Contents lists available at ScienceDirect

Energy

Rheological study of mixed cyclopentane + CO_2 hydrate slurry in a dynamic loop for refrigeration systems

Nada Chami [a,b,*], Yasmine Salehy [b], Dennis Burgner [d], Pascal Clain [c,b], Didier Dalmazzone [a], Anthony Delahaye [b], Laurence Fournaison [b]

[a] UCP/ENSTA Paris, Institut Polytechnique de Paris, Palaiseau, France
[b] Université Paris-Saclay, INRAE, FRISE, 92761, Antony, France
[c] Léonard de Vinci Pôle Universitaire, Research Center, 92916, Paris la Défense, France
[d] Benjamin Levich Institute and Department of Chemical Engineering, The City College of New York, Grove School of Engineering, New York, NY, 10031, United States

ARTICLE INFO

ABSTRACT

The use of CO_2 hydrates as phase change materials is promising for secondary loop refrigeration, as these compounds present adjustable dissociation temperature that can be higher than 273.15 K and have high enthalpy of dissociation. In the present work, by using various promoters, cyclopentane (CP) in this study, the formation pressure of hydrates may be significantly lowered than CO_2 hydrates. For their application as a secondary refrigerant, the rheological properties of mixed CP + CO_2 hydrate slurry need to be controlled. The flow properties of CP and mixed CP + CO_2 hydrate slurries were studied in a dynamic flow loop at different cyclopentane contents ranging from 3 wt% to 15 wt%, using a capillary viscometer based on Rabinowitch and Mooney equation. Rheological parameters (viscosity, flow behavior...) related to these two slurries were compared. The experimental results demonstrate that CP and mixed CP + CO_2 hydrates slurries exhibit a shear thinning behavior and the viscosity values vary between 3 and 12 mPa.s-1 at [100–1000 s^{-1}] for CP hydrates slurries and between 2 and 10 mPa s^{-1} at [100–1200 s^{-1}] for CP + CO_2 hydrates slurries. CP hydrate and CP + CO2 hydrate slurry viscosity is close to that of TBPB hydrate and lower than that of CO_2 hydrate. Moreover, mixed CP + CO_2 have shown a time-evolution of the rheological behavior.

1. Introduction

With 20% of electricity consumption worldwidel, refrigeration and air conditioning (RAC) industry is one of the most energy-intensive sectors [1]. Among the solutions to reduce RAC carbon footprint, it is possible to implement environment-friendly fluids in indirect refrigeration systems which roled is to carry thermal energy from the cold production machine (containing primary refrigerant) to the places of use. indirect refrigeration systems using secondary refrigerants thus greatly reduces primary refrigerant amount (by about a factor of 10) [2]. Currently, the use of phase change materials (PCM) in indirect refrigeration systems (to form PCM slurry) is an innovative design in development. They improve the process by increasing the energy density of the fluid [3].

For air conditioning purposes, the phase change material slurry must have specific physical requirements such as a phase change temperature between 273 K and 285 K, a high enthalpy of dissociation, low viscosity, good thermal stability and conductivity, and must not present a significant environmental impact (GWP<10).

Ice slurries are widely used in industry, but there are other of slurries are under development such as hydrates. Other kind of slurries could be considered such as gas hydrates, which present the advantage of having a melting temperature above 273 K and are stable under moderate pressure conditions (0.1–0.4 MPa). Gas hydrates have the advantage of being produced by non-mechanical methods by simple gas injection in a pre-cooled solution [4]. One of the most studied gas hydrates in the refrigeration field is carbon dioxide. The latent heat of CO_2 hydrate is 500 kJ.kg_{water}^{-1}, which is higher than that of ice (333 kJ. kg_{water}^{-1}) [5]. The phase change temperatures of CO_2 hydrate range of 273–283 K, corresponding to the temperatures suitable for air-conditioning systems, and high formation pressures (1.5–4.5 MPa).

Considering the importance of having favorable formation conditions for hydrates to support safe and cost-effective indirect refrigeration applications, several studies have been developed to evaluate the

---

* Corresponding author. UCP/ENSTA Paris, Institut Polytechnique de Paris, Palaiseau, France.
 E-mail address: nadachami65@gmail.com (N. Chami).

formation conditions to reach the appropriate pressure-temperature with the combination of several promoters to form mixed hydrates. Frequently used promoters are tetrahydrofuran (THF) to form mixed THF + CO_2 hydrates [6], tetrabutylammonium bromide (TBAB) [7], tetra-*n*-butylphosphonium bromide (TBPB) [8] and cyclopentane C_5H_{10} (CP) [9]. These additives are themselves able to form hydrate slurries at atmospheric pressures and low temperatures contrary to gas hydrates [10]. Cyclopentane is a low volatility and low-pressure alkane. It is known to be a good PCM material for cold storage applications. The formation conditions of CP hydrate are realized at the temperature range of 279–285 K at formation pressures between 0.01 and 0.02 MPa, which is well within the operating conditions of conventional air conditioners. However, the latent heat of CP hydrate is 252.2 kJ kg$_{water}^{-1}$, half the value of CO_2 hydrate, which reduces the cold storage density. Zhang et al. [11] studied the formation of CP hydrate in emulsion. CP hydrates require a high degree of subcooling to form, due to CP's low solubility in water, but this can cause ice crystals to form, impeding hydrate growth. The subcooling is also a problem for applications of CP hydrates, as it lowers the temperature required for the phase change, reducing the efficiency of RAC systems. CP can be used as thermodynamic promoter to form mixed CP + CO_2 structure II hydrates which are more stable than CO_2 hydrates in the same equilibrium conditions. These hydrates also present favorable equilibrium conditions of formation [8,11] and kinetic characteristics [16]. These studies have shown that CP + CO_2 hydrate slurry form in the temperature range of 279–285 K at formation pressures between 0.01 and 0.45 MPa and have a high dissociation enthalpy (462.5 ± 1.5 kJ$_{water}^{-1}$) and a heat capacity value not too much further away from that of ice slurries (1479.09 ± 137.43 J K^{-1}.kg$_{hydrate}^{-1}$ at 0.25 MPa) [12]. Nevertheless, in order to be implemented as phase change material slurries in secondary loop refrigeration, these hydrate slurries must present good flowability in the pipes. For this reason, a rheological characterization of mixed CP + CO_2 hydrate slurry is essential. Therefore, a rheological characterization of mixed CP + CO_2 hydrate slurry is essential.

However, until now, no research work has been conducted to explore the rheological properties of mixed CP + CO_2 hydrate slurry but some rheological studies dedicated to CP hydrate have been presented [17, 18]. Table 1 summarizes various studies on rheological parameters of CP hydrate slurries such as viscosity, stress, strain using typical experimental rheometers. The effects of various parameters on the slurries viscosity has been studied, mainly the dependence on the water content in the W/O emulsions .

The studies conducted by Ahuja et al. [19] showed that CP hydrate slurry exhibit a shear-thinning behavior for shear stresses ranging from about 5 to 4600 Pa between 16% and 30% water cut. Majid et al. [18] compared between two types of systems: (1) non-emulsified system (2) emulsified system. They concluded a non-emulsified system can be characterized into five different stages (cooling, initial impeller growth, adhesion to wall, sloughing, steady state), and three different stages (cooling, initial hydrate formation, steady state) for the emulsified

system. Additionally, decreases in viscosity were found to be caused by the break-up of the hydrate particles and their rearrangement. To understand the role of water to hydrate conversion on rheological properties, Karanjkar et al. [20] proposed a mechanism in which the hairy and porous hydrate growth, combined with the enhanced agglomeration due to liquid bridges formed by wetted water, to explain the viscosity evolution during CP hydrate slurries formation in an oil-emulsions system. The hydrate slurry viscosity was determined to increase with the water volume fraction in the emulsions (the viscosity ranges from 0.4 Pa s for 10% of water to 200 Pa s for 45% of water).

