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Rheological study on CO_2 hydrate slurries for secondary refrigeration

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To help the fight against climate change, the Kigali deal has planned to eliminate hydrofluorocarbon's use (HFC) in industrial systems. HFCs are powerful greenhouse gases with a high global warming potential. Moreover, HFCs are commonly used as a refrigerant within secondary refrigeration processes for cold production. A solution to limit their negative environmental impact would be to reduce the amount of HFC by using a phase change slurries (PCS) in the secondary loop. A PCS is composed of solid phase change particles (solid-liquid) in a liquid transportation phase. Clathrate hydrates are crystalline particles where gas molecules are trapped in water cages. Due to their high energy densities, hydrate slurries, in particular CO_2 hydrates, are relevant two-phase secondary fluids because they enhance the energy efficiency of secondary refrigeration systems. In this study, the rheological behaviour of CO_2 hydrate slurries in various experimental conditions on a dynamic loop for cold distribution was investigated. An exhaustive state-of-the-art rheological study of hydrate slurries in aqueous solution has pointed out that hydrate slurries are non-Newtonian fluids. However, the rheological behaviour could be different for the same kind of hydrate slurry according to the literature. Moreover, the literature review also highlighted that the most used measurement method for the apparent viscosity is the capillary viscometer. We used a semi-empirical Herschel-Bulkley's model for determining the apparent viscosity of the CO_2 hydrate slurry as a function of the hydrate slurry fraction. This work is primordial for designing and sizing a new efficient refrigeration system based on this innovative material.

Keywords: CO_2, hydrate slurries, rheology, dynamic loop, secondary refrigeration

INTRODUCTION

In many industrial fields the production of cold is primordial, especially in agroalimentary, chemistry or transport. Producing the necessary energy for refrigeration has a real environmental impact. Indeed, it is responsible for approximately 8% of greenhouse gas emissions. To reduce this negative impact, the problematics has been discussed during international protocols, such as Kyoto in 1977 or Montreal in 1985 and more recently at Kigali in October 2016. The need to find new refrigerants, neutral for the environment is an urgent matter.

Secondary refrigeration is a method that consists of using an environmental neutral fluid for the transport of cold in order to reduce the use of hydrofluorocarbon that has a negative greenhouse effect. Two-phase refrigerants (solid-liquid) are relevant because of their energetic density higher than single-phase refrigerants thanks to the latent heat in melting. These refrigerants are composed with phase change material (PCM) as solid particles in a liquid transportation phase. The most common phase change slurry (PCS) used in the industry is ice slurry. However, an important amount of energy is lost by the mechanical processes needed with ice slurries. Relevant two-phase refrigerants for secondary refrigeration are hydrate slurries formed by hydrates crystals in aqueous solution [1].

Hydrate clathrates are caged structures formed from water molecules connected by hydrogen bonds. A guest molecule (CO_2, CH_4 …) is trapped inside the clathrates cages that suits the molecule size. CO_2 hydrates have a higher dissociation enthalpy (550 kJ kg_{water}^{-1} or 374 kJ $kg_{hydrate}^{-1}$) [2] than water (333 kJ kg^{-1}). To form hydrate slurry, the suitable temperature is more than 273 K, which is in the range of temperature for refrigeration application such as air conditioning, cold production for fridges, etc.

To use hydrate slurries in refrigeration applications, good fluids conditions at the pressure and temperature equilibriums are required. In order to get those conditions, multiple studies have been made to understand the kinematic and rheological behaviour of CO_2 hydrate slurries.

