of some authors have been used in their article for this equation, Finally the correct units of this equation were discovered.

In 1991, Motiee suggested Eq. 4 for natural gas mixtures (Motiee, 1991):

$$T = -238.24469 + 78.99667 \log P \quad (4)$$

$$- 5.352544(\log P)^2$$

$$+ 349.473 - 150.85465\gamma^2$$

$$- 27.604065\gamma \log P$$

Where P is in PSI, T is in Fahrenheit.

In 2005, Towler and Mokhatab proposed a relatively simple equation for estimating hydrate temperatures as a function of the pressure and the gas gravity (Towler & Mokhatab, 2005):

$$T = 13.47 \ln P + 34.27 \ln \gamma - 1.675 \ln \gamma \ln P \quad (5)$$

$$- 20.35$$

Where P is in PSI, T is in Fahrenheit.

In 2009, Bahadori and Vuthaluru presented one correlation for estimating HFT and one correlation for estimating HPT (Bahadori, 2009):

$$\ln T = a + b \left(\frac{1}{P} \right) + c \left(\frac{1}{P} \right)^2 + d \left(\frac{1}{P} \right)^3 \quad (6)$$

$$\ln P = a + b \left(\frac{1}{T} \right) + c \left(\frac{1}{T} \right)^2 + d \left(\frac{1}{T} \right)^3 \quad (7)$$

where P is the pressure in kPa and T is the temperature in K.

Depending on the ranges of pressure, temperature and gas molecular weight, different sets of adjustable parameters have been recommended. Totally any of these equations have 16 adjustable parameters.

In 2015, Safamirzaei proposed a T-explicit correlation for $0.55 \leq \gamma \leq 1$ (Safamirzaei M., 2015):

$$T = A\gamma^B (\ln P)^C \quad (8)$$

Where:

A=194.681789

B=0.044232

C=0.189829

In this equation, P is in kPa and T is in K.

In addition to the introduced equations, there are other equations such as Kobayashi (Kobayashi, Song, Sloan, & Bradley, 1987), Ameripour and Barrufet (Ameripour & Barrufet, 2009) and etc.

The main advantages of these empirical correlations are portability and simplicity. Indeed, required input data are accessible and they are applicable even with a simple calculator. The results are in excellent agreement with the experimental data in most cases and even better than the results from commercial simulators in some cases.

Despite of many advantages, these correlations have some limitation. For example, most of them can be used in the defined ranges of pressure, temperature and gas molecular weight and for the other ranges, show high errors. Also, some of them are accurate only for sweet natural gas mixtures or some of them work quite well for pure formers.

There are some equations which have been implemented by the artificial neural network (ANN) (Zahedi, Karami, & Yaghoobi, 2009) (Elgibaly & Elkamel, 1998) (Khomehchi, Shamohammadi, & Yousefi, 2013). These equations are often complicated and are not suitable for calculations performed by hand (Safamirzaei M., 2015).

3. Analysis Method

In this study, more than 2000 experimental data collected from literature (Guo & Ghalambor, 2005) (Sloan & Koh, Clathrate Hydrates of Natural Gases, 2007), and some of empirical correlations have been evaluated for these data separated in three groups:

1- Simple natural gas components included methane, ethane, propane, isobutane, carbon dioxide, nitrogen, and hydrogen sulfide.

2- Binary guest mixtures

3- Gas mixture similar to natural gas

Evaluated empirical correlation included: Motiee, Towler and Mokhatab, Hammerschmidt, Safamirzaei, Bahadori, Berg and new equation presented in this study.

For doing calculation the experimental hydrate pressure and specific gravity of a composition has been put into an equation. Then calculated temperature has been compared to experimental temperature for calculating the accuracy of the equation.

In this study, average relative deviation (ARD) and average absolute deviation (AAD) have been implemented to assess different equations deviations.

$$AAD = \frac{100}{n} \sum_{i=1}^{i=n} (T^{exp} - T^{cal}) \quad (9)$$

$$\%ARD = \frac{100}{n} \sum_{i=1}^{i=n} \frac{T^{exp} - T^{cal}}{T^{exp}} \quad (10)$$

The results of evaluating have been presented in tables 1-4 and Figures 1-15 in the next section.

Since some of the equations have temperature, pressure, or specific gravity restrictions, so some experimental data may not be used for some equations. The NOD¹ column in tables represents the number of data that can be used in the corresponding equation.

By using experimental data and a simple mathematic model, a new equation is presented here for estimating HFT as a function of gas pressure and specific gravity.

This equation is developed by fitting a polynomial function to 100 experimental data points using curve fitting of MATLAB software.

This equation has 3 adjustable parameters:

$$T = 242 \times \gamma^{0.02} \times P^{0.021} \quad (11)$$

where P is the pressure in kPa and T is the temperature in K.

The R-squared value for this equation is 0.9988.

4. Discussion

4.1. Comparison the Results of the First Group Data

The result of comparison the experimental temperatures with temperatures calculated by

the equations for the first group of data are plotted in graphs which are shown in Figures 1-9.

Figure 1 shows that for the pressures above 200 MPa, proposed empirical correlation in the present study and Towler and Mokhatab (Towler & Mokhatab, 2005) equation presents the closest results to experimental data.

For pressures lower than 200 MPa, Motiee (Motiee, 1991) and Bahadori's (Bahadori, 2009) represent the most accurate results.

Figure 2 shows hydrates formation temperature for ethane in low pressures. It can be seen that proposed empirical correlation in the present study and Motiee equation provide the best corresponding. For high pressure, Figure 3 is applicable.

According to Figure 4, for pressures above 1000 kPa, Hammerschmidt equation (Hammerschmidt, 1934) calculated the temperature of the propane hydrate formation accuracy. For pressures less than 1000 kPa, proposed empirical correlation in the present study and Safamirzaei equation (Safamirzaei M., 2015) are in good agreement with the experimental data. With respect to Figure 5, for pressures higher than 0.893 MPa, Hammerschmidt equation and for lower pressures, proposed empirical correlation in the present study shows the best fit with experimental data.

Figure 6 shows for pressures lower than 900 kPa, Motiee and proposed empirical correlation in the present study always provide the most accurate temperatures for isobutane hydrates. For pressures higher than 900 kPa and lower than 50 kPa, Hammerschmidt equation shows good performance.

Figure 7 can be divided into several parts and in each section, Motiee or Safamirzaei equations is selected for calculations the Nitrogen hydrate formation temperature.

According to Figure 8, for hydrogen sulfide at pressures below 57 kPa, Motiee and Safamirzaei equations are almost correspond with experimental data. For the pressure between 57 to 90 kPa, proposed empirical correlation in the present study shows very satisfactory results. Towler and Mokhatab equation is the best equations for pressures higher than 90 kPa.

Figure 9 shows for the pressures below 3385 kPa, Motiee equation (Motiee, 1991) is the best, and for higher pressures, Hammerschmidt equation (Hammerschmidt, 1934) and proposed empirical correlation in the present study provide good results for carbon dioxide.

¹ Number of Data

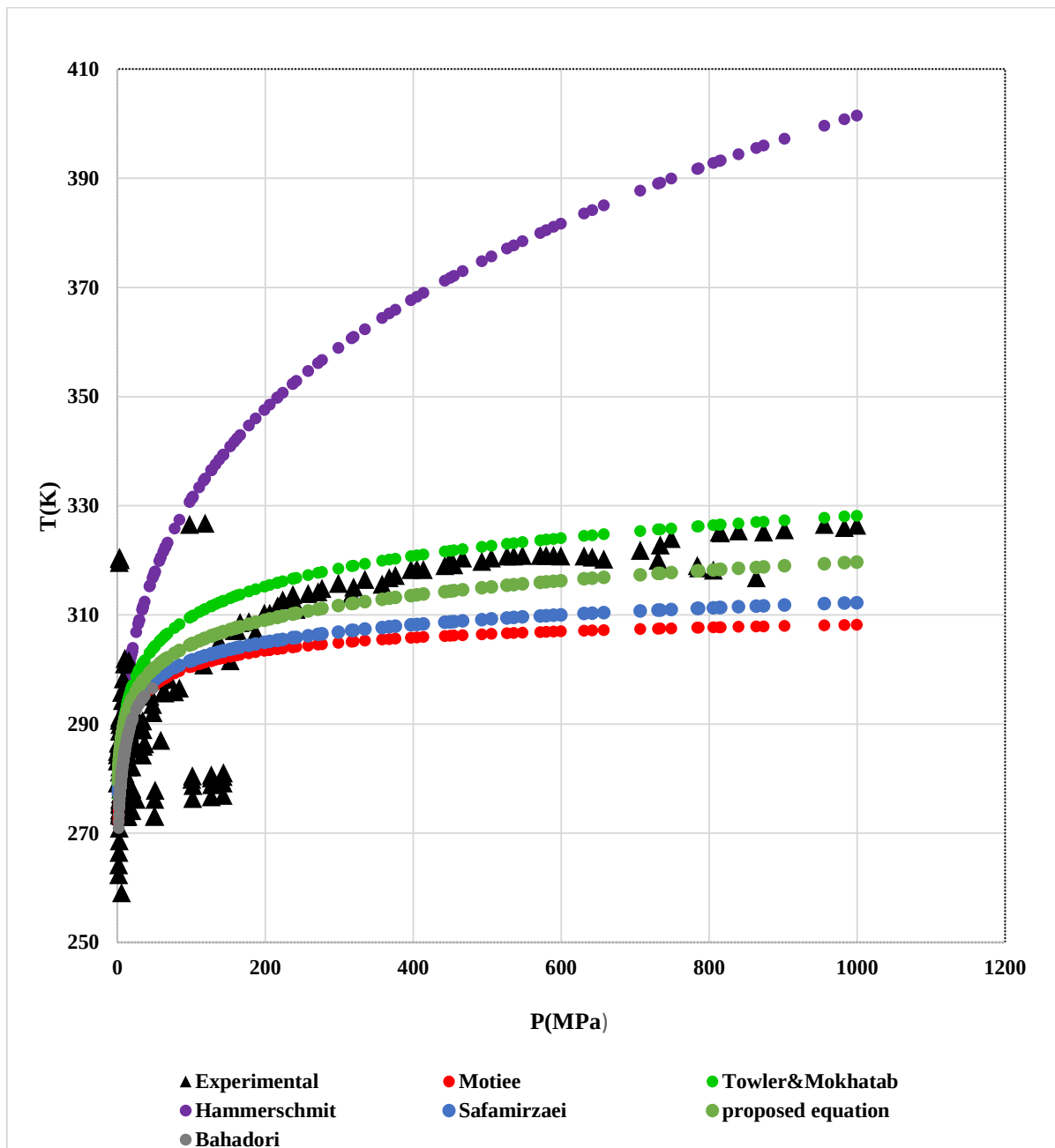


Figure 1. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for methane.