Sandoval et al. [20] present a rheological study of CP hydrate slurry in a model water in oil emulsion. They found that the CP hydrate formation occurred only when a subzero temperature pretreatment was imposed on the sample. The CP hydrate slurry presents elasticity below a yield stress and a shear thinning behavior above it. Ahuja et al. [22] studied emulsions of water in a continuous organic phase containing kerosene and cyclopentane. The hydrate slurry exhibited shear-thinning behavior when cycled up and down in shear rate. Zylyftari et al. [23] compared the rheological properties of two types of emulsions, emulsions forming CP hydrate and forming - ice emulsion. The relative viscosity of CP hydrate slurry forming an emulsion was found to be two orders of magnitude higher. Liu et al. [24] performed hydrate formation experiments and rheological tests in both a flow loop and a stress-controlled rheometer with different wax contents. The rheological results conducted in the flow loop revealed a thixotropic behavior of waxy hydrate slurries that decreases with the increasing wax content. In an attempt to improve the flow quality of CP hydrates slurries, Chen et al. [25] chose to add wax at different concentrations to W/O emulsion mixtures. They studied the impact of wax on the viscosity of the CP hydrate slurry for a content of 3 wt% to 5 wt% wax using a stress-controlled rheometer. They concluded that the final viscosity of the hydrate slurry and shear stress increase with the wax content.

In this work, the rheological characteristics of oil-in-water CP hydrate slurries that forms at atmospheric pressure measured in a capillary viscometer are presented, which is a novelty given that previous rheological studies on CP hydrate slurries were performed with rotational rheometer and very often using water-in-oil emulsions. In addition, the rheological behavior of mixed CP + CO_2 hydrate slurry (also performed in a capillary viscometer) are presented for the first time.

2. Materials and methods

The following section describes materials and experimental procedure used to form hydrate slurries and to study their rheology in loop.

2.1. Materials and set-up

The fluids used in the experiments were distilled and degassed water and cyclopentane purchased from Acros Organics (Molar purity: 0.97). Carbon dioxide was obtained from Air Liquide (Molar purity: 0.99995).

Table 1
Summary of rheological behavior of CP hydrate slurries.

References	Solution	Measurement method	Water cut (%)	Rheological behavior	Shear rate (s^{-1})
Zylyftari et al. [23]	Water-in-oil emulsion	Stress-control-type rheometer	40	Viscoelasticity	1–100
Ahuja et al. [22]	Water-in-Kerosene emulsion	Stress-control-type rheometer	40	Viscoelasticity	1–100
Ahuja et al. [19]	Water-in-oil emulsion	Stress-control-type rheometer	18	Thixotropic	1–100
Karanjkar et al. [20]	Water-in-oil emulsion	Stress-control-type rheometer	10–45	Shear thinning	1–100
Majid et al. [18]	Water-in-oil emulsions & non-emulsified system	Stress-control-type rheometer	10 excess of cyclopentane	Thixotropic	1000
Chen et al. [17]	Waxy water-in-oil emulsion	Stress-control-type rheometer	20–30	Shear thinning	1–300
Sandoval et al. [21]	Water-in-oil emulsion	Stress-controlled rheometer	20–30	Shear thinning	0.1–10
Liu et al. [24]	Waxy water in oil emulsion	Stress-controlled rheometer + Flow loop	20	Thixotropic	50–600
Chen et al. [25]	Waxy and wax-free emulsion	Stress Controlled rheometer	20–35		100–600

Table 2
Cyclopentane and carbon dioxide data.

Name	Formula	Solubility in water (cm^3/100 g of water)	Molar mass (g.mol^{-1})	Density (g. dm^{-3})	ΔH_{vap} (kJ. mol^{-1})	Phase
Carbon dioxide	CO_2	90.1 (at 293 K)	44.01	1.87	15.33	Gas
Cyclopentane	C_5H_{10}	Almost none	70.13	751	28.8	Liquid

All materials were used without further purification (Table 2).

Experiments were carried out in a dynamic loop as shown in Fig. 1, composed of 344 ml stainless steel pipes with an 8 mm internal diameter and a 10 mm external diameter. It is also equipped with seven T-type thermocouples (± 0.3 K), two pressure gauges (0–400 mbar $\pm 0.04\%$) from Sensit and Transintruments (0–5 MPa, $\pm$ 0.05%), an electromagnetic flowmeter (IFM6080K-type Vatiflux, 0.5%) (0–1800 l h-1 $\pm$ 2.5%), and a pump (220-type, Maximum flow rate = 0.17 m3.h-1). The loop is equipped with a ABB 266 DSH differential pressure gauge to measure pressure drops generated by the slurry ($\Delta X = \pm 0.125\%$) (Fig. 1).

2.2. Experimental procedure

The experimental procedure was developed to study the flow characteristics and rheological behavior of cyclopentane and mixed CP + CO_2 hydrate slurries at different fractions of cyclopentane. The rheological characterization is first conducted for CP hydrate slurry (hydrate slurry that forms using only cyclopentane) at different CP fractions (3 wt %, 5 wt %, 7 wt %, 10 wt %, 12 wt %, and 15 wt %) in order to achieve different hydrate fractions. The same procedure is followed, and the same CP fractions are used to characterize the mixed CP + CO_2 hydrate slurries. The following steps are the procedure for preparing each of the CP mixtures. First, the mixture is prepared by mixing water and a given amount of CP, depending on the desired percentage. This mixture is then converted into an emulsion of O/W using a homogenizer (IKA T25 digital ULTRA TURRAX) operating at the speed of 18,000 rpm for 15 min. The homogenized emulsion is immediately transferred into the dynamic loop, which is located in a controlled cold room providing a homogenous temperature inside the whole loop. In order to define the experimental protocol of hydrate slurry formation, and to perform rheological characterization, the thermo-physical properties (density, solid fraction, CO_2 fraction …) used in this paper were evaluated using the thermodynamic conditions (P, T …) at the equilibrium. To form CP hydrate slurries, the temperature in the loop is set at 272 K (since CP hydrate equilibrium temperature in pure water range from 279.3 to 280.7 K) [10], with an initial flow rate of 120 l. h^{-1} and at atmospheric pressure. In the case of mixed CP + CO_2 hydrate slurry, the formation stage is obtained by cooling the CP-Water emulsion to a temperature of 280 K after applying a pressure around 1.5 MPa using a calibrated injection (4 ml. min^{-1}) of gas by a syringe pump 1000D ISCO. The flow rate in the loop is identical to that of CP hydrate slurry, 120 l. h^{-1}. During the temperature decrease, a sudden increase in pressure drop occurs when CP or mixed CP + CO_2 hydrate slurries appear.

After hydrate slurry formation and stabilization of the system, the rheological analysis is achieved using an indirect method based on the capillary viscometer principal, also known as Ostwald viscometer, described in previous work [26,27]. It consists of circulating a fluid and determining its rheological parameters by relating the flow rate (or velocity) of the fluid to the pressure drop it generates in a straight pipe. The capillary viscometer geometry is well suited to slurries where basic configuration is to circulate in a flow loop. Additionally, the local heating that can lead to partial melting of the PCMs (and therefore modify the solid fraction of the slurry) is limited to a capillary viscometer, unlike the rotary rheometers that have small air gaps between their moving parts (cylinders, cones, etc.) and therefore areas of potential heating and melting.

The relationship between pressure drop and flow rate is based on a force balance [28], with several assumptions such as a laminar regime and the absence of wall slip, and whose principle is as follows: a specific quantity of fluid passing through a tube with a certain flow rate generates a pressure drop induced by the friction of the fluid at the wall. The assumption related to the laminar regime will be checked in the present paper. The absence of wall slip will be admitted in the first approach. The equation resulting from this force balance then expresses the flow rate as a function of the shear stress and the shear rate:

$$Q/_{\pi R^3} = {}^1\!/_4 \left(8u/_D \right) = {}^1\!/_{\tau_w^3} \int_0^{\tau_w} \tau^2 \dot{\gamma} d\tau \qquad (Eq.\ 1)$$

With Q the volume flow, R the pipe radius, $\dot{\gamma}$ the shear rate, τ the shear stress. τ_w is the shear stress at the wall, related to regular pressure drops ΔP in a pipe of length L and diameter D by the following equation:

$$\tau_w = D\Delta P/_{4L} \qquad (Eq.\ 2)$$

After derivation of the (1), the Rabinowitsch-Mooney equation, expressing shear rate at the wall, can be deduced [29]:

$$\dot{\gamma}_w = \left(8u/_D \right) (3n+1)/_{(4n)} \qquad (Eq.\ 3)$$
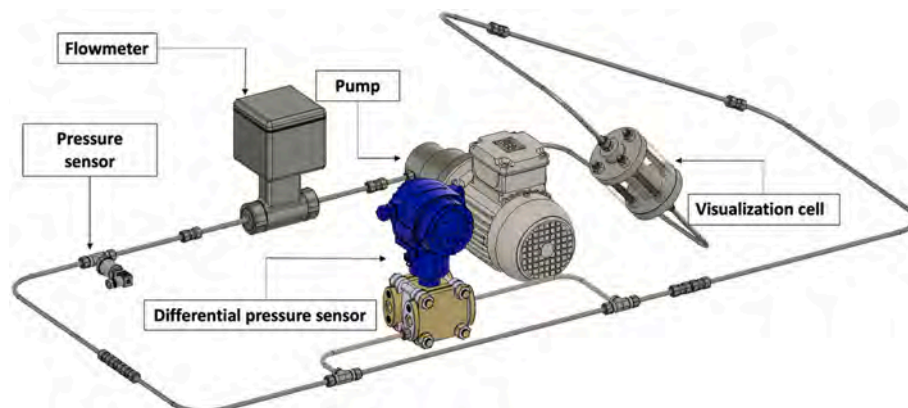
with *n* the behavior index defined as:

