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# PECTIN AS A BIOLOGICAL KINETIC INHIBITOR ON THE NUCLEATION OF GAS HYDRATES

**Bárbara Louise Lemos Drumond Silva**

**Bruna Carolina Lemos Drumond Silva**

**Bonifácio de Oliveira Fialho**

**José Adilson de Castro**

Laboratório de Fluídos e Termociências, Departamento de Engenharia Metalúrgica e Materiais, Universidade Federal Fluminense, Avenida dos Trabalhadores N° 420, CEP 27225-125, Volta Redonda, RJ, Brasil.

barbara.drumond@gmail.com

xbrunadrumondx@hotmail.com

bonifaciofialho@id.uff.br

joseadilsoncastro@id.uff.br

**Adriana Teixeira**

Centro de Pesquisa e Desenvolvimento Leopoldo Américo Miguêz de Mello, Avenida Horácio de Macedo N° 950, CEP 21941-598, Rio de Janeiro, RJ, Brasil.

adriteix@petrobras.com.br

**Abstract.** *The study of hydrate formation has increasingly attracted the world of science as a matter of immediate application and of high importance, mainly in the oil and gas industries. Understanding the kinetics of hydrate formation and its dissociation is very important. The formation of gas hydrate can cause blockage of ducts in oil unit production and transportation with subsequent loss of production and possible safety problems. Traditionally, the prevention of hydrate-plug formation has been done with thermodynamic inhibitors, however, economic and environmental factors allied to technical problems associated with thermodynamic inhibitors have motivated research and new development to identify technological alternatives such as kinetic inhibitors. Among the kinetic inhibitors polysaccharides such as pectin are potential candidates. The present work aims to study the effect of pectin as a biological kinetic inhibitor on the nucleation of gas hydrates. The experimental runs were carried out on a high pressure cell and the pectin performance was compared with the well-known inhibitor ethanol. The pectin showed superior inhibition effect under temperature range of 2 to 6 °C, demonstrating potential for using as biological hydrate inhibitor.*

**Keywords:** *Gas Hydrate, Kinetic Inhibitors, Pectin.*

## 1. INTRODUCTION

Gas hydrates are crystalline solids composed of water and gases of small molecular weight (Fig.1) formed at low temperatures and high pressure (Machado, 2009). Hydrate crystallization is a process that consists of two stages: nucleation and growth. In the nucleation stage, the first hydrate nuclei (clusters) are formed, and these must achieve a critical radius before further growth becomes thermodynamically favourable. Nucleation can be induced (through crystal seeds) or can occur spontaneously through random molecular interactions (Kaschiev, 2000). The conditions of formation and stability of gas hydrates are determined by the relationship between three variables: concentration of the hydrate-forming gas, temperature and pressure (Oliveira *et al.*, 2010).

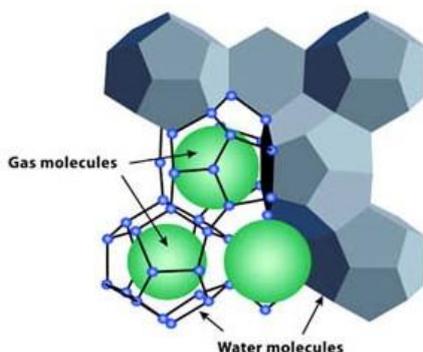


Figure 1. Gas Hydrate formation and structural aspect (Gundersen, 2013)

The three main families of gas hydrates are the cubic structures I and II and the H hexagonal structure (TRUEBA *et al.*, 2014) as can be seen in Fig. 2.