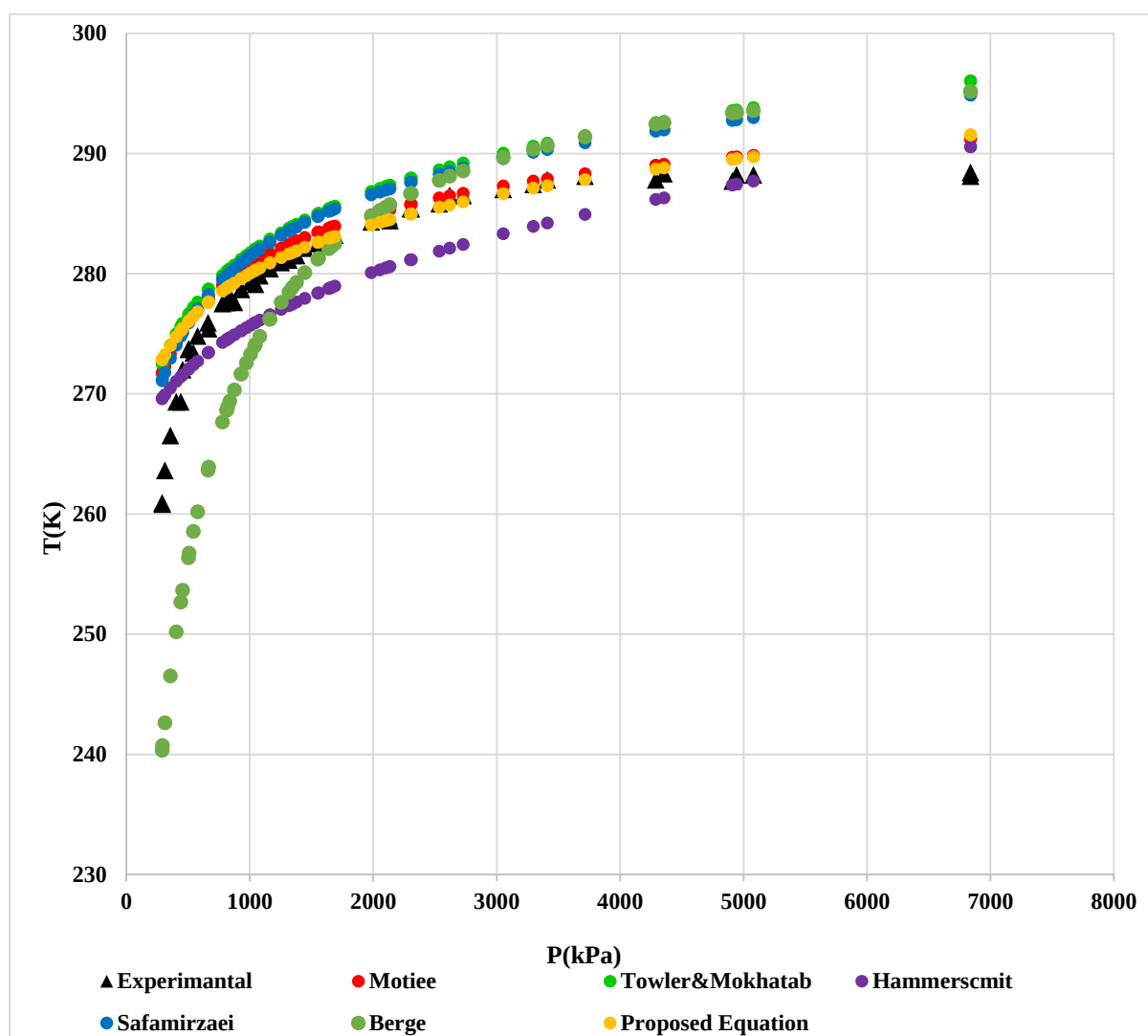


Figure 2. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for ethane at low pressure.

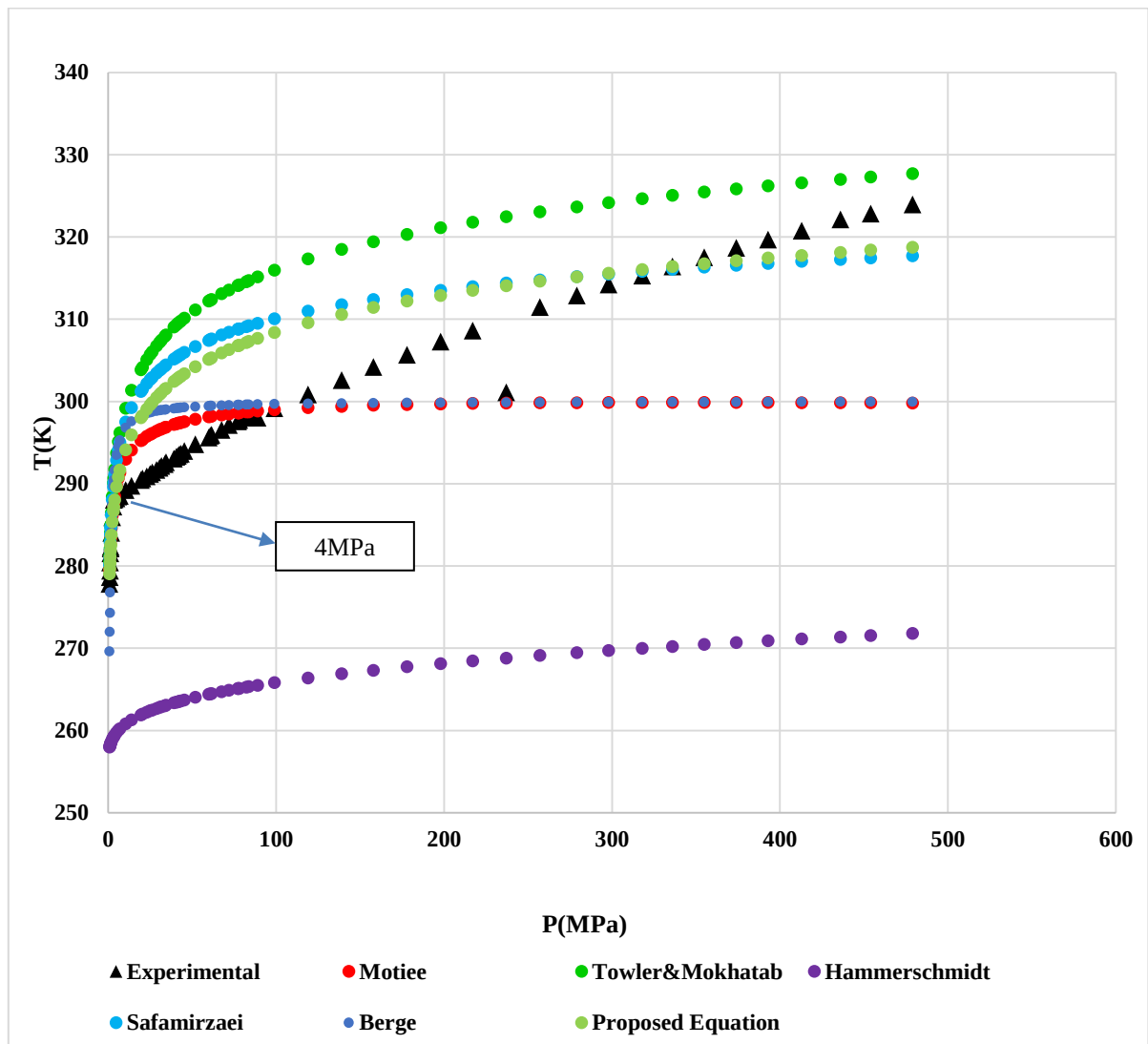


Figure 3. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for ethane at high pressure.