Fig. 1. Experimental loop.

$$n = d(\ln \tau_w) \Big/ d \ln \left(8u/D \right) \qquad \text{(Eq. 4)}$$

To implement the capillary viscometer method, various flow rates and pressure drops must be applied in order to correlate ΔP to U and in turn, τ_w to $\dot{\gamma}$. Fig. 2 shows an example of experimental data obtained when applying various flow rates resulting in various pressure drops and Fig. 3 show the appearance of hydrates after formation in the circulation loop.

Finally, the rheological behavior of the fluid can be modeled based on the pressure drop and flow velocity, using Herschel-Bulkley's model:

$$\tau_w = \tau_0 + k \, \dot{\gamma}_w^n \qquad \text{(Eq. 5)}$$

where k and τ_0 are the consistency index and the yield stress, respectively.

In addition, the apparent viscosity μ_{app} of the slurry can be defined as the ratio between the stress and the shear rate [30]:

$$\mu_{app} = \tau_w / \dot{\gamma}_w \qquad \text{(Eq. 6)}$$

In the present procedure, flow rate plateaus are applied from the highest to the lowest values, and then increasing from the lowest to the highest flow rate (Fig. 2) in order to determine the evolution as a function of time of the rheological properties of cyclopentane and mixed CP + CO_2 hydrate slurries.

Finally, for each plateau, the pairs (ΔP, Q) can be converted into the couple curve (τ_w, $8U/D$), based on previous equations. Then the behavior index n, as described by (4), corresponds to the slope of the representative curve of the function $\tau_w = f(8U/D)$. Likewise, the consistency index k and the yield stress τ_0, as described by (5), corresponds to the slope and the intercept of the representative curve of the function $\tau_w = g\left(\left(\frac{8U}{D}\right)^n\right)$, respectively.

The goal will be to study the behavior of CP hydrate and mixed CP + CO_2 hydrate slurries, compare the behavior between two types of hydrate slurries, and develop a semi empirical model that could better characterize the effect of CP as a thermodynamic promoter on the CO_2 hydrates.

3. Results and discussion

An analysis of the experimental results of CP hydrate and mixed CP + CO_2 hydrate slurries is detailed in this section. An empirical rheological model based on a Herschel-Bulkley equation for each type of hydrate slurry is proposed from these results.

To define the errors propagation for the measurements of different rheological parameters, two types of uncertainty can be determined: the degree of the uncertainty related to the experiments, which can be provided by the instrument manufacturer (Section 2.1). The second uncertainty is related to the measurement noise corresponding to each measured experimental plateau (this method is more representative since it also includes instrument-related errors).

The statistical uncertainty propagation related to measurement noise was evaluated in this work using the Student's law within a 95% confidence [31] to determine the measurement errors on pressure drop ΔP and flow rate Q for each measured experimental plateau, each having a sample size of 100 measurements. Then, the propagation of these errors on the rheological parameter calculations (shear stress, shear rate, behavior index …) was determined to have a student coefficient of 2.9467, using a 99% confidence interval. Additionally, the method also allowed verification of the point distribution within the 95% confidence interval.

The loop was loaded with various CP fractions: 3, 5, 7, 10, 12, and 15 wt %. Rheological results in the loop were performed and presented as a function of the CP fractions used, as it is the case for the other rheological work on CP hydrate slurry. From a theoretical point of view and as explained by Ref. [10], the CP fractions studied ranging from 3 to 15 wt % correspond to CP hydrate solid fractions ranging from 17 to 84%, which is a very high solid fraction.

In addition, there is no method described in the literature to determine experimental fractions of CP hydrate or mixed CP + CO_2 hydrate slurries, like there is for the case of CO_2 hydrate slurries where a mass balance can be directly resolved from PVT data [32,33]. Indeed, in the case of CP hydrate slurry, the mass balance requires knowing the rate of conversion of CP to hydrate, which can be partial and heterogeneous (crystallization only at the surface of the CP droplets). For mixed CP + CO_2 hydrate slurry, CO_2 can dissolve in both water and CP, which complicates the balance. The use of the circulation loop makes determining this fraction in an exact and detailed way complicated. This requires the presentation of results as a function of CP fraction in order to avoid a misinterpretation of solid fraction values and to be consistent with data from literature. The final discussion of these results in term of a hydrate fraction will be only theoretical.
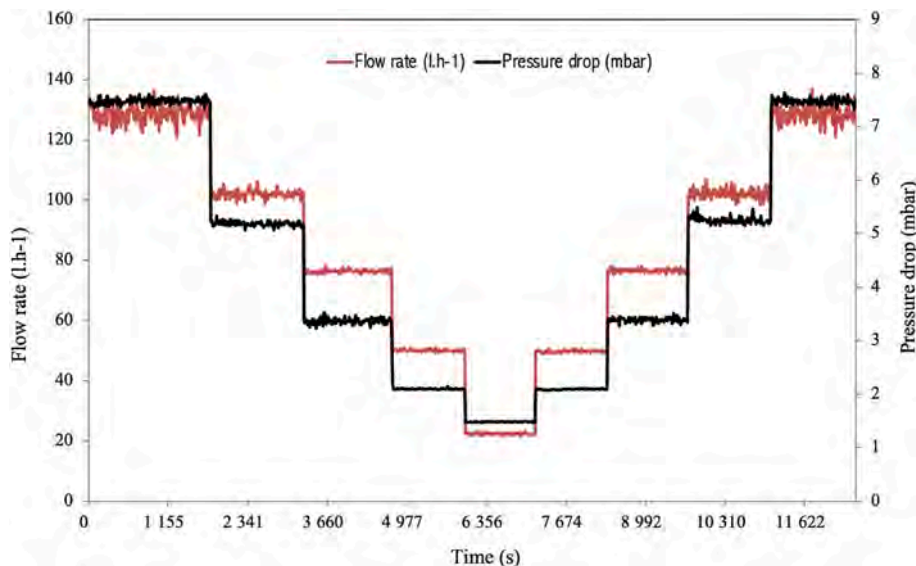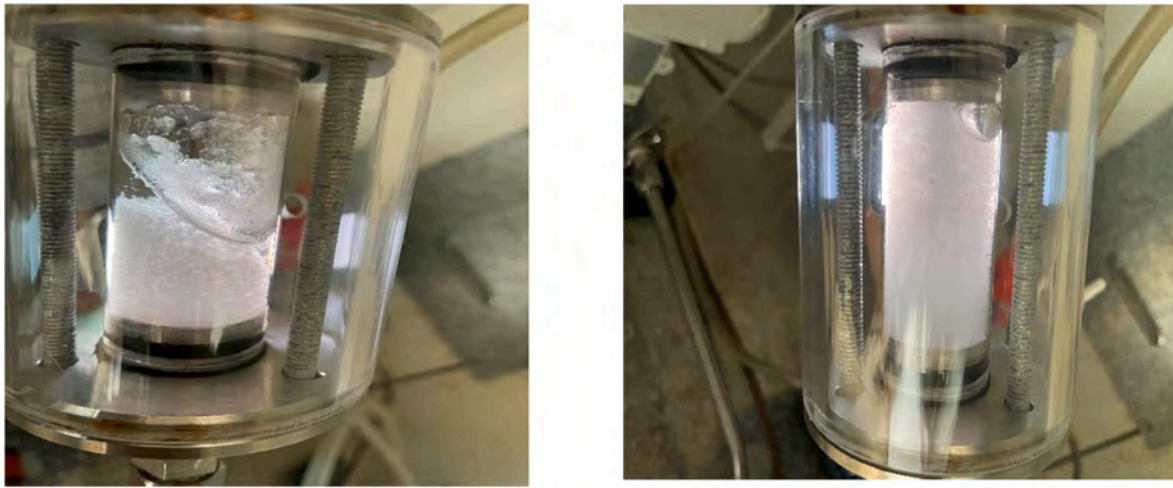

Fig. 2. Experimental protocol.