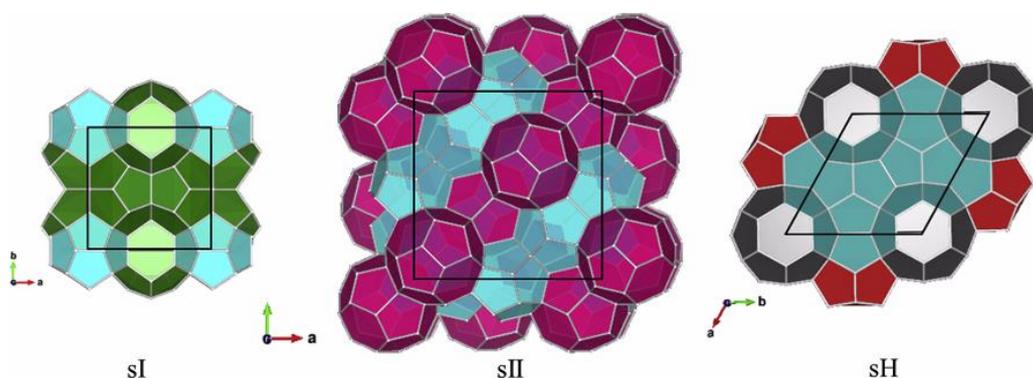


Figure 2. Gas Hydrate Families (RIPMEESTER *et al.*, 2016)

These compounds are common in the continental margins of the entire globe, forming an immense reservoir of natural gas. A study by the United States Geological Survey (USGS) estimates that the amount of natural gas stored as hydrates in permafrost and ocean sediments is twice that of all other fossil fuels combined (Gandara *et al.*, 2015). However, hydrate blockages also hinder oil/gas pipeline transportation, and, despite their huge potential as energy sources, our insufficient understanding of hydrates has limited their extraction (Sa *et al.*, 2016). According Daraboina *et al.* (2014), the formation of gas hydrates is one of the major challenges of the oil and gas industry in the last decades.

Companies in the oil sector are continually working to increase the exploration and production of oil and gas. In some systems, the fluids from the reservoir (gas, oil and water) are directed to the platform through a pipeline, where processing is performed. These pipes remain under extreme conditions of low temperatures and high pressures, providing favourable conditions for the formation of gas hydrates (SERPA, 2015).

Thus, understanding the kinetics of hydrate formation and its dissociation is very important for the oil industry in general, which wants the unrestricted flow of oil and gas into pipelines (ANDRADE, 2009).

Traditionally, prevention of hydrate formation has been done with thermodynamic inhibitors, commonly methanol or glycol, at high dosages (Daraboina *et al.*, 2011). In Brazil the usage of ethanol is common. However, economic and environmental factors and technical problems associated with thermodynamic inhibitors have motivated research and development to identify alternative technologies such as low dosage hydrate inhibitors (LDHIs) (Daraboina *et al.*, 2013). Some LDHIs prolong the induction time for hydrate nucleation (kinetic hydrate inhibitor, KHIs), while others prevent the agglomeration of hydrate crystal (anti-agglomerants) (Daraboina *et al.*, 2011).

There are few researchers that develop natural inhibitors, for example, chitosan, tapioca, amino acid, and antifreeze protein (Xu, *et al.*, 2010; Lee and Englezos, 2007; Daraboina *et al.*, 2011; Sa *et al.*, 2013; Walter *et al.*, 2015; Sa *et al.*, 2016; Perfeltd *et al.*, 2014; Xu, P. *et al.*, 2016). These natural products showed positive effects on the hydrate inhibition. The polysaccharides pectin is also among the environmentally friendly alternatives kinetic inhibitors and has recently been studied by Xu, S. *et al.* (2016) and Xu, P. *et al.* (2016). According to Xu, S. *et al.* (2016), pectin has good inhibition performance coupled with high biodegradability and competitive cost.

Pectin, a family of complex heteropolysaccharides consisting predominantly of partially methoxylated galacturonic acid residues, is extensively found in almost all of the fruits and vegetables as the structural unit of fresh cells and the

junction between the cells. Its structure (Fig. 3) is based on 1, 4-linked  $\alpha$ -D-galacturonic acid, interrupted by L-rhamnose residues with side-chains of neutral sugars, mainly D-galactose and L-arabinose (Guo *et al.*, 2014).