During the last decades, lots of rheological studies to determine hydrate slurries behaviour have been carried out. Different methods have been used to define the rheology of this refrigerant. Depending on the chosen equipment, the study phase (aqueous, organic or with additives) and the method, diverse behaviours of hydrate slurries have been found. In previous works, CO_2 hydrate slurries have been studied in aqueous phase [3–7]. HC hydrate slurries are usually studied in an organic phase [8–19]. Viscometer methods to categorize the behaviour of the slurry can be of several types: capillary, rotating, magnetic or plate. The most used one in rheological studies is the capillary viscometer method (describe in paragraph 2.3). Oyama et al. [3] have characterized the dynamic viscosity of CO_2 hydrate slurries in aqueous phase as increasing before nucleation starts and then decreasing. In 2008, Delahaye et al. [4] have performed rheological study of CO_2 hydrate slurries in aqueous phase using the capillary viscometer method by which they have defined the slurries' behaviour as Ostwald-de Waele shear thickening, Hershel-Bulkley shear thinning and with an apparent viscosity from 4 to 42 mPa s. A few years later, Jerbi et al. [5] tested CO_2 hydrate slurries in a different system and described the fluid's behaviour as Ostwald-de Waele and shear thinning.

To characterise the fluids, Clarke and Bishnoi measured CO_2 hydrates particle size distribution with a focused beam reflectance method (FBRM) probe [20]. Their results show that the chord length and diameter variate between 0 and 18 microns.

To work with CO_2 hydrate slurries, the formation of these hydrates happens at a pressure higher than 1 MPa. The addition of promoters, as quaternary salt is a solution to reduce the equilibrium pressure. Previous studies revealed that TBPB (tetra-n-butylphosphonium) can be an effective promoter [21]. Indeed they have the ability of being stable at the atmospheric pressure.

This article presents the rheological research of mixed CO_2 and TBPB hydrate slurries carried out on a dynamic loop. The behaviour of hydrate slurries is measured with the capillary viscometer method.

MATERIALS AND METHODS

Dynamic loop

During precedent studies [7, 15, 22], a dynamic loop (Fig. 1) was used to characterize rheological properties of hydrate slurries. The loop is composed of stainless steel pipes with an internal diameter of 8 mm and a thickness of 2 mm. The total length of the loop is 2 m. The loop is placed in a thermo-regulated by PID cold room, equipped with a control opening. The loop is equipped with a visualisation glass tube, with an inner volume of $3\ 10^{-5}$ m^3 for detecting the formation of hydrate particles. The liquid is flowing thanks to a pump (AxFlow GC-M25) that has a maximum flow rate for pure water of 0.08 $m^3\,h^{-1}$. The device is also composed of a differential pressure gauge

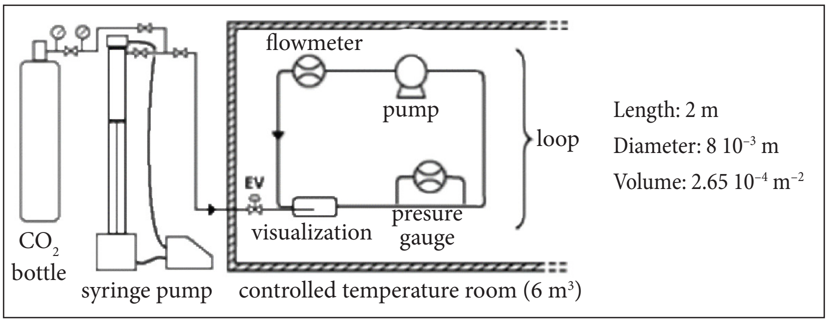

Fig. 1. Scheme of the dynamic loop

(ABB 265 DS, up to 0.02 MPa, ±0.04%), placed on a straight line that measures the pressure drop due to the fluid flow. The maximum pressure inside the loop is kept at 3.5 MPa by a safety valve that frees gas above this maximum pressure. The loop is equipped with 6 T-type thermocouple (±0.3 K) and 2 pressure gauges within a range of 0 to 5 MPa (accuracy 0.05%).

The materials used for this experiment are water, TBPB salt, and CO_2 gas that is injected in the loop, as described in the following paragraph.