Fig. 3. 12 wt% of mixed CP + CO2 hydrate slurry in the loop at (a) t = 0 (b) t = 16 h

3.1. Rheological properties of CP and mixed CP + CO$_2$ hydrate slurries

As described in the methodology part, the rheological behavior is characterized by several criteria as the behavior index, n. Fig. 4, represents the evolution of the behavior index n of CP and mixed CP + CO$_2$ hydrate slurries. The behavior index decreases with the increase of the CP fraction used x_{CP}, meaning that CP hydrate slurry exhibits a non-Newtonian behavior increasingly with the increase of the amount of CP hydrate slurry formed in the loop. Fig. 4 shows also that the behavior index value above 1 for cyclopentane fraction below 5 wt%. The behavior index was approximated by (7) for CP hydrate slurry and by (8) for mixed CP + CO$_2$ hydrate slurry:

$$n = -3.33\,x_{CP} + 1.16 \qquad \text{(Eq. 7)}$$

$$n = -3.58\,x_{CP} + 1.27 \qquad \text{(Eq. 8)}$$

From this 5 wt% CP fraction and above, the behavior index is lower than 1. This difference suggests that the shear-thinning behavior of CP hydrate and mixed CP + CO$_2$ hydrate slurries is not validated for all CP fraction used. Another explanation could be related to the limit of application of the method since inertial terms, meaning that laminar/turbulent transition regime is not controlled, can also explain a behavior index higher than 1.

The evolution of the consistency index k as a function of the CP fraction is modeled in the same way from experimental data. (9) and (10) represent the consistency index k for CP hydrate slurry and mixed CP + CO$_2$ hydrate slurry respectively:

$$k = 0.0014\,e^{25.344 x_{CP}} \qquad \text{(Eq. 9)}$$

$$k = 0.0004\,e^{29.893 x_{CP}} \qquad \text{(Eq. 10)}$$

In addition, the yield stress can be neglected. As shown in Fig. 5, the consistency index k increases exponentially with the CP fraction, which means that the viscosity of the CP and mixed CP + CO$_2$ hydrate slurries increase significantly with the increase of CP fraction used, which is usual for slurries when the behavior index n is below 1 (shear-thinning behavior).

3.2. Effects of CP fraction on viscosity values of hydrate slurries

Karanjkar et al. [20] have shown that shear-thinning behavior of CP hydrate slurry (Chen et al. Majid et al.), [17,19] pointed out a
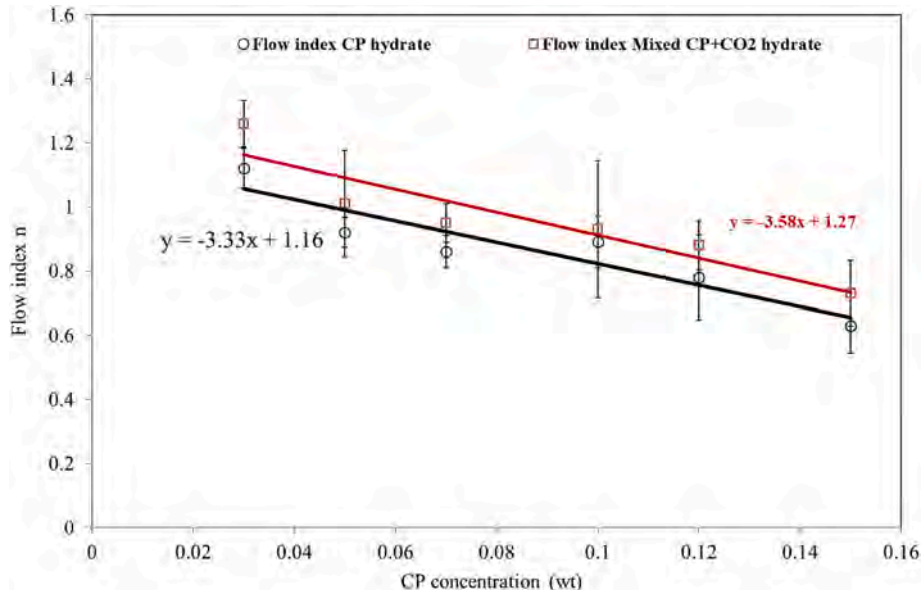

Fig. 4. Behavior index n as a function of CP fraction for CP hydrate and mixed CP + CO$_2$ hydrate slurry.
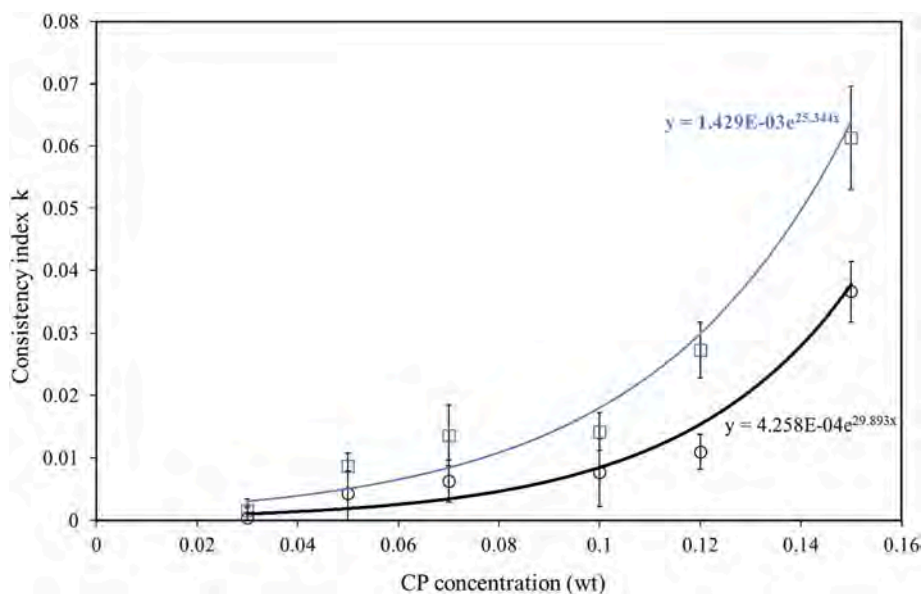
Fig. 5. Consistency index k as a function of CP fraction for CP hydrate and mixed CP + CO_2 hydrate slurry.

thixotropic behavior, and Ahuja et al. [22] have found a viscoelasticity behavior by using a stirring rheometer. This divergence between results shows the need for a rheological analysis of CP hydrate slurry in the circulation loop. These differences provide essential information to understand whether stirred rheometers and capillary viscometers provide the same kind of results.

Based on the abovementioned method [34], the data of apparent viscosity can be represented as a function of CP fraction. Figs. 6 and 7 show experimental rheogram for CP and mixed CP + CO_2 hydrate slurries respectively, for CP fractions between 3 and 15 wt%. These experimental points have been modeled using Herschel-Bulkley's (HB) model (5). However, considering a negligible the yield stress, this HB model can be reduced to a power law model. Finally, the rheological behavior for CP hydrate slurry and mixed CP + CO_2 hydrate slurry can be modeled respectively by:

$$\tau_w = k \, \dot{\gamma}_w^n \tag{Eq. 11}$$

$$\tau_w = \left(0.0014 e^{25.344 x_{CP}}\right) \cdot \dot{\gamma}_w^{-3.33 x_{CP} + 1.16} \tag{Eq. 12}$$

$$\tau_w = \left(\mathbf{0.0004} e^{\mathbf{29.893 x_{CP}}}\right) \cdot \dot{\gamma}_w^{-\mathbf{3.58 x_{CP} + 1.27}} \tag{Eq. 13}$$

A good agreement between experimental data and model fittings (cf. (12) and (13)) is observed for CP hydrate slurry as opposed to mixed CP + CO_2 hydrate slurry, especially noticeable at low CP fraction 3 and 5 wt %.