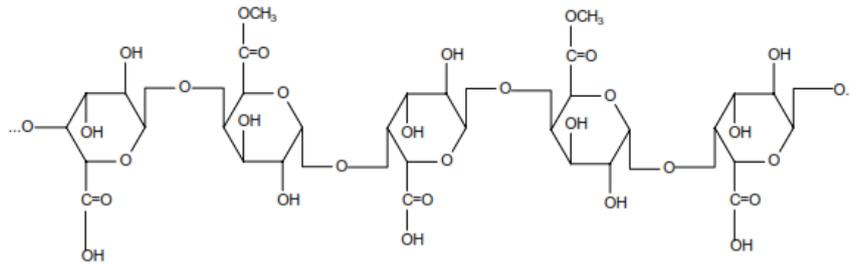


Figure 3. Pectin Structure (Bobbio and Bobbio, 1995)

Pectin, as a well-known food additive, is widely used as thickener, emulsifier and stabilizer in a variety of industrialized food, pharmaceutical and cosmetic products. Pectin has been extracted from various agricultural by products, including orange peel, apple pomace, lemon and sugar beet pulp, specifically, the orange peel and apple pomace are abundant and contain high levels of pectin polysaccharides (Guo *et al.*, 2014).

The present work aims to extend the understanding of the mechanisms of gas hydrate formation and inhibition as well as to evaluate the performance of polysaccharide pectin as a biological kinetic inhibitor on the nucleation of gas hydrates.

## 2. EXPERIMENTAL PROCEDURE

The experiments were carried out in the Hydrates laboratory of the Leopoldo Américo Miguez de Mello Research and Development Center (CENPES) and in the Laboratory of Fluids and Thermosciences of the Engineering School of the Universidade Federal Fluminense (UFF).

The solutions for the experiment were prepared by diluting the pectin (Dinâmica, Brazil) or ethanol in deionized water. The study evaluated the pectin and ethanol at the concentrations of 0.3% and 10%, respectively. Pectin concentration was chosen based on the article by Xu, S. *et al.* (2016) and ethanol concentration was defined according to the desired modification in the hydrate envelope curve (Fig. 4).

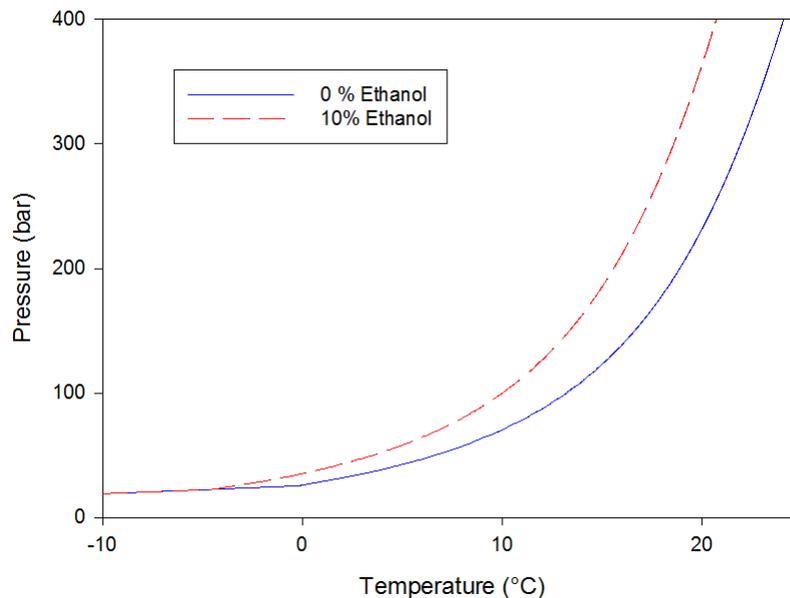


Figure 4. Hydrate Formation Curve for Gas Standard Mixture (CENPES, 2016)

At first, the gas hydrate formation studies were performed in the Hydrates laboratory of the Leopoldo Américo Miguez de Mello Research and Development Center using a Top Industrial high pressure cell with the Proline RP845 bath from Lauda (Germany), coupled. The analyses for the evaluation of the solutions of 0,3% pectin and 10% ethanol as inhibitors were done at the temperature of 4°C and pressure of 100 bar, using a standard gas mixture (87,06% C<sub>1</sub>,

10% C<sub>2</sub>, 2% C<sub>3</sub>, 0,05% i-C<sub>4</sub>, 0,04% n-C<sub>4</sub>, 0,03% i-C<sub>5</sub>, 0,02% n-C<sub>5</sub>, 0,4% N<sub>2</sub>, 0,4% CO<sub>2</sub>) as the hydrate-forming for sub cooling of 15.5°C.