Protocol for gas injection

After filling the loop with water, the temperature is decreased to the minimum conservation temperature. Once the temperature is reached, the loop is injected with gas. In order to control the injection of CO_2 inside the loop, a syringe pump (1000D ISCO) is used. At first, the syringe pump, which is a cylinder of the volume of 1000 cm^3, is filled with gas. By knowing the pressure, temperature and volume inside the cylinder, we are able to calculate with the real gas equation the number of CO_2 gas moles inside the syringe pump. The pressure inside the syringe pump decreases once the gas is injected in the loop. As the volume and temperature of the cylinder are constant, the number of CO_2 gas moles injected inside the loop can be calculated by the difference between the number of moles when the pump was filled and the one after the injection.

Capillary viscometer

Rheology allows us to determine the fluid flow properties and study the deformation of the fluid subjected to stress. Fluids are classified into two principal categories, Newtonian or non-Newtonian fluid. If shear stress has an impact on the fluid viscosity, the fluid is called non-Newtonian. Otherwise the fluid is Newtonian, as water's viscosity is independent of shear stress.

Non-Newtonian fluids behaviour independent of time can be classed as pseudoplastic or shear thinning, dilatant or shear thickening, Bingham or Herschel-Bulkley, depending on the influence of the yield stress. To describe the behaviour of these fluids, we use the Bingham generalized model:

$$\tau - \tau_c = k\dot{y}, \tag{1}$$

where τ is the shear stress (Pa), $\dot{y}$ is the shear rate (s^{-1}), τ_c is the yield stress, k is the fluid consistency coefficient ($Pa.s^n$), and n is the behaviour index. If n is different from 1, then the fluid is non-Newtonian. On the contrary, if $n = 1$ and $\tau_c = 0$, then the fluid is called Newtonian.

For the dynamic loop presented, the experimental method that will be used to determine the fluid's rheogram is the capillary viscometer. In order to apply this method, some hypotheses were taken. The fluid is incompressible; the flow is laminar, with no-slip and no heat condition to the walls. With the balance equation, we can use the generalized form of Rabinowitsh and Mooney's equation. The shear rate can be expressed with the shear rate at the walls:

$$\frac{Q}{\pi R^3} = \frac{1}{\tau_w^3}\int_0^{\tau_p} \tau \dot{y}_w d\tau, \tag{2}$$

where Q is the volume flow ($m^3.s^{-1}$), R is the pipe radius (m), $\dot{y}_w$ and τ_w, are, respectively, the wall shear rate and shear stress at the walls. The shear stress is calculated as a function of the experimental data obtained for the pressure drop ΔP. The pipe length is called L and its diameter D:

$$\tau_p = \frac{D\Delta P}{4L}. \tag{3}$$

The shear rate is expressed as a function of the flow rate

$$\dot{y}_p = \frac{8U_d}{D}\left(\frac{3n+1}{4n}\right). \qquad (4)$$

Thus, the index n can be determined as follows, from the experimental data:

$$n = \frac{d\ln\left(\frac{D\Delta P}{4L}\right)}{d\ln\left(\frac{8U_d}{D}\right)}. \qquad (5)$$

The apparent viscosity is expressed as the ratio between the shear stress and the shear rate at the walls:

$$\mu_{app} = \frac{\tau_p}{\dot{y}_p}. \qquad (6)$$

RESULTS AND DISCUSSION

Liquid water in the dynamic loop

In order to verify the proper accuracy of the method and the equipment, the first experiment was carried out on liquid water. As the water behaviour is known as Newtonian at 274 K and under atmospheric pressure.

At a different flow rate (from approximately 25 l h^{-1} to 80 l h^{-1}), temperature inside the loop and pressure drop were measured. To find the behaviour index and thus to characterise the fluid, the method of capillary viscometer (as described in the precedent paragraph) was used. The behaviour index obtained with experimental data was around 1, as it should be for a Newtonian fluid. Moreover, the yield stress τ_c was equal to 0.

Mixed CO_2-TBPB hydrate slurry

The experiment was carried out in the system described on paragraph 2 with tetra-n-butylphosphonium bromide (TBPB) and CO_2 gas injected in a cold liquid (in our case, the liquid is water). TBPB is quaternary salt used for gas separation and cold transportation. TBPB hydrate can trap a small gas molecule, such as CH_4 or CO_2. Moreover, TBAB hydrate slurries are already used as a secondary refrigerant in various air-conditioning systems [22].