After obtaining the shear stress from the Herschel Bulkley model, the evolution of viscosity of CP and mixed CP + CO_2 hydrate slurries as a function of shear rate based on the experimental data is presented. Fig. 8 shows the viscosities of CP hydrate slurry at different CP fractions. Similar trends can be founded for mixed CP + CO_2 hydrate slurry at the same CP fraction (Fig. 9). As expected, it can be clearly seen that the viscosity increases with the increasing amount of CP, and therefore of hydrate fraction, and the viscosity decreases when the applied shear rate increases for CP fractions above 7 wt% in cyclopentane, since the
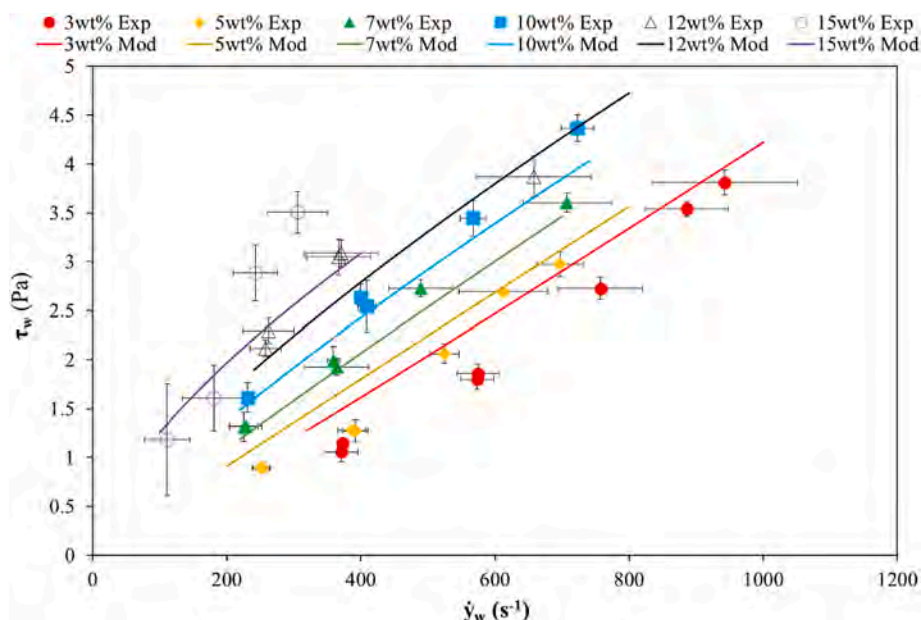

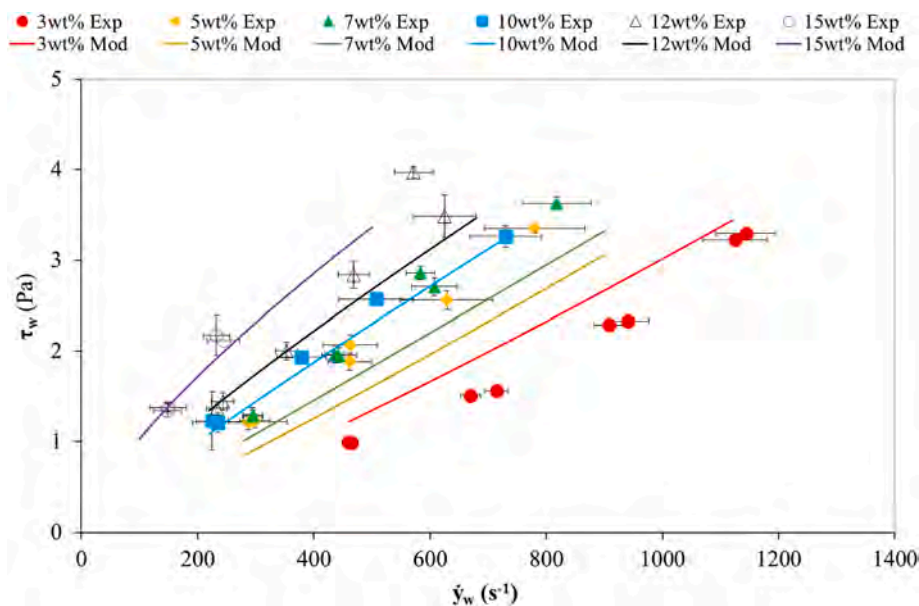**Fig. 6.** CP hydrate slurry rheograms for CP fraction between 3 and 15 wt%.

Fig. 7. Mixed CP + CO$_2$ hydrate slurry rheograms for CP fraction between 3 and 15 wt%.
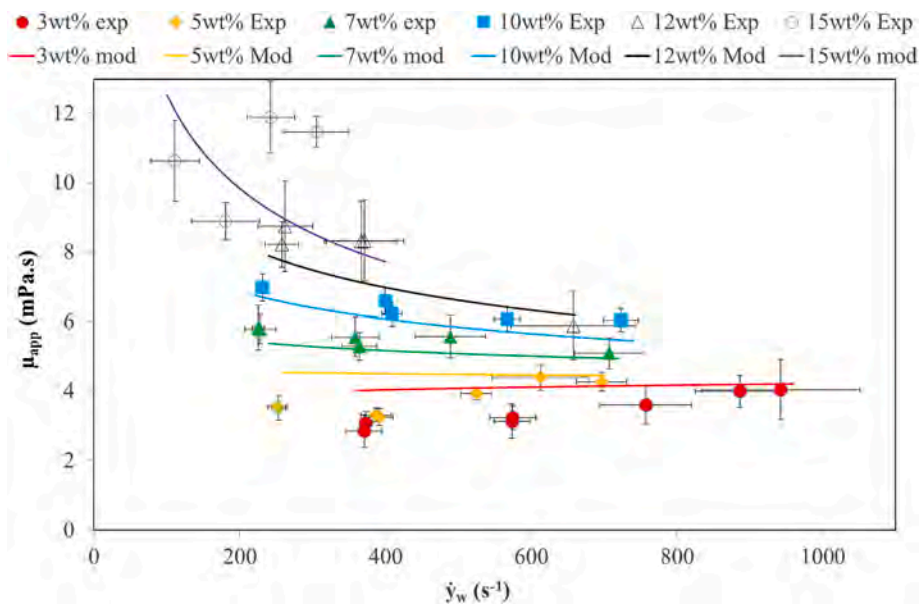

Fig. 8. Apparent viscosity of CP hydrate slurry for CP fraction between 3 and 15 wt %.

behavior index *n* is lower than 1. In addition, for CP fraction at 3 and 5 wt%, the viscosity does not show any dependence of the shear rate, since the behavior index is close to 1.

It is noticed that the data predicted by the model are generally in good agreement with those determined experimentally, with a slight difference that can be explained by an overestimation of the correlation of the consistency index *k*. Thus, a better agreement is obtained for CP hydrate slurry.

Since all the experiments were performed with oil in water emulsions in a capillary viscometer, unlike previous studies on CP hydrate slurry (water in oil) in rotative rheometer, the comparison of viscosity values at the same shear rate (Table 3) should be considered with caution. Yet, Table 3 shows that the viscosity values found for hydrates formed from direct W/O emulsion and for hydrate slurries formed from inverse O/W emulsion are close to each other and are of similar order.

As previously mentioned, and from a theoretical point of view, the

literature results at 20% water cut, corresponding to 25% (by mass balance) of hydrates formed, present lower viscosity values compared to the viscosity values at 90% water cut obtained in this work which corresponds to 55% of hydrate slurry formed. This difference in results may be related to two causes: the first may be attributed to the difference between how the two emulsions were prepared, which suggests that CP hydrate slurry are more easily formed with an inverse O/W emulsion. The second cause may be related to the forming device. Since the circulation loop is considered to be a dynamic system, hydrate particles can circulate continuously, which probably helps with the prevention or limitation of the aggregates and thus may decrease the apparent viscosity.