In a second moment, the evaluation of the 0,3% pectin solution was performed in the Laboratory of Fluids and Thermosciences of the Engineering School of the Universidade Federal Fluminense using a high pressure cell from Hydrafact Ltd (United Kingdom) with the refrigerated/heating circulator F25 from JULABO (Germany), coupled. The experiments were performed over a range of temperatures (2°C~6°C) and pressure of 100 bar, using the methane as the hydrate-forming gas for sub cooling of 11°C, 9°C and 7°C, respectively (Fig.5).

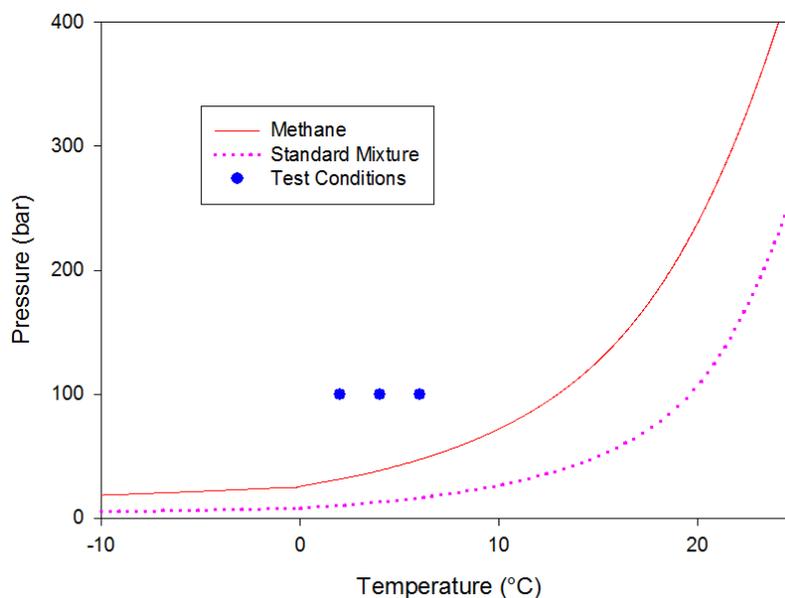


Figure 5. Hydrate envelope curve (CENPES, 2016)

The approximate amount of gas in the system per time period was calculated using Eq. 1 and the gas consumption rate during the experiment is calculating using the relation shown in Eq. 2.

$$n = PV/RT \quad (1)$$

$$\text{Gas consumption rate} = dn/dt \quad (2)$$

Where  $n$  is the number of moles (mol),  $P$  is the pressure (Pa),  $V$  is the gas volume (m<sup>3</sup>),  $R$  is the universal gas constant ( $R=8.31 \text{ m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ),  $t$  is time and  $T$  is the temperature (K) in the reactor cell.

### 3. RESULTS AND DISCUSSION

The experiments performed evaluated the gas hydrate formation curve for the studied systems (Fig. 6 and 7). In these experiments is possible to see the pressure drop due to incorporation of gas in the solution and the consumption of gas due to gas hydrate formation. In Figure 6, the result for the solution with 10% of ethanol shows both events clearly: a first little drop due to the solution saturation, and a second drop (at 2 h) due to gas hydrate formation. Sometimes both events happen at the same time, as in the test with 0,3% of pectin in the same figure. The result with pure water shows this two events occurring till 2h, and then a sharp decrease of pressure associated to a increased rate of conversion of hydrates.