The temperature of the water in the loop is about 10°C and the pressure studied is about 12 bar. In the slurry, three different volume solid fractions were formed: we tried to compare the experimental rheological behaviour of mixed TBPB-CO_2 hydrate slurry with the ones found in the previous studies. By using the experimental data of the differential pressure and the flow rate, we were able to describe the behaviour of the slurry.

First, the behaviour index n is found with the experimental data. The method is represented in Fig. 2. The behaviour index is determined by the slope steering coefficient for each volume solid fraction. For a solution with mixed CO_2-TBPB hydrates, the behaviour index is really different from 1, which characterize these slurries as non-Newtonian.

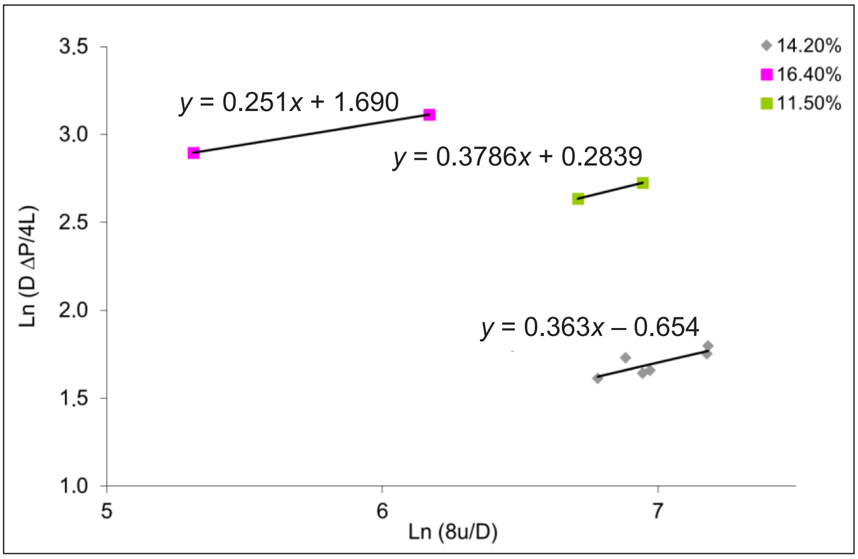

Fig. 2. Determination of the behaviour index n of a mixed CO_2-TBPB hydrate slurry for differentvolume solid fraction

For the cases with 11.50% and 16.40% volume fraction, there are only two points to draw the line. In these cases, the hydrates are not sufficiently stable. Indeed, the agglomeration of the particles happens too fast to allow more readable experiments. However, the error of each point is less than 5% and is based on the numerous experimental data that have been carried on.

Figure 3 presents the behaviour index *n* evolution of the mixed hydrate slurries of CO_2 and TBPB for a volume hydrate fraction from 0% to 16.4%. The index is decreasing as the volume hydrate fraction is increasing, which characterize the fluid as pseudoplastic. For 0%, the behaviour is significantly above 1, which presents the fluid as non-Newtonian.

The evolution of the consistency coefficient *k* is presented in Fig. 4 with a comparison with some previous works on TBPB hydrate slurries [1] and CO_2 hydrate slurries [2].

The coefficient becomes more than 1 above 15% of the volume solid fraction.

As for other results in the literature, the Ostwald-de Waele behaviour is obtained as the yield stress is considered equal to 0. The apparent viscosity law is expressed as a function of the volume solid fraction:

$$\mu_{app} = 5.0.10^{-4}\exp(52.78 \cdot \varphi_s)\dot{\gamma}_w^{\,1.387\exp(-10.307\,\varphi s)}. \quad (7)$$

Figure 5 is a comparison of the apparent viscosity obtained with the model and the one obtained with the experimentation. The model describes precisely the experimental values. However, the fluid behaviour changes depending on the volume solid fraction, and it can be