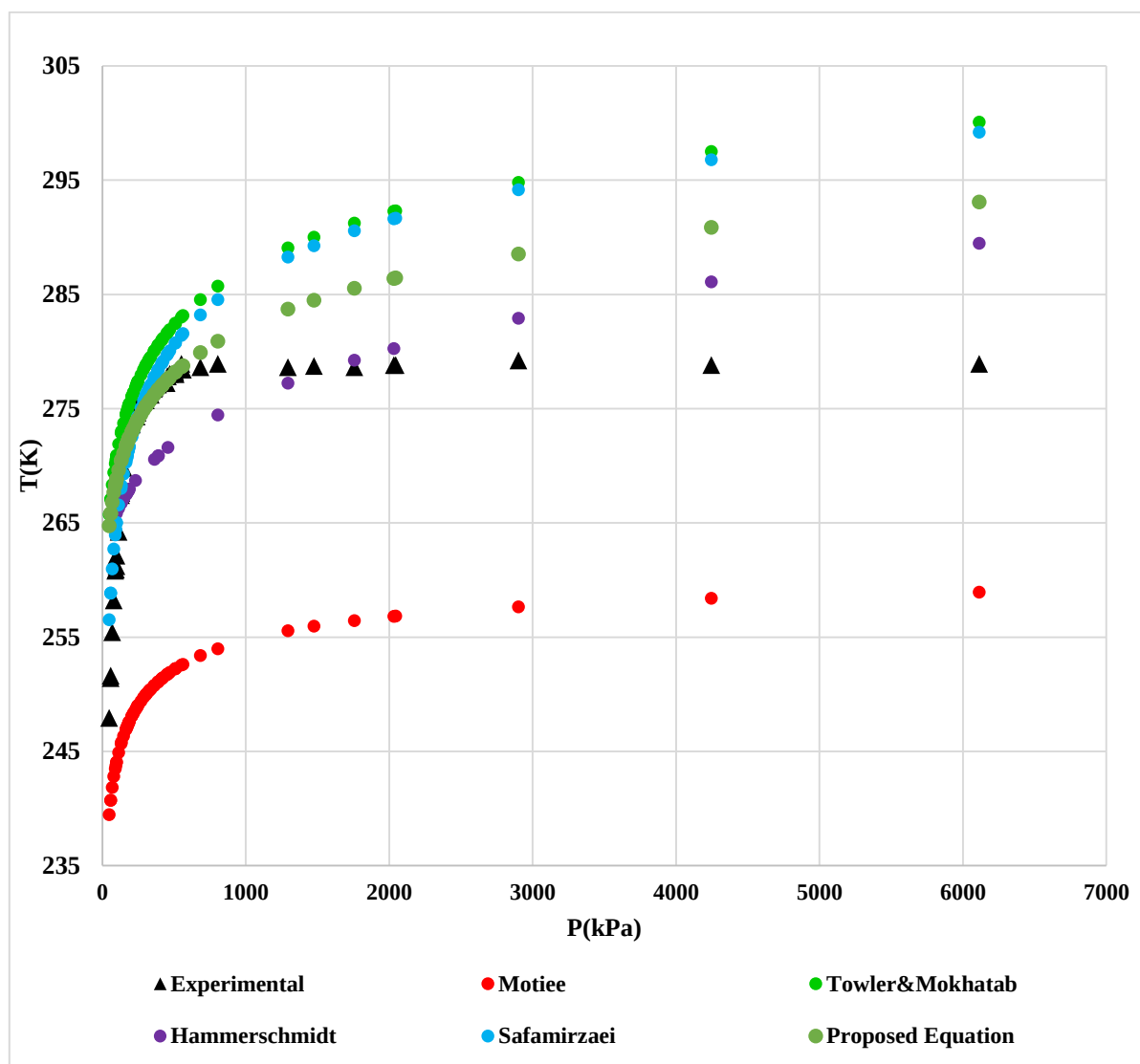


Figure 4. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for propane at low pressure.

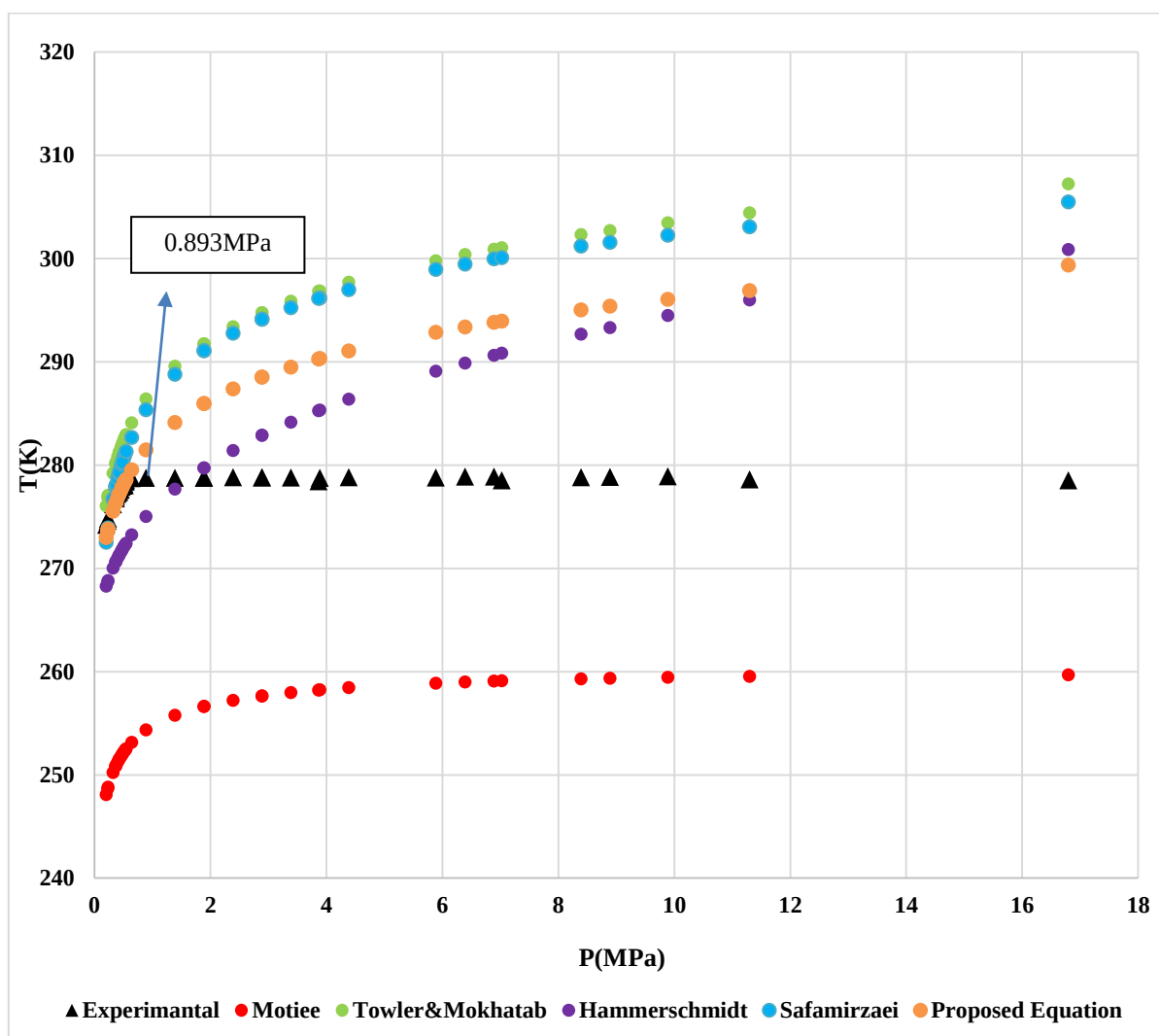


Figure 5. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for propane at high pressure.

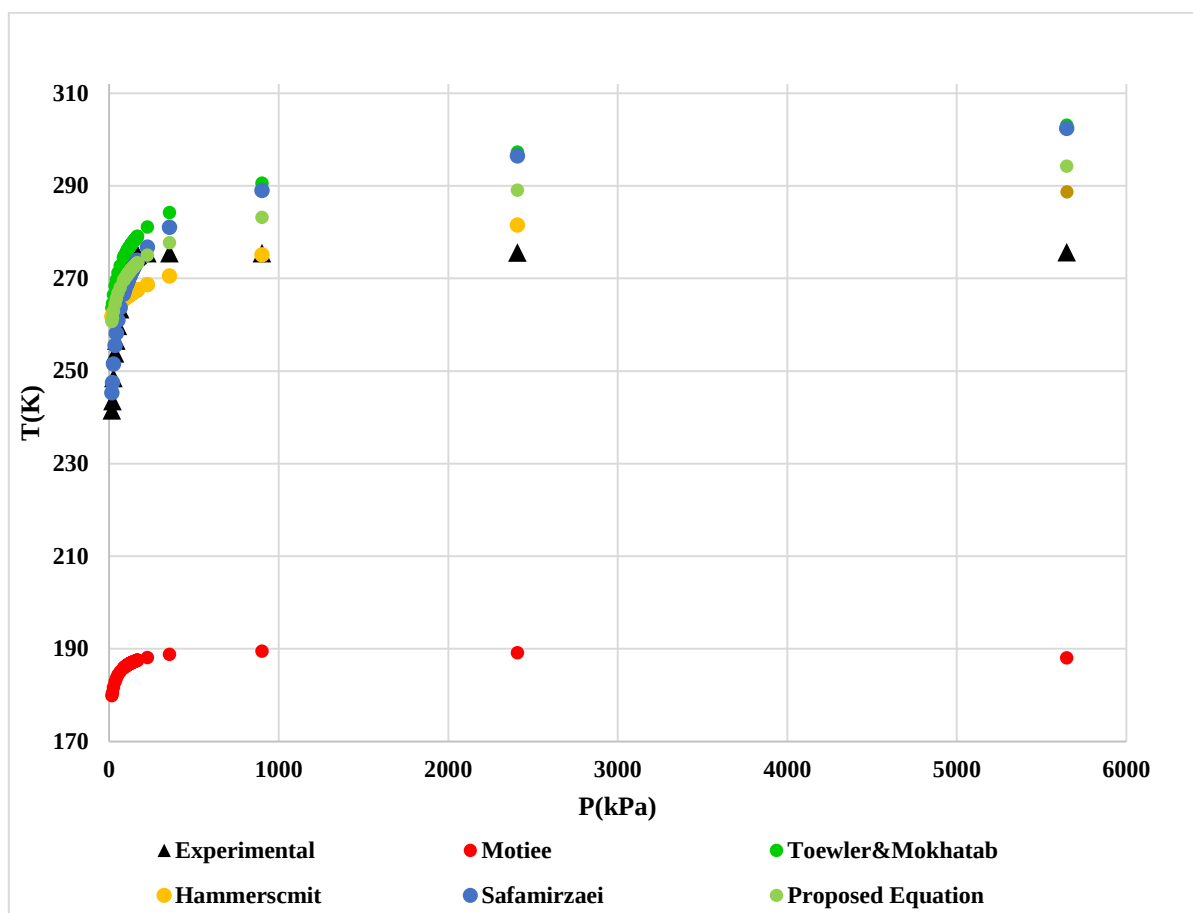


Figure 6. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for Isobutane.