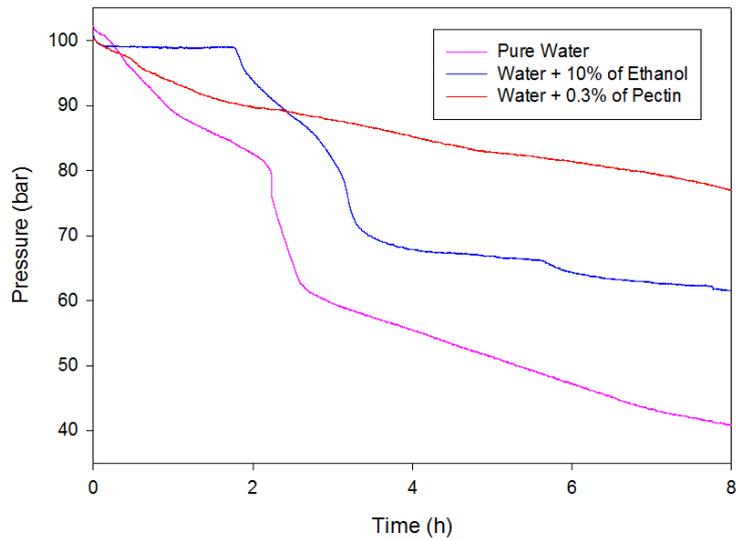


Figure 6. Pressure *versus* time plot for the CENPES studied systems at 4°C, using the gas mixture

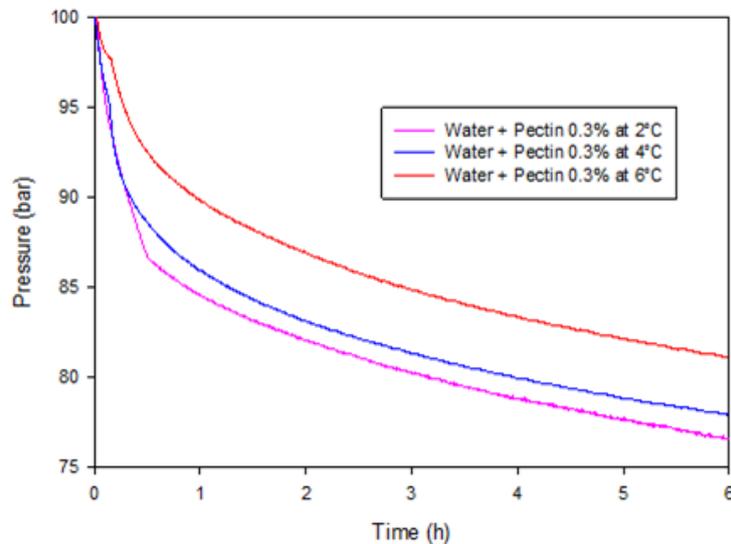


Figure 7. Pressure *versus* time plot for the UFF studied systems, using methane

Figure 6 shows that there was a lower formation of hydrates in the water + ethanol system compared to the pure water system. This may be explained by the lower subcooling in the presence of ethanol. Its possible to observe too that water + pectin system delayed the gas hydrate formation when compared with pure water system. Figure 7 demonstrates that increasing subcooling (by lowering the temperature), increases the rate of hydrate formation. This behavior is confirmed by Bai and Bai (2012), for them, when subcooling increases, the hydrate formation time decreases exponentially.

It is worth mentioning that the hydrates formed in the presence of the Standard Mixture gas (CENPES studied systems) have a type II structure, whereas the hydrates formed in the presence of the Methane gas (UFF studied systems) have a expected type I structure.

The volume of hydrate formed in the water + standard gas mixture system was analyzed on the basis of gas consumption, which in turn was obtained by pressure variation throughout time (Fig. 8).

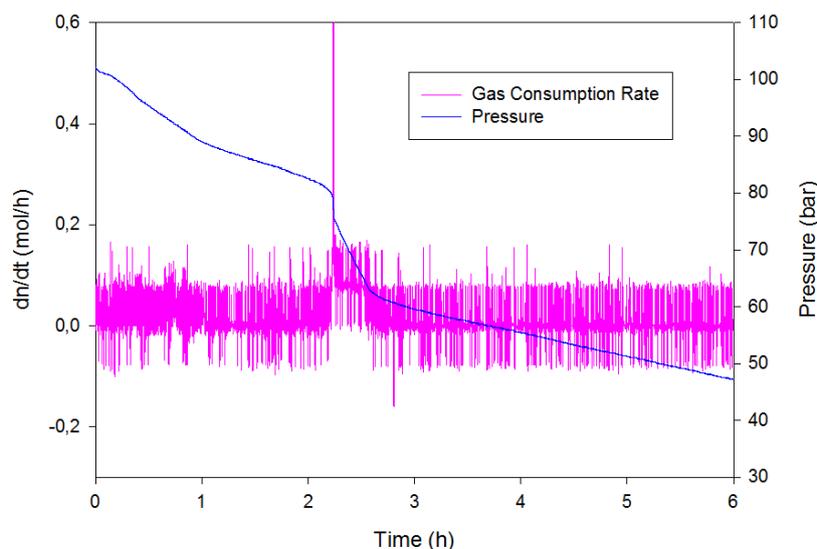


Figure 8. Gas consumption rate and the pressure curve over time for the water + standard gas mixture system at 4°C