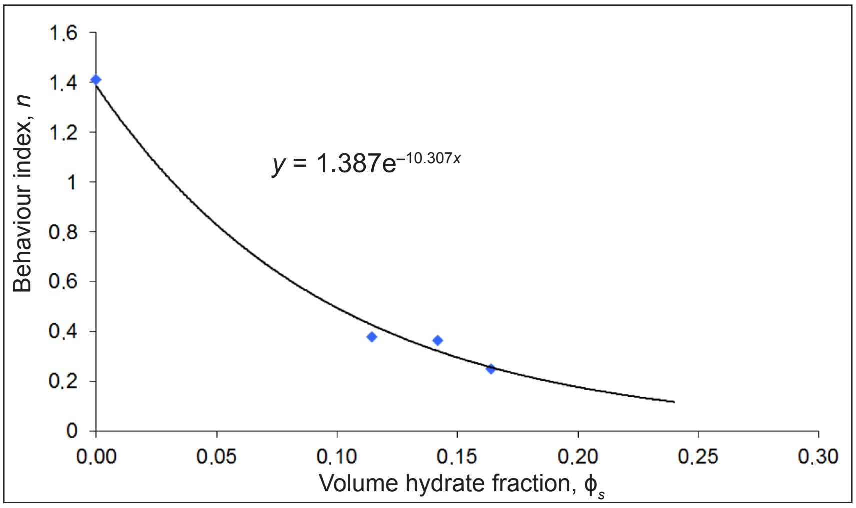

Fig. 3. Variation of the behaviour index *n* as a function of volume hydrate fraction

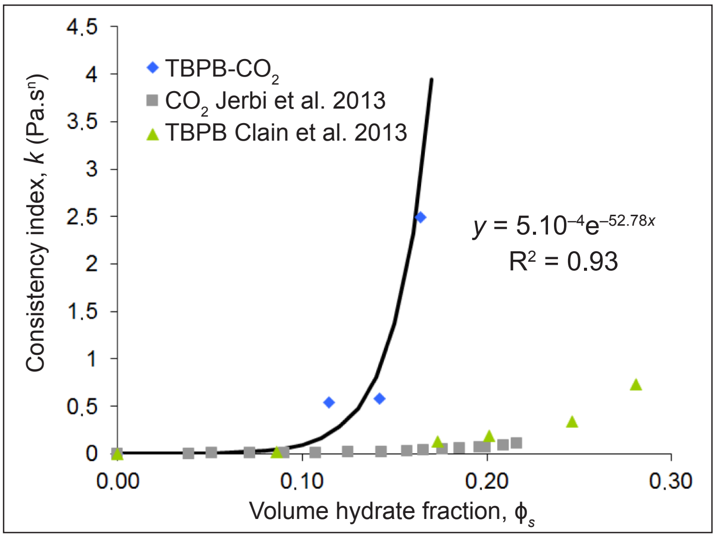

Fig. 4. Variation of the consistency coefficient *k* as a function of the volume solid fraction

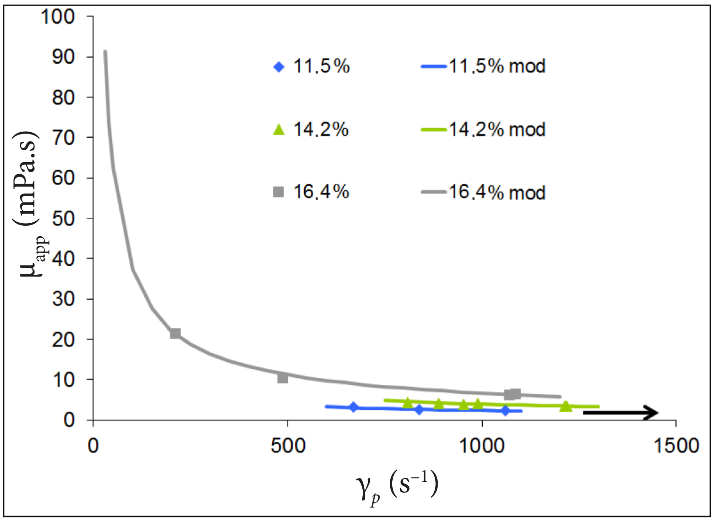

Fig. 5. Apparent viscosity of the mixed CO_2-TBPB hydrate slurries

discussed. It is difficult to explain the shear thickening behaviour of the slurry without hydrates and the change of behaviour when the volume fraction increases.