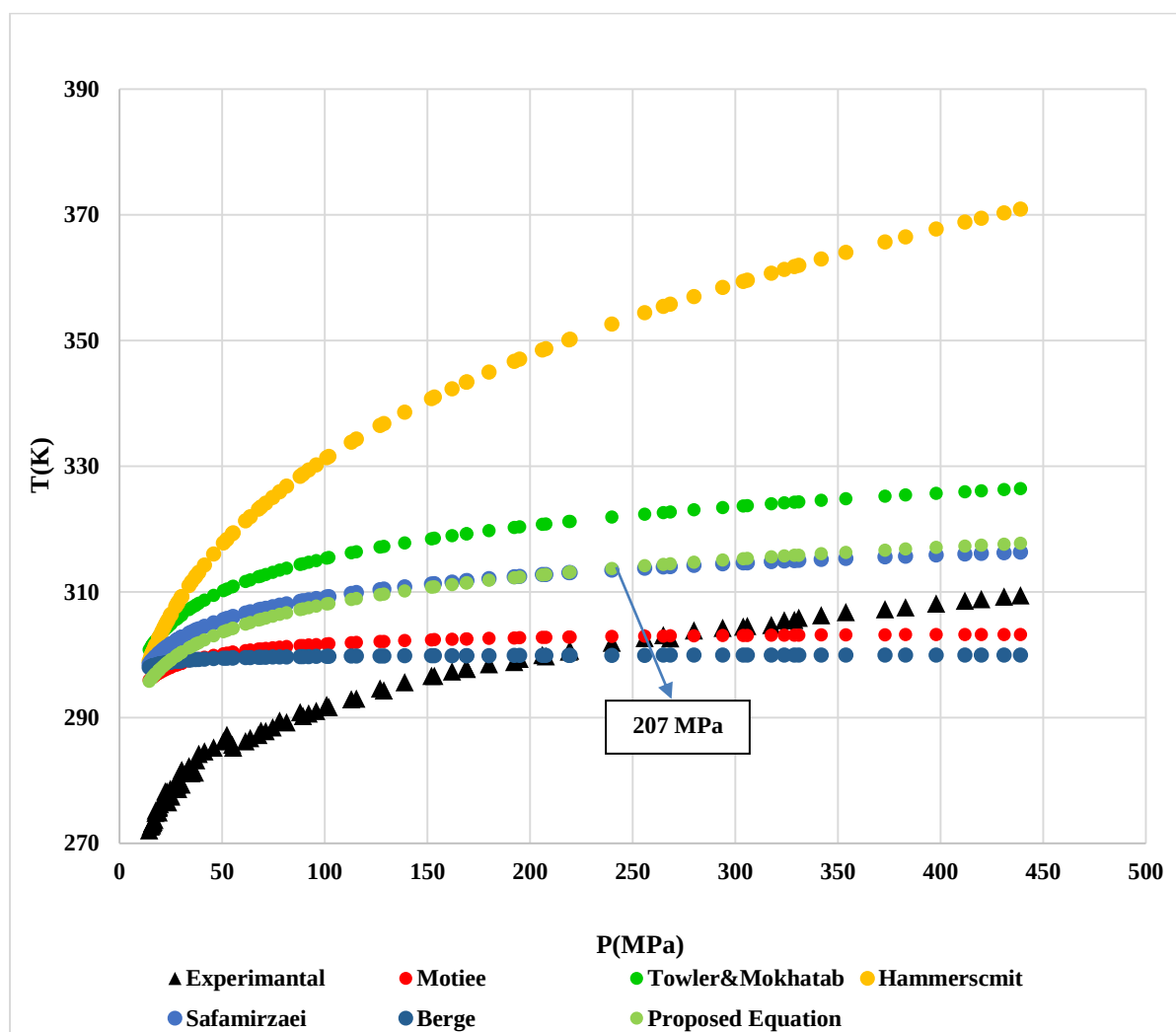


Figure 7. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for nitrogen.

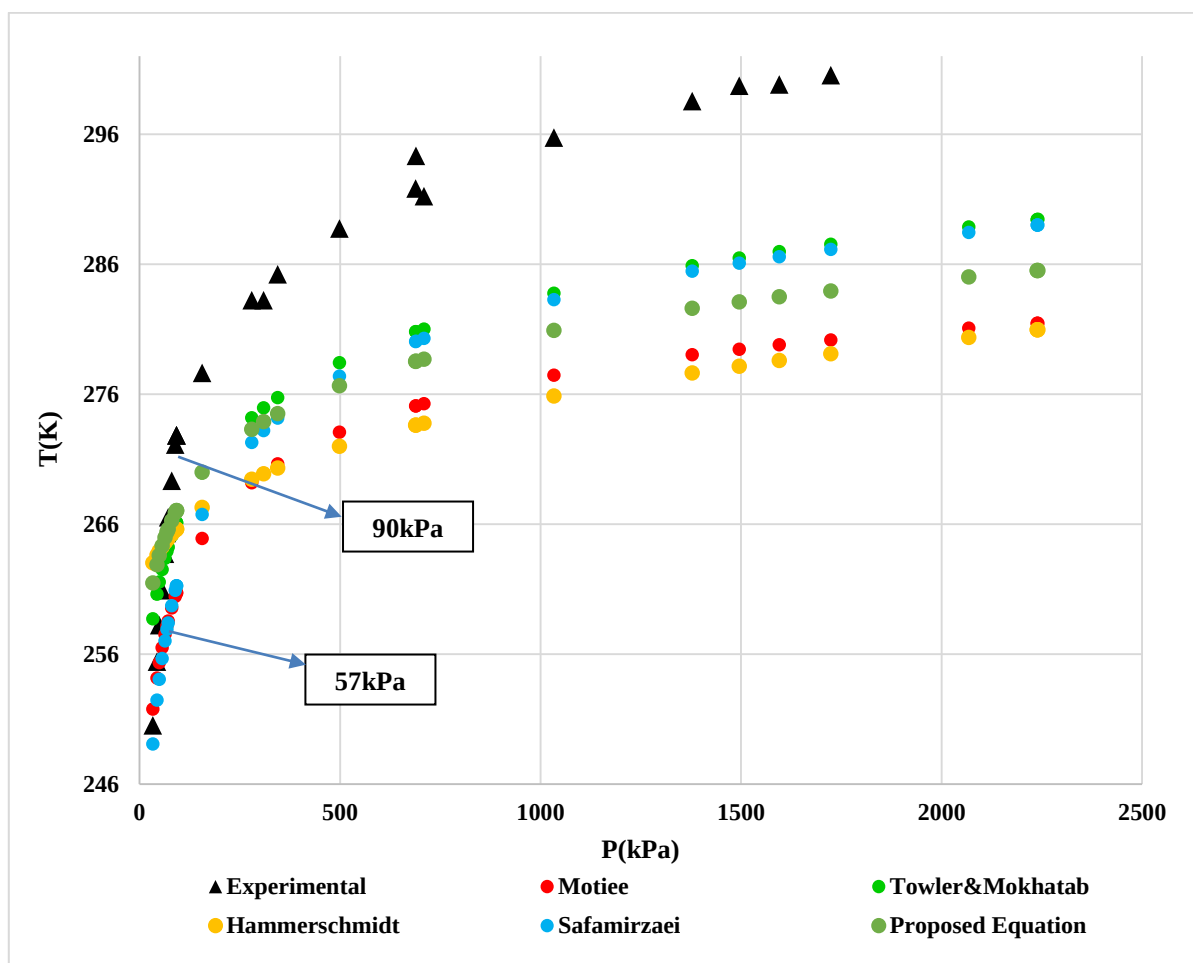


Figure 8. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for hydrogen sulfide.