Another comparison can be made between various types of hydrate slurries formed in the same circulation loop. Fig. 10 shows the variation of viscosity as a function of shear rate for CP, CO$_2$, TBPB [34], SDS-CO$_2$ [35] and mixed CP + CO$_2$ hydrate slurries. This comparison shows that
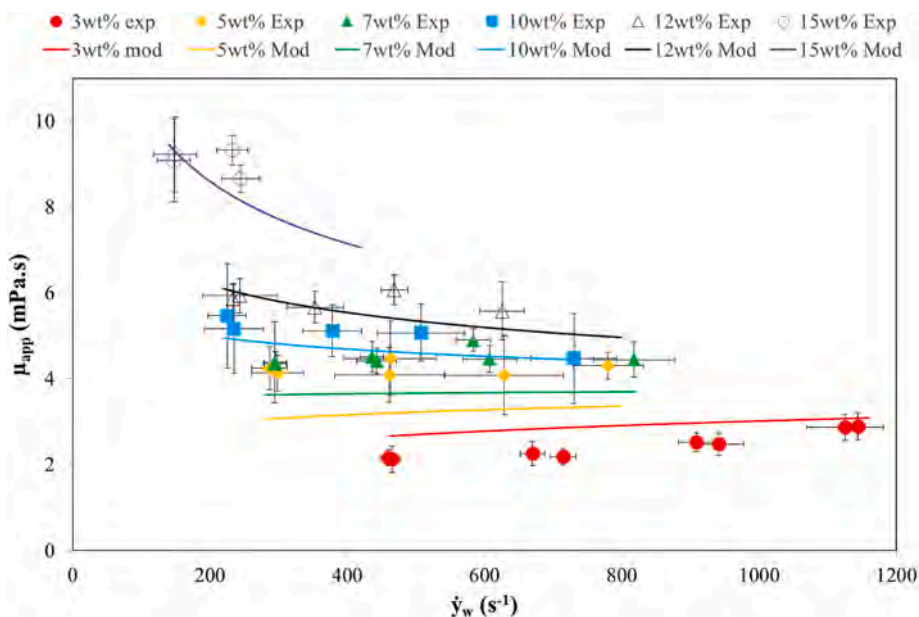
Fig. 9. Apparent viscosity of mixed CP + CO$_2$ hydrate slurry for CP fraction between 3 and 15 wt%.

Table 3
Comparison of viscosities of CP hydrate slurry.

Reference	Water cut (%)	Shear rate(s^{-1})	Viscosity (Pa. s)
Chen et al. [25]	20	300	0.017 ± 0.002
Liu et al. [24]	20	300	0.014
This work (CP hydrate)	85	300	0.011 ± 0.0005
	88		0.008 ± 0.0015
	90		0.007 ± 0.0010
	93		0.006 ± 0.0006
	95		0.004 ± 0.0002
	97		0.003 ± 0.0005

CP and CP + CO$_2$ hydrate slurries present low viscosity, close to that of TBPB hydrate slurries, which is favorable for flow in pipes. This behavior will be verified using other experiments to validate these observations in another paper.

3.3. Time effect on mixed CP + CO$_2$ hydrate

It is well known that hydrate plugs can easily occur over time in transportation pipelines, and many researches have shown a certain change of hydrate slurry behavior with time [18,19]. Therefore, tests involving a long period of circulation are essential to study the flow characteristics of the hydrate slurries over time in order to ensure that these hydrate slurries can be effectively used in a transport application, like secondary loop refrigeration. In this work, the rheological characterization of hydrate slurry was done at two different measurement times. The first measurement was done directly after the hydrate formation (t = 0 h). The second measurement was made 16 h after the hydrate formation (t = 16 h).

For each CP fraction, the following process has been applied: **(1)** hydrate formation **(2)** stabilization of pressure drop in system **(3)** rheological characterization at t = 0 h **(4)** continuous circulation of hydrate slurry under the same conditions (the same operating conditions
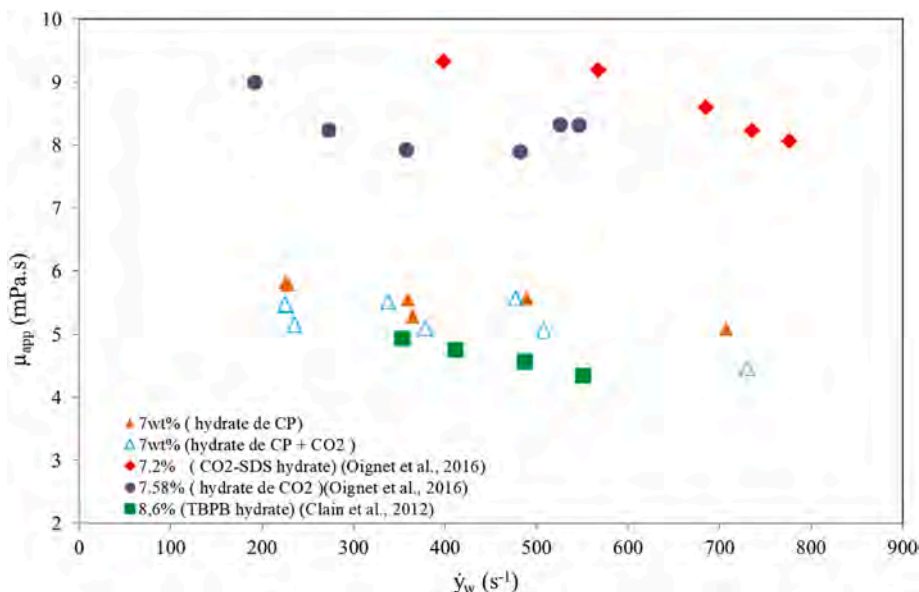

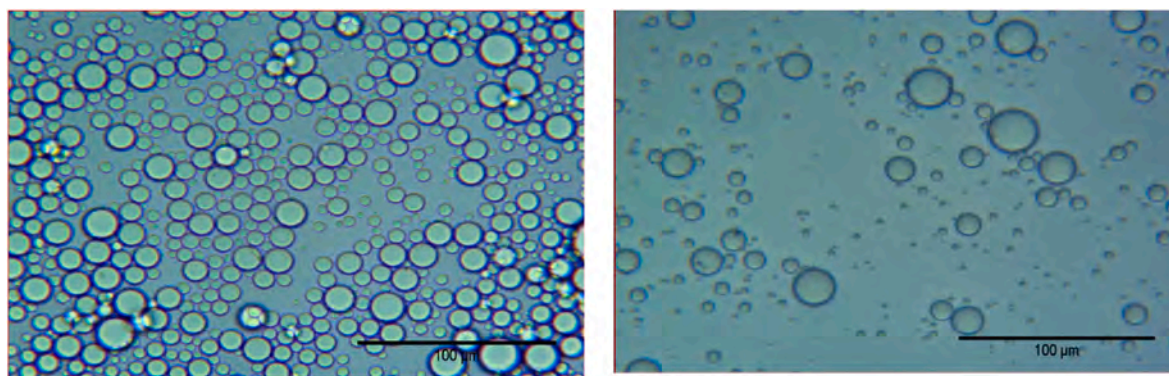**Fig. 10.** Comparison between different types of hydrates.

Fig. 11. Microphotographs of the 10 wt % cyclopentane in water emulsion at different time periods: (a) before hydrate formation (b) after hydrate dissociation.

of pressure, temperature and flow rate are kept for 16 h) **(5)** rheological characterization of hydrate slurry after 16 h of circulation.

This characterization at different times showed a change in behavior index *n* values when CP fraction varies from 3 to 10 wt% (lower than 1 at t = 0 h, except the point at 3 wt%, and higher than 1 at t = 16 h) (Fig. 12). The evolution of experimental and modeled viscosity of mixed CP + CO_2 hydrate slurry as a function of shear rate for different CP fractions ranging from 3 to 10 wt % was presented in Fig. 15. The viscosity of mixed CP + CO_2 hydrate slurry shows an increase with the shear increase, contrary to what was found at t = 0 h when the mixed CP + CO_2 hydrate slurry have exhibited typical shear-thinning behavior, which is strengthened with increasing of CP fraction. This finding proves the effect of time on the rheological results and the slurry seems to have a shear-thickening behavior, which can be unusual behavior for a slurry especially at relatively low CP fraction (see Fig. 16).

To verify this assumption, it is first necessary to analyze the flow regime when hydrate slurry is subjected to a long period of circulation, in order to verify the potential existence of any inertial terms. Indeed, this rheological study is based on the capillary method relying on two assumptions: laminar flow and no wall slip. Referring to the method used by Clain et al. [34], which allows the verification of the system regime, the Re_{MR} number [29] and the Fanning friction factor have been determined. If the Fanning factor and the Re_{MR} number can be correlated using the Hagen-Poiseuille method, then the dominant regime in the system is laminar.