On Fig. 6, the variation of the apparent viscosity of simple and mixed hydrate slurries for a volume solid fraction between 0 and 16% is presented. The shear rate is fixed at 400 s^{-1} and compared to the results obtained for CO_2 [2], TBPB [1] and CO_2 with SDS (Sodium Dodecyl Sulphate – anti-agglomerate surfactant) [3] hydrate slurries. The simple hydrate slurries (gas or salt) exhibit a conventional shear-thinning behaviour. Their apparent viscosity increases when the solid fraction is greater because the resistance of the flow increases due to the stronger particle–particle interactions. The mixed hydrate slurry also behaves as a shear-thinning up to 12% vol. with very reasonable viscosities and close to those of the CO_2 hydrate slurries alone. Beyond this, the viscosity increases rapidly. At low shear rates, the flow velocity is too low to ensure good homogeneity and sufficient dispersion of the hydrates in the slurry. Agglomeration phenomena occur and the apparent viscosities increase to reach very high levels. The addition of gas to the simple hydrates of TBPB appears to increase markedly and to amplify the agglomerant character of the slurry. The addition of a kinetic inhibitor is therefore necessary to maintain easy flow conditions. Finally, these results call into question the hypothesis of considering the yield stress as null, in particular beyond the solid fraction of the slurry of 15% vol.

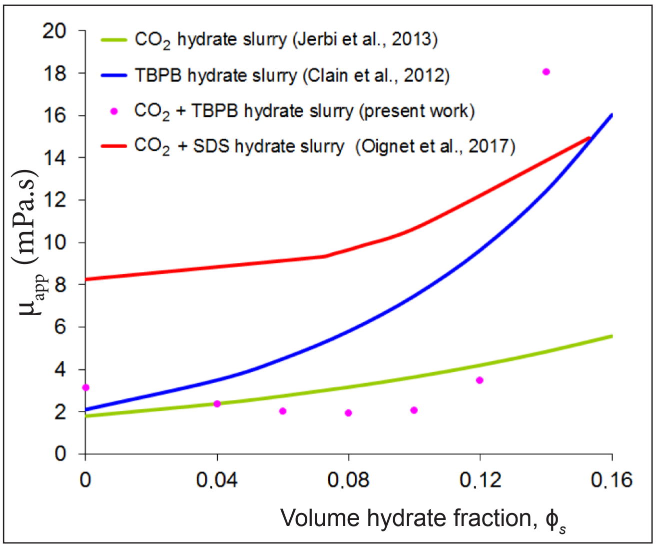

Fig. 6. Comparison of the apparent viscosities of hydrates slurries for a shear rate at 400 s^{-1}

CONCLUSIONS

A lower equilibrium pressure and higher temperature make mixed CO_2-TBPB hydrate slurries a good phase change material for cold storage application.

The behaviour of the mixed hydrate of CO_2 slurries in the presence of TBPB was studied in a dynamic loop with a capillary method. The slurries were characterised as non-Newtonian and for the presence of the volume solid fraction, the behaviour of the fluid becomes shear thinning. The apparent viscosity of the mixed hydrate slurry follows the Ostwald-de Waele law. However, beyond the solid fraction of 15% vol., the apparent viscosity of the slurry increases significantly and reaches very high values. The addition of an antiagglomerant agent may then be necessary to maintain proper flow conditions. This study must be followed to obtained more results in order to approve the model developed. Moreover, different volume solid fractions can be studied (above 16.4% vol.).