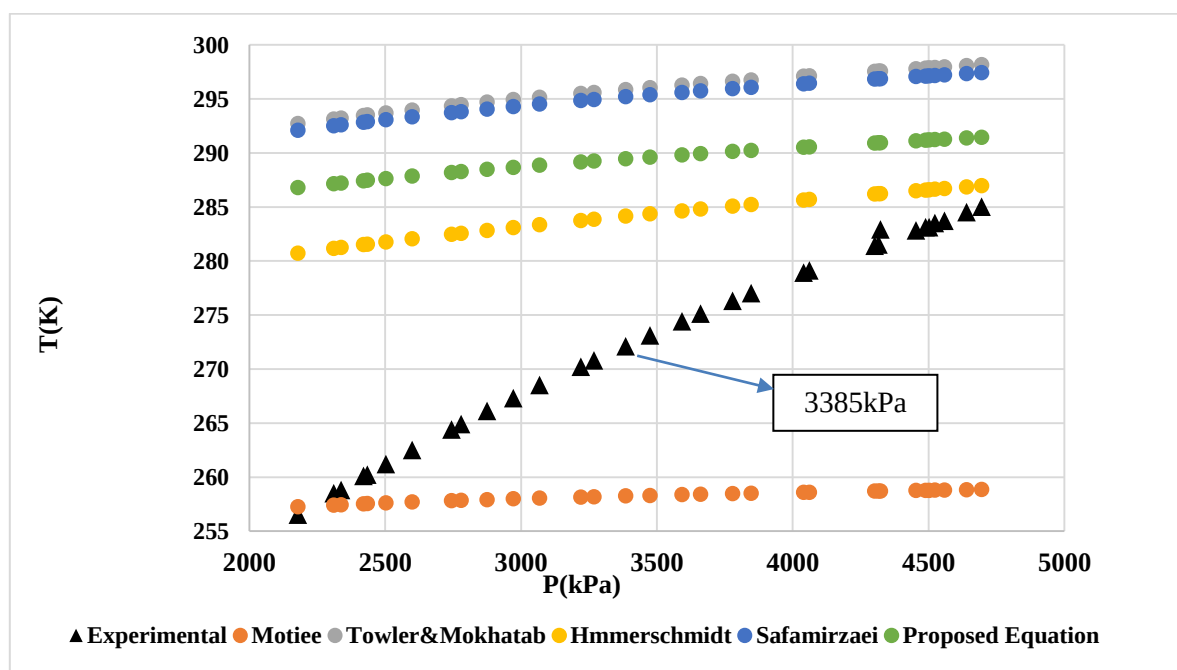


Figure 9. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for carbon dioxide.

4.2. Comparison the Results of the Second Group Data

Figures 10 through 13 show the calculated result in compared to experimental data. The curves of equations that show a large deviation have been omitted.

According to table 2 and Figure 15, it can be seen that Hammerschmidt (Hammerschmidt, 1934) presents the best result for ethane-containing mixtures, so it is not necessary to plot the graph. This is true for the mixtures containing Normal butane. The reason for superiority of Hammerschmidt equation for these mixtures may be due to the fact that ethane, propane, and isobutane

molecules only enter the large cages of their respective hydrate. And in the large cages, there is a high degree of occupancy. So, for ethane, propane, and isobutane, the composition of the hydrate does not appear to be a function of the temperature or the pressure.

On the other hand, Hammerschmidt equation is the only equation in which the molecular weight of the component is not affected, so it is expected that this equation gives good results for these compounds. As shown in table 2, Hammerschmidt equation for Propane also has a very good result.

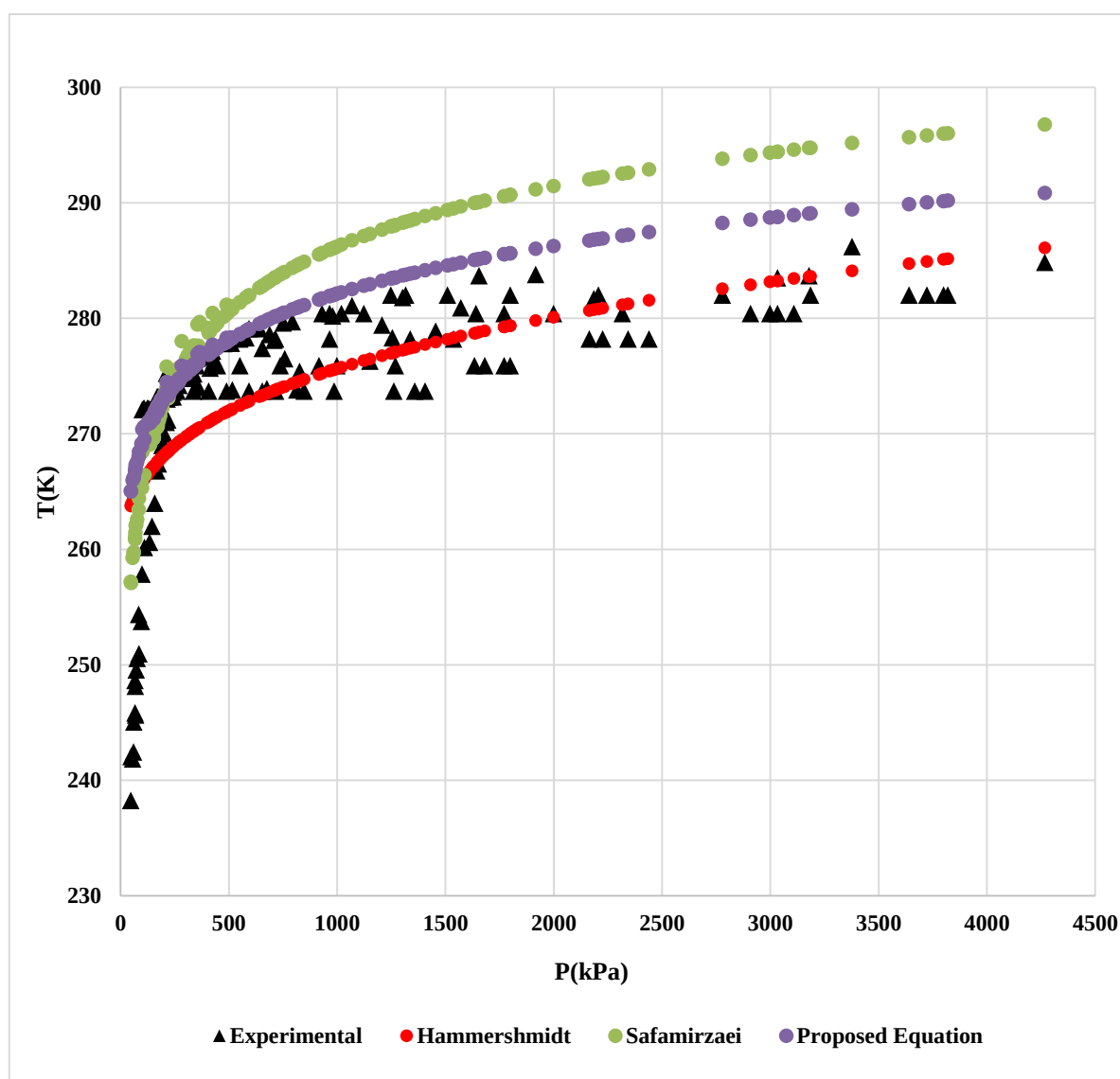


Figure 10. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for mixtures containing propane at low pressures.

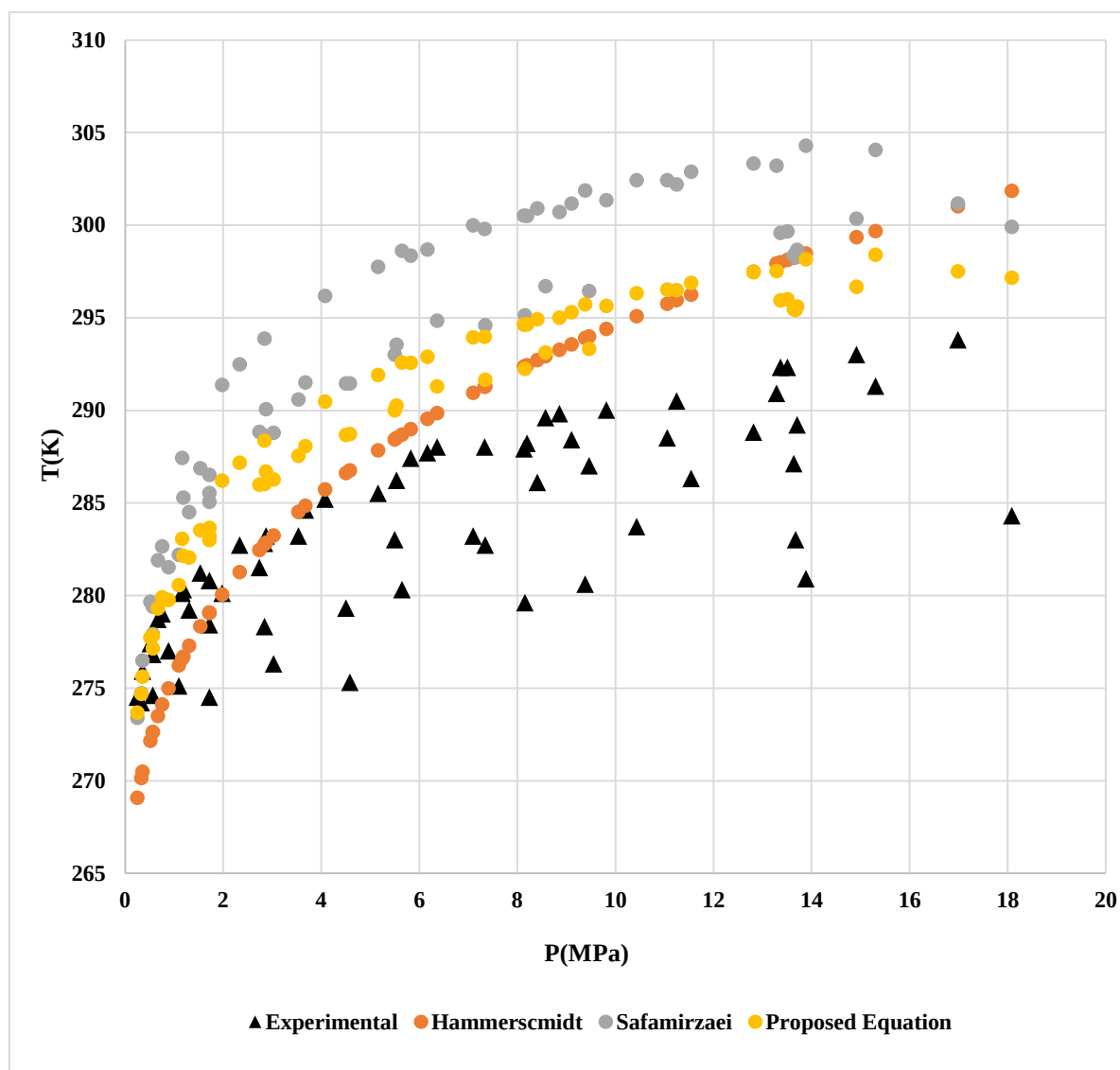


Figure 11. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for mixtures containing propane at high pressures.