Fig. 13 shows the experimental data of the Fanning factor as a function of the Re_{MR} number. This plot offers a good agreement with the prediction of the Hagen-Poiseuille equation, which proves that the regime is laminar after 16 h for mixed CP + CO_2 hydrate slurry. Another
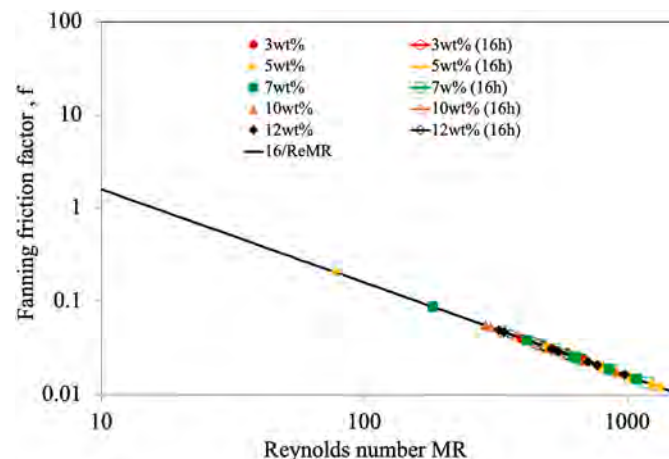

Fig. 13. Friction factor of CP + CO_2 hydrate slurry as a function of Reynolds number MR for various CP fractions after hydrate formation, and 16 h after hydrate formation.
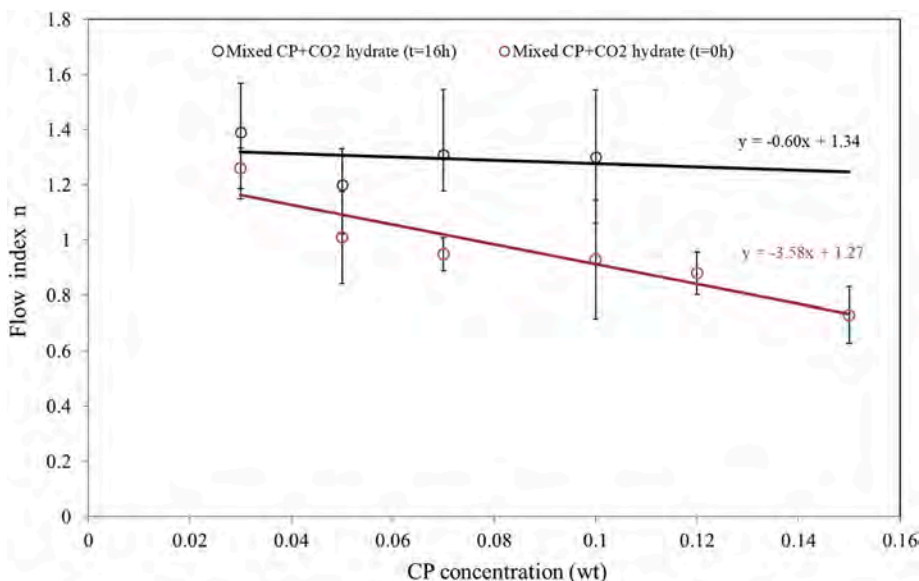

Fig. 12. Flow index as a function of CP fraction for mixed CP + CO_2 hydrate slurry at t = 0 h and after 16 h.

method was also used to characterize the regime in the loop, the representation of pressure drop as a function of the flow rate (Fig. 14). The relationship between the pressure drop and the flow rate is linear which shows that the regime is laminar.

Therefore, the changes in rheological behavior after 16 h of mixed CP + CO2 hydrate slurry are not related to a regime change in the system but instead to another phenomenon.

Fig. 14 shows the variation of only experimental viscosity of mixed CP + CO_2 hydrate slurry as a function of the shear rate at different time periods. For all CP fractions, the viscosity at t = 16 h was measured to increase slightly with increasing shear rates, unlike the viscosities at t = 0 h. Furthermore, the value of the viscosity is a little higher at t = 16 h than at t = 0 h which becomes more obvious at the 10 wt% concentration.

This behavior change over time can be attributed to a change in hydrate fraction or distribution, possibly due to the microscopic structure of the hydrate slurry. In order to ensure that the cyclopentane in water emulsion did not undergo a structural change, microscopic investigations were carried out. The characterization was done using an OMAX Microscope AC 100–240 V. Fig. 11 shows the micrographs for the CP-in-water emulsion at the start before hydrate formation and directly after hydrate dissociation, which shows the ability of the emulsion to stay stable over time, without having a phase separation or a phase inversion [36]. Nevertheless, the number of cyclopentane drops was significantly lower after the hydrate dissociation, which was also reported by Ref. [21]. They noticed that the emulsion destabilizes at the end of the experiments through an optical and rheological analysis. This may hypothetically be due to the fact that the hydrate slurry is subjected to various changes over a long period of circulation, which could be related to the reduction of adhesive force between the hydrate particles in motion. This could mean that the structure is modified, possibly due to the competition between cohesion and shear forces, resulting in a change of hydrate slurry behavior after 16 h. The same behavior was observed even earlier by Karanjkar et al. [20] using a hysteresis loop for CP hydrate slurry. Webb et al. [37] reported that once hydrate particles convert to hydrate, they are free to move around and collide with other hydrate particles or water droplets, which may lead to aggregation and result in increased viscosity of hydrate slurries.

4. Conclusion

A rheological study of CP and mixed CP + CO_2 hydrate slurry in loop was carried out to understand the potential of this fluid for transportation application, such as secondary loop refrigeration, and to determine the impacts of several operating conditions. The CP fraction as well as the effect of time circulation on the rheological properties were studied. The following conclusions were drawn:

- The experimental results demonstrate that the CP hydrate and mixed CP + CO_2 hydrate slurries exhibit mostly a shear-thinning behavior. This behavior becomes more evident with increasing CP concentration, significantly above 7 wt%.
- Semi-empirical models were proposed to describe the effect of CP fraction on the rheological behavior of the CP hydrate and mixed CP + CO_2 hydrate slurries.
- This first rheological study shows that CP and mixed CP + CO_2 hydrate slurry in a circulation loop can be suitable for RAC applications.
- The measurement at different times indicates the mixed CP + CO_2 hydrate slurry exhibit a behavior change, while the laminar regime was verified.
- Due to the influence of times on hydrate slurry behavior illustrated in this work, future work will focus on investigating CP hydrate and mixed CP + CO_2 hydrate slurries formation at different measurement times using a controlled stress rheometer. Since no realistic method exists on the determination of CP hydrate fraction in flow, detailed
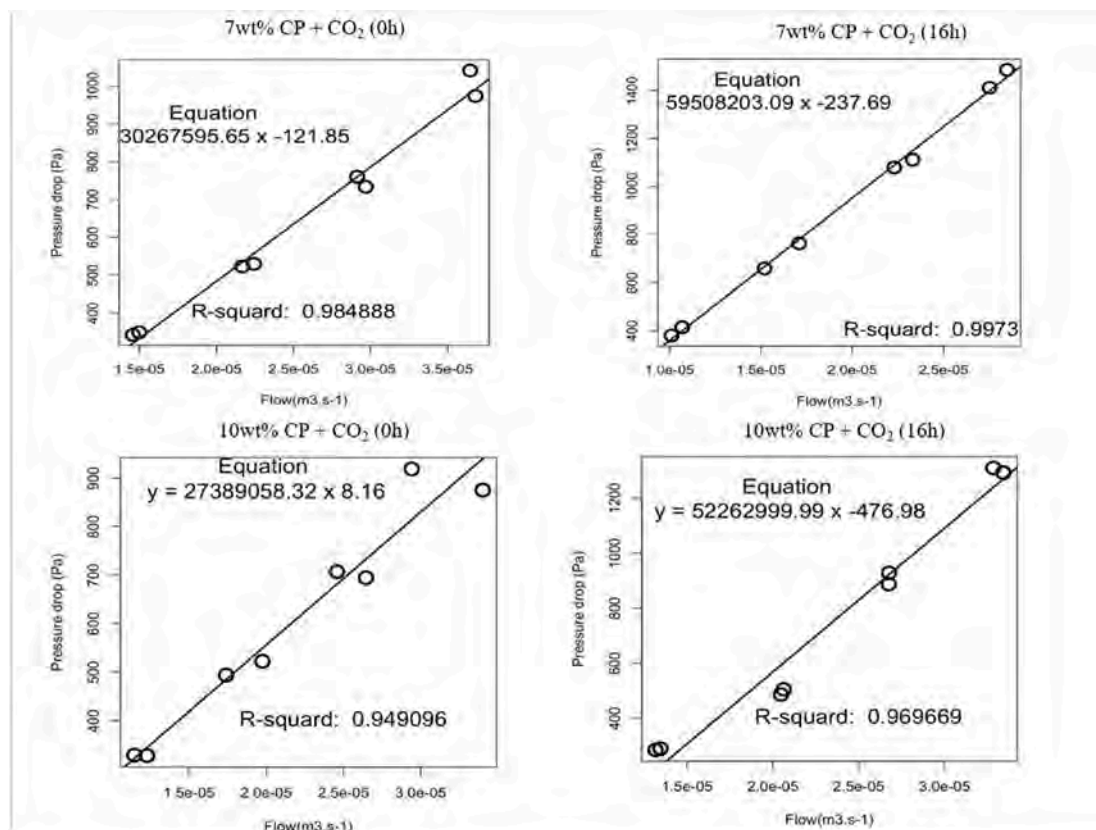