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References

1. Clain P., Delahaye A., Fournaison L., Mayoufi N., Dalmazzone D., Fürst W. Rheological properties of tetra-n-butylphosphonium bromide hydrate slurry flow. *Chemical Engineering Journal.* 2012. Vol. 193–194. p. 112–122.
2. Jerbi S., Delahaye A., Oignet J., Fournaison L., Haberschill P. Rheological properties of CO_2 hydrate slurry produced in a stirred tank reactor and a secondary refrigeration loop. *International Journal of Refrigeration.* 2013. Vol. 36. P. 1294–1301.
3. Oignet J., Delahaye A., Torré J.-P., Dicharry C., Hoang H. M., Clain P., Osswald V., Ziad Y., Fournaison L. Rheological study of CO_2 hydrate slurry in the presence of Sodium Dodecyl Sulfate in a secondary refrigeration loop. *Chimical Engineering Sciences.* 2017. Vol. 158. P. 294–303.
4. Fukushima S., Takao S., Ogoshi H., Ida H., Matsumoto S., Akiyama T., Otsuka T. Development of high density cold latent heta with clathate hydrate. *NKK Technical Report*. 1999. Vol. 166. P. 65–70.
5. Delahaye A., Fournaison L., Jerbi S., Mayoufi N. Rheological properties of CO_2 hydrate slurry flow in the presence of additives. *Industrial & Engineering Chimical Research*. 2011. Vol. 50. P. 8344–8353.
6. Marinhas S., Delahaye A., Fournaison L. Solid fraction modelling for CO_2 and CO_2-THF hydrate slurries used as secondary refrigerants. *International Journal of Refrigeration*. 2007. Vol. 30. P. 758–766.
7. Oyama H., Ebinuma T., Shimada W., Takeya S., Nagao J., Uchida T., Narita H. Viscosity increase before nucleation of CO_2 gas hydrate. *Proceedings of the 4th International Conference on Gas Hydrates, Yokohama, Japon*, 2002.
8. Delahaye A., Fournaison L., Marinhas S., Martinez M. Rheological study of CO_2 hydrate slurry in a dynamic loop applied to secondary refrigeration. *Chemical Engineering Science*. 2008. Vol. 63. P. 3551–3559.
9. Andersson V., Gudmundsson J. Flow experiments on concentrated hydrate slurries. *Proceedings of the 1999 SPE Annual Technical Conference and Exhibition: 'Production Operations and Engineering – General', Houston, TX, USA*, 1999.
10. Austvik T., Bjorn M. The transportability of hydrates in pipes. In: *Multiphase Transportation III. Roros, NPS*, 1992.
11. Fidel-Dufour A., Herri J.-M. Formation and transportation of methane hydrate slurries in a flow loop reactor: influence of a dispersant. *Proceedings of the International Conference on Multiphase Flow, Alba, Italy*, 2002.
12. Peysson Y., Maurel P., Vilagines R. Hydrate transportability in multiphase flow. *Proceedings of the International Conference on Multiphase: Extending the Boundaries of Flow Assurance*, 2003.
13. Webb E., Koh C., Liberatore M. Rheological properties of methane hydrate slurries formed from AOT+Water+Oil microemulsions. *Langmuir*. 2013. Vol. 29. P. 10997–11004.
14. Webb E., Koh C., Liberatore M. High pressure rheology of hydrate slurries formed from water-in-mineral oil emulsions. *Industrial & Engineering Chemical Research*. 2014. Vol. 53. P. 6998–7007.