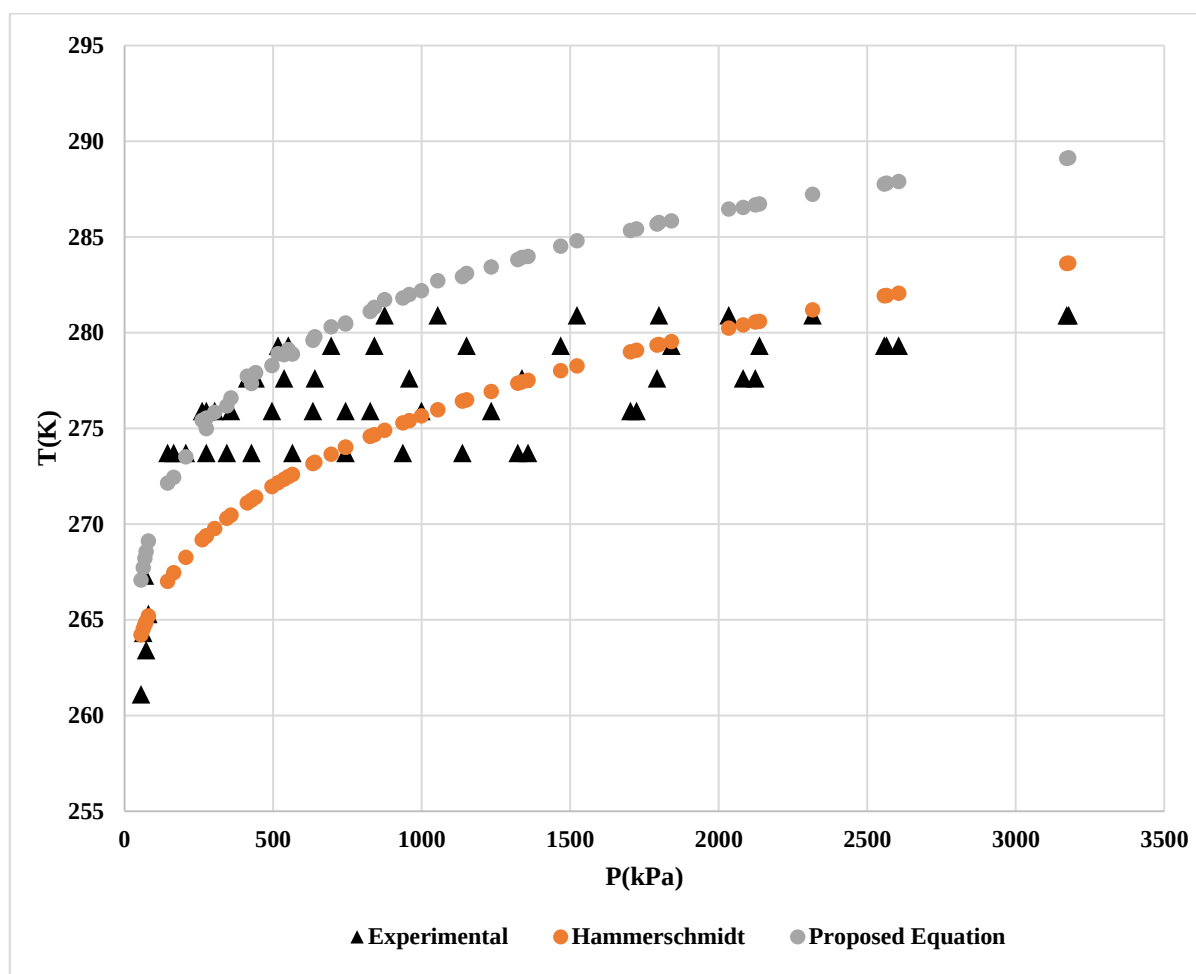


Figure 12. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for mixtures containing isobutane.

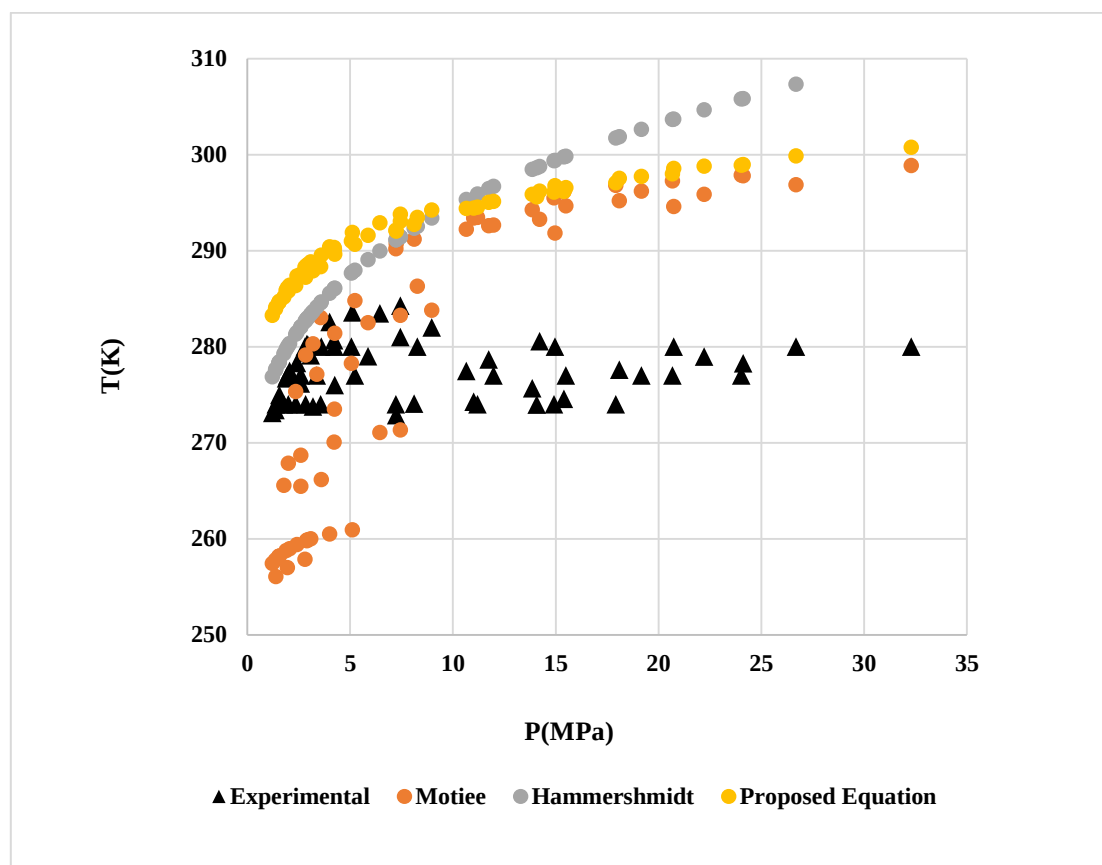


Figure 13. Comparison of the experimental temperature of hydrate formation with the results calculated by equations for mixtures containing nitrogen.

4.3. Comparison of the Results of the Third Group Data

Due to the high density of data, use of the diagram is not suitable and it is better to use the results of calculations presented in table 3.

4.4. Conclusion about Empiricalequations

4.4.1. Motiee

This equation is applied for natural gas mixtures. As shown in table 1 and Figure 14, for pure ethane and nitrogen, presents the best results and for pure methane is one of the best, but for pure propane and butane shows high deviations. The reason for is that Motiee equation is presented for natural gas, and the presence of propane and butane in pure form, displaces the sample from the natural gas mixture.

Table 4 shows that for the mixture of methane and ethane, Motiee calculates the most exact result. This equation is relatively accurate for gas mixture similar to the natural gas but for binary gas mixtures according to table 2, the results show high errors. Since that this equation has no limitations for pressure, temperature or gas molecular

weight, it has been applied for all the experimental points used in this paper.

4.4.2. Towler and Mokhatab

This equation has no limitation like Motiee. According to the tables, this equation has always reported moderate results and this is one of the most important advantages of this equation.

4.4.3. Hammerschmidt

The equation represented by Hammerschmidt is very simple and has only two parameters. Since that this equation has no limitations for pressure, temperature or gas molecular weight, it has been applied for all the experimental points used in this paper.

Tables 1 and 2 show that the performance of this equation for binary gas mixtures is better than pure compounds. So for the mixture of ethane, butane or nitrogen with other compounds it presents the best result.

4.4.4. Safamirzaei

This equation is presented for natural gas mixtures ($0.55 \leq \gamma \leq 1$), but has been evaluated for heavier hydrocarbon mixtures in this study.

As shown in table 3, for the natural gas mixtures, Safamirzaei presents the best result compared to other equations. Also, for pure propane and butane, or mixtures containing propane with other compounds, the results are excellent. The weakness of this equation is for pure nitrogen and pure sulfide, or mixtures containing them.