It can be observed that where there is greater pressure drop, there is also a higher consumption of gas, showing that in these regions the formation of hydrates occurs.

Xu, S. *et al.* (2016) also found that pectin could retard methane hydrate formation and suppress the hydrate growth. According Xu, S. *et al.* (2016), with lots of oxygen or hydroxyl groups in the pectin structure, pectin could form hydrogen bonds with water molecules, perturbing the water structure. They indicated that water molecules could break the hydrogen bonds between hydroxyl and carbonyl groups of pectin through water and pectin molecular forming H-bonds. At same time, these effects result in decreasing the water activity. Additionally, after nucleation, the hydrophilic structure enables pectin to retard hydrate crystal growth. Oxygen atoms of pectin bind to the surface of hydrate crystal through hydrogen bonds. Consequently, the  $\alpha$ -D-galacturonosyl units of pectin can enhance the steric hindrance and thus suppress crystal growth.

The same behavior was also observed by Xu, P. *et al.* (2016). They observed that the higher the concentration of pectin is, the better the effect of inhibition is. According Xu, P. *et al.* (2016), the double-bonded oxygen atoms of pectin combine with hydrogen atoms of water, and the hydrogen atoms of hydroxyl in pectin combine with oxygen atoms of water through hydrogen bonds, which disturbed the further growth of the methane hydrate. The role of the pectin's active groups in hydrogen bonds with water both as proton donor and as electron acceptor makes pectin have a better inhibitory effect on the growth of methane hydrate.

#### 4. CONCLUSIONS

The results confirmed the inhibitory effects of pectin demonstrated by the behavior of the pressure over the experiment time. The results relating the gas consumption rate over time indicated that was possible to identify the events where the increase in gas consumption occurred in the systems studied. It is assumed that gas consumption is directly linked to the formation of gas hydrates and therefore the hydrate formation rates were calculated. The results demonstrated the superior inhibition effects of pectin compared with the ethanol, for a certain period of time. Thus we concluded that pectin is a promising biological kinetic hydrate inhibitor for the the oil and gas industry.

#### 5. ACKNOWLEDGEMENTS

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#### 6. REFERENCES

- Bai, Y. and Bai, Q., 2012. *Subsea Engineering Handbook*. Gulf Professional Publishing, Waltham.
- Bobbio, P.A. and Bobbio, F.O., 1995. *Introdução à química de alimentos*. Varela, São Paulo, 2<sup>nd</sup> edition.
- Daraboina, N., Linga, P., Ripmeester, J., Walker, V. K. and Englezos, P., 2011. "Natural gas hydrate formation and decomposition in the presence of kinetic inhibitors. 2. Stirred reactor experiments". *Energy & Fuels*, Vol. 25, p. 4384-4391.