15. Webb E., Rensing P., Koh C., Sloan E., Sum A., Liberatore M. High-pressure rheology of hydrate slurries formed from water-in-oil emulsions. *Energy Fuels*. 2012. Vol. 26. P. 3504–3509.
16. Yan K., Sun C., Chen J., Chen L., Shen D., Liu B., Jia M., Niu M., Lv Y., Li N., Song Z., Niu S., Chen G. Flow characteristics and rheological properties of natural gas hydrate slurry in the presence of anti-agglomerant in a flow loop apparatus. *Chemical Engineering Science*. 2014. Vol. 106. P. 99–108.
17. Camargo R., Palermo T., Sinquin A., Glenat P. Rheological characterization of hydrate suspensions in oil dominated systems. *Annals of the New York Academy of Sciences*. 2000. Vol. 912. P. 906–916.
18. Cameirao A., Fezoua A., Ouabbas Y., Herri J., Darbouret M., Sinquin M., Glénat P. Agglomeration of gas hydrate in a water-in-oil emulsion: experimental and modeling studies. *International Conference on Gas Hydrates (ICGH), Edimbourg*, 2011.
19. Gainville M., Sinquin A., Darbouret M. Hydrate slurry characterisation for laminar and turbulent lows in pipelines. *International Conference on Gas Hydrates (ICGH), Edinburgh*, 2011.
20. Peng B.-Z., Chen J., Sun C.-Y., Dandekar A., Guo S.-H., Liu B., Mu L., Yang L.-Y., Li W.-Z., Chen G.-J. Flow characteristics and morphology of hydrate slurry formed from (natural gas+diesel oil/condensate oil+water) system containing antiagglomerant. *Chemical Engineering Sciene*. 2012. Vol. 84. P. 333–344.
21. Clarke M. A., Bishnoi P. Determination of the intrinsic kinetics of CO_2 gas hydrate formation using in situ particle size analysis. *Chemical Egineering Science*. 2004. Vol. 60. No. 3. P. 695–709.
22. Pascal C., Anthony D., Laurence F., Salem J., Nadia M., Didier D., Walter F. Characterization of mixed CO_2-TBPB hydrate for refrigeration applications. *Proceedings of the 7th International Conference on Gas Hydrates, Edinburgh, Scotland, United Kingdom*, 2011.

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CO_2 HIDRATŲ SUSPENSIJOS PANAUDOJIMO ANTRINIAM ŠALDYMUI REOLOGINIAI TYRIMAI

Santrauka

Kovojant su klimato kaita, vadovaujantis Kigalio susitarimu, planuojama apriboti hidrofluorangliavandenilių (HFC) dujų naudojimą pramoninėse sistemose. HFC yra šiltnamio efektą sukeliančios dujos, galinčios turėti didelę neigiamą įtaką klimatui. Be to, HFC dujos dažniausiai naudojamos kaip žemos temperatūros šaltinis šalčio gamybai antriniuose šaldymo procesuose. Neigiamą poveikį aplinkai būtų galima apriboti sumažinant HFC dujų kiekį naudojant faziniais virsmais pasižyminčias suspensijas antriniame kontūre. Fazinio virsmo suspensija yra sudaryta iš kietos agregatinės būsenos dalelių (kietasis kūnas-skystis) skystoje transportavimo fazėje. Klatrato hidratai yra kristalinės dalelės, kuriose dujų molekulės įstrigusios vandens kristaluose. Dėl didelio energijos tankio hidrato suspensija, ypač CO_2 hidratai, yra svarbūs dviejų fazių antriniai fluidai, nes jie didina šaldymo sistemų efektyvumą. Šiame darbe buvo tiriamas CO_2 hidratų suspensijos reologinis elgesys esant įvairioms sąlygoms dinaminėje šalčio pernešimo sistemoje. Išsamus hidrato suspensijų reologijos tyrimas parodė, kad hidratų suspensija yra neniutoninis skystis. Tačiau literatūroje aprašoma, kad tos pačios rūšies hidratų suspensijų reologinis elgesys gali būti skirtingas. Be to, literatūros apžvalgoje taip pat pabrėžiama, kad dažniausiai naudojamas klampos matavimo prietaisas yra kapiliarinis viszometras. Autoriai naudojo pusiau empirišką Herschel-Bulkley modelį, skirtą nustatyti CO_2 hidratų suspensijoje esamą klampumą kaip hidrato suspensijos frakcijos funkciją. Šio darbo rezultatai leis sukurti naują efektyvią šaldymo sistemą.

Raktažodžiai: CO_2, hidratų suspensija, reologija, dinaminė kilpa, antrinis šaldymas