4.4.5. Bahadori

These correlations cover molecular weight between 16 to 29 and temperatures between 265 to 298 K as well as pressures between 1200 to 40000 kPa. As shown in tables 1, 2 and 4, for pure methane, mixture of methane and ethane, as well as mixtures similar to natural gas, Bahadori has presented the best results. Due to temperature, pressure and gas molecular weight limitations for these equations, most of the data used in this article is not usable. The error of this equation results increase with decreasing purity of methane in the mixtures.

4.4.6. Berge

This equation is for $0.55 \leq \gamma \leq 1$, therefore does not work for methane, propane, butane and pure hydrogen sulfide, and mixtures with gas molecular weight out of this range. As shown in table 1, for pure nitrogen, after the Motiee, Berge shows the best result.

4.4.7. Proposed Empirical Correlation in the Present Study

This equation has no limiting conditions and according to table 1, for pure propane and isobutane, presents the best results and for pure methane and ethane is one of the best results. Also, for binary guest mixtures containing ethane, propane or nitrogen and other compounds, the results are more accurate than other equations. For mixtures similar to the natural gas, according to table 3, this equation presents acceptable results. This equation is evaluated for all the experimental points used in this paper and often presents one of the three accurate results.

Table 1. Comparison of calculated result for simple natural gas components

	Methane			Ethane			Propane			Isobutane			Nitrogen			Hydrogen sulfide			Carbon Dioxide		
	AAD (K)	ARD (%)	NOD	AAD (K)	ARD (%)	NOD	AAD (K)	ARD (%)	NOD	AAD (K)	ARD (%)	NOD	AAD (K)	ARD (%)	NOD	AAD (K)	ARD (%)	NOD	AAD (K)	ARD (%)	NOD
Motiee	7.35	2.5	271	4.24	0.69	65	23.50	8.53	107	84.81	31.22	59	12.75	4.52	96	13.60	4.71	29	14.55	5.23	32
Mokhatab	8.29	2.95	271	8.32	2.85	65	7.81	2.84	107	6.53	2.44	59	23.66	8.24	96	8.59	2.98	29	23.15	8.59	32
Hammerschmidt	24.03	8.03	271	18.67	6.27	65	6.31	2.30	107	7.64	2.83	59	38.92	13.32	96	13.19	4.55	29	11.5	4.32	32
SafaMirzaei	8.42	2.92	271	6.07	2.1	65	5.95	2.15	107	4.05	1.48	59	17.99	6.31	96	10.46	3.65	29	22.4	8.34	32
Bahadori	3.54	1.27	174	-	-	0	-	-	0	-	-	0	-	-	0	-	-	0	-	-	0
Berge	-	-	0	7.29	2.48	65	-	-	0	-	-	0	-	-	0	-	-	0	-	-	0
proposed empirical correlation in the present study	8.10	2.84	271	4.39	1.49	65	4.36	1.60	107	4.06	1.54	59	16.77	5.84	96	10.18	3.53	29	16.76	6.24	32

Table 2. Comparison of calculated result for binary guest mixtures

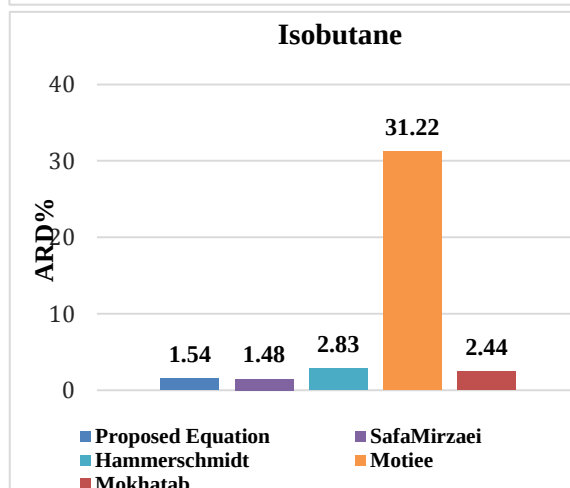
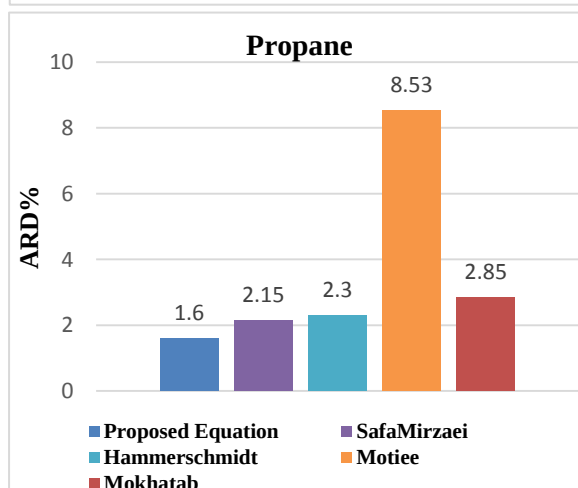
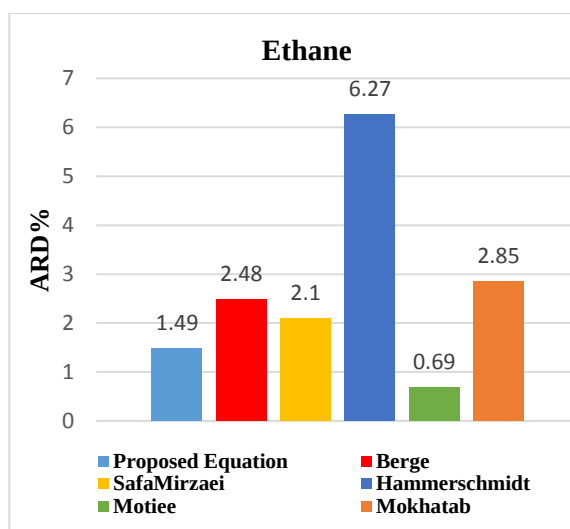
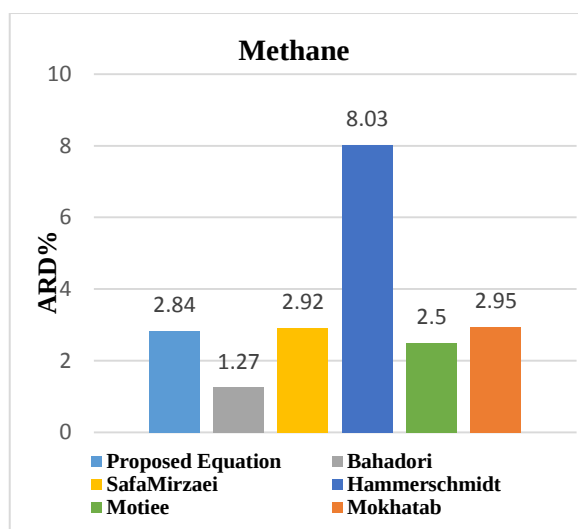
	Methane + another component			Ethane + another component			Propane + another component			Isobutane + another component			n-Butane + another component			Nitrogen + another component		
	AAD (K)	ARD (%)	NOD	AAD (K)	ARD (%)	NOD	AAD (K)	ARD (%)	NOD	AAD (K)	ARD (%)	NOD	AAD (K)	ARD (%)	NOD	AAD (K)	ARD (%)	NOD
Motiee	13.86	5.19	658	6.89	2.47	132	23.38	8.48	232	34.69	12.64	57	20.81	7.542	21	14.41	5.19	63
Mokhatab	7.91	3.08	658	10.20	3.71	132	9.57	3.49	232	9.68	3.50	57	15.27	5.53	21	19.77	7.13	63
Hammerschmidt	7.30	2.85	658	3.92	1.44	132	5.07	1.87	232	3.21	1.16	57	3.08	1.16	21	13.73	4.96	63
Safa Mirzaei	7.31	2.87	658	9.60	3.50	132	7.71	2.79	232	7.79	2.81	57	13.90	5.27	21	18.42	6.64	63
Bahadori	5.80	2.69	310	-	-	0	11.63	4.14	13	-	-	0	-	-	0	-	-	0
Berge	7.40	2.65	402	-	-	0	9.02	3.19	25	-	-	0	-	-	0	21.05	7.62	21
proposed empirical correlation in the present study	6.07	2.19	658	6.24	2.19	132	4.38	1.70	232	4.59	1.66	57	9.52	3.45	21	14.21	5.13	63

Table 3. Comparison of calculated result for gas mixture similar to natural gas

	Similar to Natural Gas (Sloan & Koh, Clathrate Hydrates of Natural Gases, 2007)			Similar to Natural Gas (Guo & Ghalambor, 2005)		
	AAD (K)	%ARD	NOD	AAD (K)	%ARD	NOD
Motiee	1.92	0.67	125	1.13	0.399	53
Mokhatab	1.18	0.41	125	1.86	0.64	53
Hammerschmidt	2.72	0.93	125	4.31	1.50	53
Safa Mirzaei	1.06	0.37	125	1.24	0.43	53
Bahadori	1.31	0.46	102	0.66	0.23	41
Berge	4.48	1.60	125	5.23	1.87	45
proposed empirical correlation in the present study	1.32	0.46	125	1.81	0.64	53

Table 4. Comparison of calculated result for methane and ethane mixture

	Methane + Ethane (Elgibaly & Elkamel, 1998)		
	AAD (K)	%ARD	NOD
Motiee	1.06	0.37	30
Mokhatab	2.93	1.04	30
Hammerschmidt	5.03	1.77	30
Safa Mirzaei	2.56	0.91	30
Bahadori	1.36	0.48	27
Berge	2.80	1.01	30
proposed empirical correlation in the present study	2.78	1.00	30