- Daraboina, N. Malmos, C. and Solms, N. V., 2013. "Investigation of kinetic hydrate inhibition using a high pressure micro differential scanning calorimeter". *Energy & Fuels*, Vol. 27, p. 5779-5786.
- Daraboina, N., Linga, P., Ripmeester, J., Walker, V. K. and Englezos, P., 2014. The unusual growth behavior of methane/ethane/propane hydrate crystals in the presence of inhibitor at low pressure. In *Proceedings of the 8th International Conference on Gas Hydrates*. Beijing, China.
- Gandara, R., Liguori, F. A., Casazza, F., Rodeguer, M. G., Maisonnave, P. P. and Bermann, C., 2015. Aproveitamento energético do hidrato de metano. In *10º Congresso sobre Geração Distribuída e Energia no Meio Rural*. São Paulo, Brasil.
- Gundersen, A., 2013. *Evaluation of Methods for Drilling and Production of Hydrate Formations*. Norwegian University of Science and Technology, Trondheim, Noruega.
- Guo, X., Zhao, W., Pang, X., Liao, X., Hu, X. and Wu, J., 2014. Emulsion stabilizing properties of pectins extracted by high hydrostatic pressure, high-speed shearing homogenization and traditional thermal methods: A comparative study. *Food Hydrocolloids*, Vol. 35, p. 217-225.
- Kaschiev, D., 2000. *Nucleation: Basic Theory and Applications*. Butterworth-Heinemann, New York.
- Lee, J. D.; Wu, H. and Englezos, P., 2007. Cationic Starches as Gas Hydrate Kinetic Inhibitors. *Chemical Engineering Science*, Vol. 62, p. 6548-6555.
- Machado, C. X., 2009. *A importância do hidrato de gás como fonte de energia alternativa e como possível agente das mudanças climáticas*. Universidade Federal de Santa Catarina, Santa Catarina, Brazil.
- Oliveira, M. B., Castro, J. A. and Silva, A. J., 2010. Formação de hidratos de gás em escoamento monofásico. In *Proceedings of the VI Congresso Nacional de Engenharia Mecânica*. Campina Grande, Brazil.
- Perfeldt, C. M., Chua, P. C., Daraboina, N., Friis, D., Kristiansen, E., Ramlov, H., Woodley, J. M., Kelland, M. A. and Solms, N. V., 2014. Inhibition of gas hydrate nucleation and growth: efficacy of na antifreeze protein from the Longhorn Beetle *Rhagium mordax*. *Energy & Fuels*, Vol. 28, p. 3666-3672.
- Ripmeester, J. A. and Alavi, S., 2016. Some current challenges in clathrate hydrate science: Nucleation, decomposition and the memory effect. *Current Opinion in Solid State and Materials Science*, Vol. 20, p. 344-351.
- Sa, J. H.; Kwak, G. H.; Lee, B. R.; Park, D. H.; Han, K. and Lee, K. H., 2013. Hydrophobic Amino Acids as a New Class of Kinetic Inhibitors for Gas Hydrate Formation. *Scientific Reports*, Vol. 3, p. 2428.
- Sa, J. H., Kwak, G. H., Han, K., Ahn, D., Cho, S. J., Lee, J. D. and Lee, K. H., 2016. Inhibition of methane and natural gas hydrate formation by altering the structure of water with amino acids. *Scientific Reports*, Vol.6, p. 31582.
- Serpa, S. F., 2015. Estudo do comportamento termodinâmico e cinético de misturas água + MEG na presença de CO<sub>2</sub> e sais. Universidade Tiradentes, Aracajú.
- Trueba, A. T., Kroon M. C., Peters, C. J., Moudrakovski, I. L., Ratcliffe, C. I., Alavi, S. and Ripmeester, J. A., 2014. Inter-cage dynamics in structure I, II, and H fluoromethane hydrates as studied by NMR and molecular dynamics simulations. *The Journal of Chemical Physics*, Vol. 140, 214703.
- Walker, V. K., Zeng, H., Ohno, H., Daraboina, N., Sharifi, H., Bagherzadeh, S. A., Alavi, S. and Englezos, P., 2015. Antifreeze proteins as gas hydrate inhibitors. *Canadian Journal of Chemistry*, Vol. 93, p. 839-849.
- Xu P., Lang X., Fan S., Wang Y. and Chen J., 2016. Molecular dynamics simulation of methane hydrate growth in the presence of the natural product pectin. *The Journal of Physical Chemistry C*, Vol. 120, p. 5392-5397.
- Xu, S., Fan, S., Fang, S., Lang, X., Wang, Y. and Chen, J., 2016. Pectin as an Extraordinary Natural Kinetic Hydrate Inhibitor. *Scientific Reports*, Vol.6, p. 23220.
- Xu, Y. J., Yang, M. L. and Yang, X. X., 2010. Chitosan as Green Kinetic Inhibitors for Gas Hydrate Formation. *Journal of Natural Gas Chemistry*, Vol. 19, p. 431-435.

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