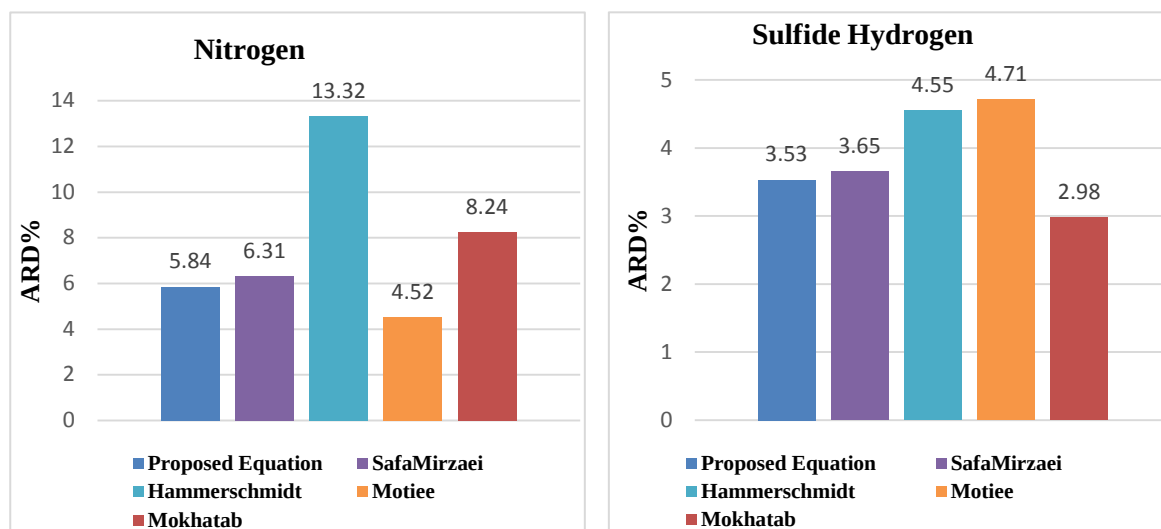
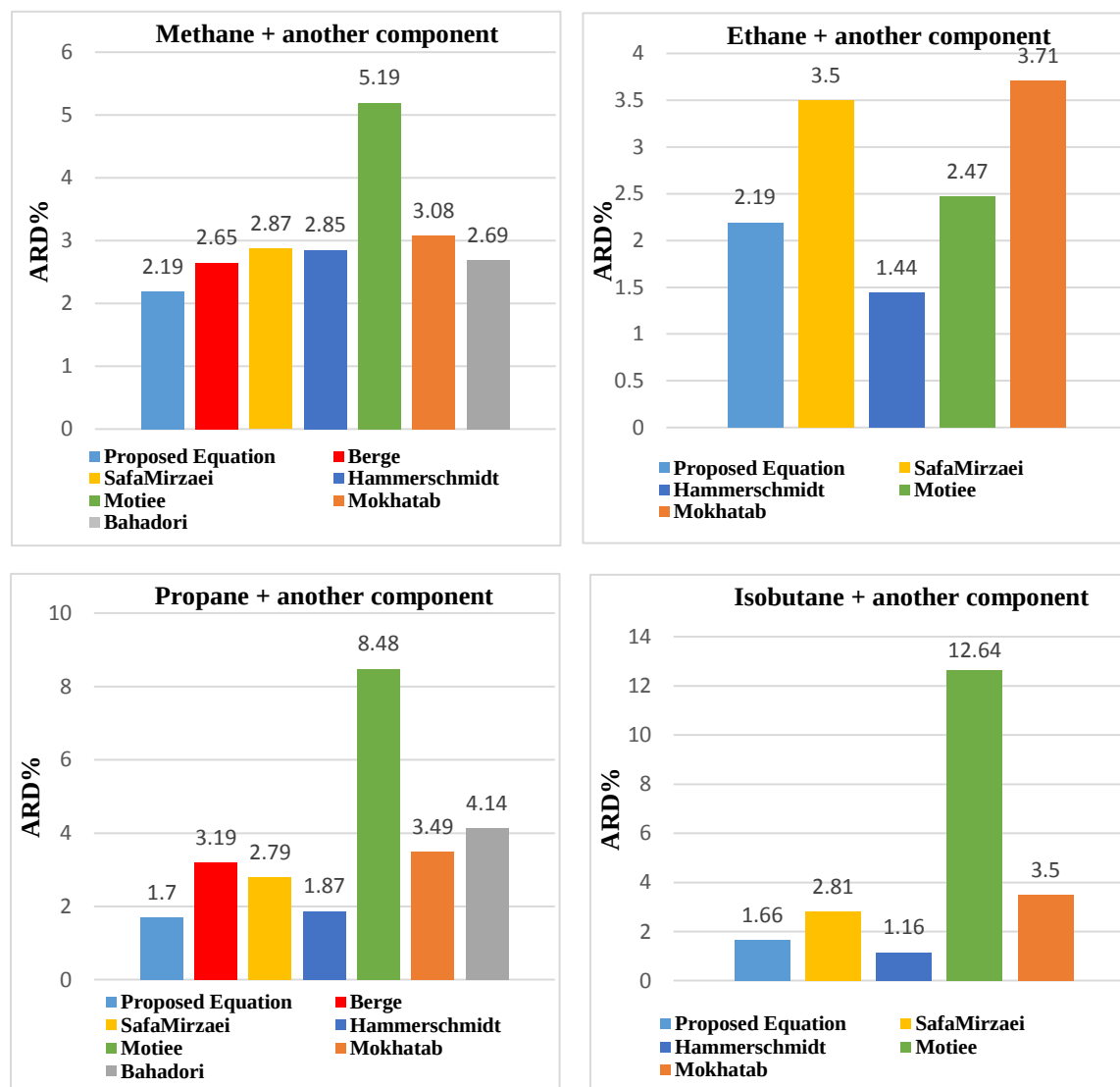


Figure 14. Comparison of calculated result for simple natural gas components



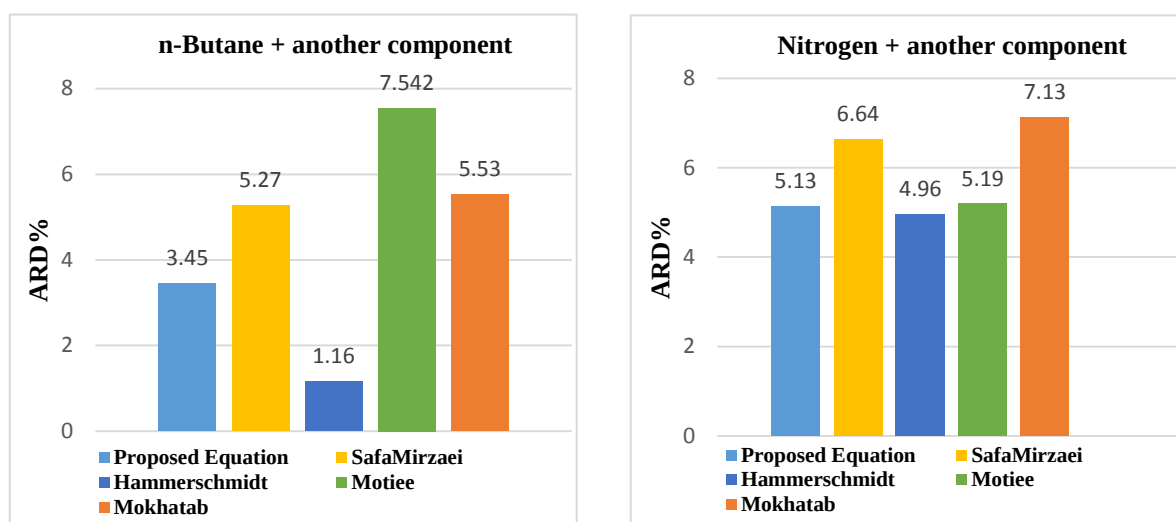


Figure 15. Comparison of calculated result for binary guest mixtures

5. Conclutions and Recommendation

In this study, the methods and empirical correlations have been reviewed and their predictive capabilities have been evaluated with the use of more than 2000 experimental data collected from the literature. These data have been separated in three groups: (1) simple natural gas components included methane, ethane, propane, isobutane, carbon dioxide, nitrogen, and hydrogen sulfide (2) binary gas mixtures and (3) gas mixture similar to natural gas. After expressing the restriction of each empirical correlation included Motiee, Tolwer and Mokhatab, Hammerschmidt, Safamirzaei, Bahadori, Berg and proposed empirical correlation in the present study, the results of evaluating have been presented in several tables and curves.

It is clear that each empirical equation has some limitations. In some cases, in addition to the specific gravity of the mixture, its composition and purity of the components also has a significant effect on some of the results. It is possible an equation covers intended molecular weight, but the result is not accurate which may be related to the lack of purity of component, the presence of some sour compounds, and so on.

Sometimes the average absolute deviation (AAD) for a group of experimental data is the minimum but it doesn't mean this equation is superior to other equations since it is seen; the maximum deviation is related to this equation. For this reasons, precautions should be taken in using the equations. It is preferred to apply all the suitable equation for a given point.

According to this study, for pure methane, mixture of methane and ethane, as well as

mixtures similar to natural gas, Bahadori has presented the perfect results. Safamirzaei provides the most accurate equation for the natural gas mixtures.

For the mixture of ethane, butane or nitrogen with other compounds, Hammerschmidt presents the precisest result. Motiee calculates the most exact result for the mixture of methane and ethane.

The proposed empirical correlation in the present study has shown reliable performance for both simple natural gas components and mixtures. Despite the existence three adjustable parameters, the accuracy of this equation shows the ranking 1 to 3 compare to the rest of the equations.

Since the type of hydrate formed depends on their former and each of the equation provides the best results for a particular group of compounds, it is proposed to investigate the relationship between the type of hydrate and the equations.

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