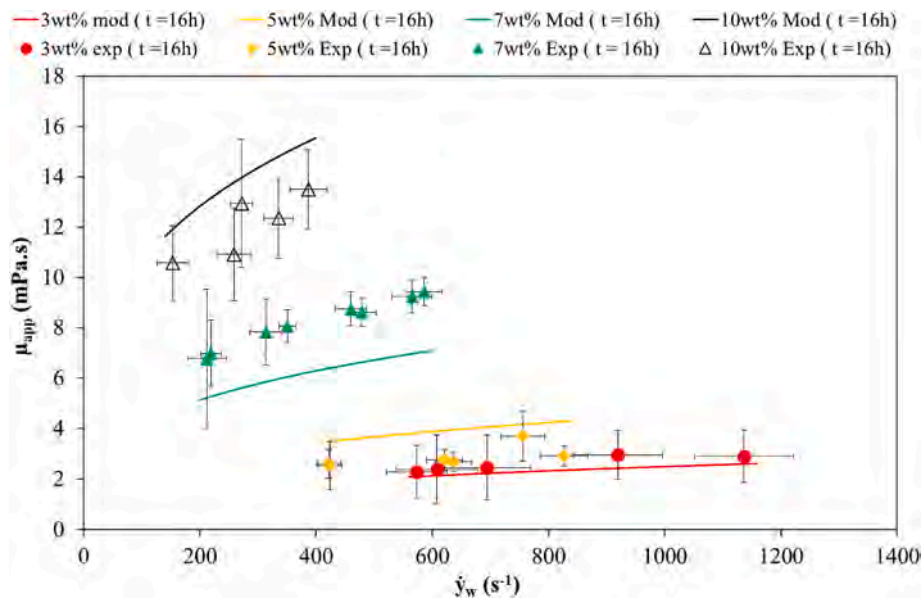**Fig. 14.** Variation of pressure drop as function of flow rate for mixed CP + CO_2 hydrate slurry.

Fig. 15. Apparent viscosity of mixed CP + CO$_2$ hydrate slurry for CP fraction between 3 and 12 wt% 16 h after hydrate formation.
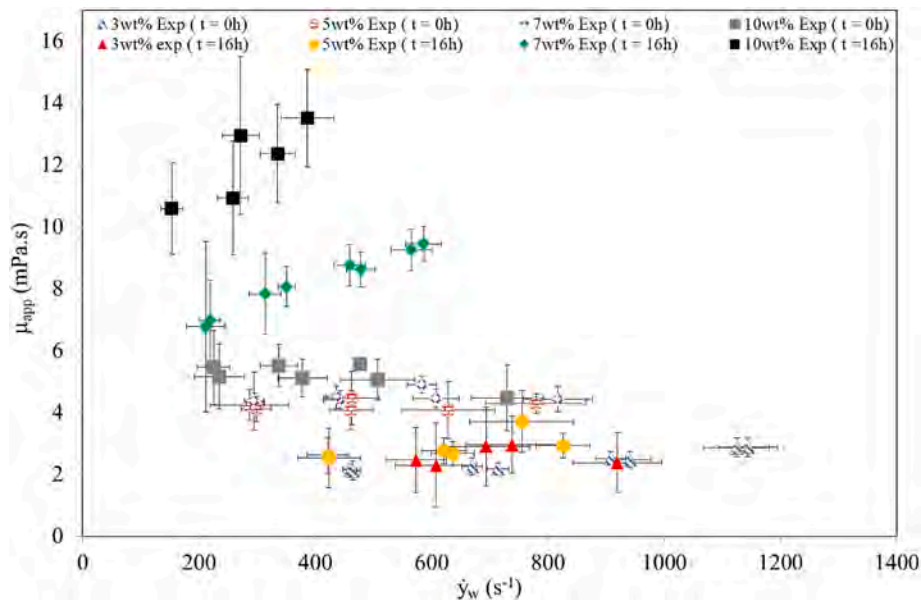

Fig. 16. Comparison between the viscosity of mixed CP + CO$_2$ hydrate slurry at 0 h and the viscosity after 16 h.

verification of this data with complementary characterization methods in the loop will be presented in a further work.

- The absence of wall slip will be checked in further work, since, there are no study performed on hydrate slurries in the literature.

Credit author statement

Nada CHAMI: Investigation, Formal analysis, Writing- Original Draft. **Yasmine SALEHY**: Formal analysis, **Pascal CLAIN**: Validation, Writing review. **Anthony DELAHAYE**: Supervision, Methodology, validation, Writing-review & editing. **Laurence Fournaison:** Supervision, Methodology, validation, Writing-review & editing. **Didier DAL-MAZZONE**: Methodology, validation, Writing-review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

Abreviations

CP	cyclopentane
ΔP	Pressure drop
τ_w	Shear stress
τ_0	Yield stress
$\dot{\gamma}_w$	Shear rate
Q	Flow rate
n	Flow index
k	Consistency index
x_{CP}	Cyclopentane fraction
μ_{app}	Apparent viscosity
Re_{MR}	Modified Reynolds number
f	Friction factor
D	Internal diameter
GPW	Global warming potential
RAC	Refrigeration and air conditioning

References

[1] Dupont J, Domanski P, Lebrun P, Ziegler F. The role of refrigeration in the global economy. 2019. https://doi.org/10.18462/iif.NItec38.06.2019 [En ligne] Disponible sur:.

[2] Wang K, Eisele M, Hwang Y, Radermacher R. Review of secondary loop refrigeration systems. Int J Refrig 2010;33(2):212–34. https://doi.org/10.1016/j.ijrefrig.2009.09.018.

[3] Tanasawa I, Takao S. Low-temperature thermal storage using ClathrateHydrate slurries of tetra-n-butylammonium bromide: thermophysical properties and morphology of ClathrateHydrate crystals. In: présenté à International Heat Transfer Conference Digital Library; 2002.

[4] Chatti I, Delahaye A, Fournaison L, Petitet J-P. Benefits and drawbacks of clathrate hydrates: a review of their areas of interest. Energy Convers Manag 2005;46(9):1333–43. https://doi.org/10.1016/j.enconman.2004.06.032.

[5] Fournaison L, Delahaye A, Chatti I, Petitet J-P. CO2 hydrates in refrigeration processes. Ind Eng Chem Res 2004;43(20):6521–6. https://doi.org/10.1021/ie030861r. sept.

[6] Kang S-P, Lee H, Ryu B-J. Enthalpies of dissociation of clathrate hydrates of carbon dioxide, nitrogen, (carbon dioxide+ nitrogen), and (carbon dioxide + nitrogen+ tetrahydrofuran). J Chem Therm 2001;33(5):513–21. https://doi.org/10.1006/jcht.2000.0765.

[7] Darbouret M, Cournil M, Herri J-M. Rheological study of TBAB hydrate slurries as secondary two-phase refrigerants. Int J Refrig 2005;28(5):663–71. https://doi.org/10.1016/j.ijrefrig.2005.01.002.

[8] Clain P, Ndoye FT, Delahaye A, Fournaison L, Lin W, Dalmazzone D. Particle size distribution of TBPB hydrates by focused beam reflectance measurement (FBRM) for secondary refrigeration application. Int J Refrig 2015;50:19–31. https://doi.org/10.1016/j.ijrefrig.2014.10.016. févr.

[9] Zhang JS, Lee JW. Equilibrium of hydrogen + cyclopentane and carbon dioxide + cyclopentane binary hydrates. J Chem Eng Data 2009;54(2):659–61. https://doi.org/10.1021/je800219k. févr.

[10] Nakajima M, Ohmura R, Mori YH. Clathrate hydrate formation from cyclopentane-in-water emulsions. Ind Eng Chem Res 2008;47(22):8933–9. https://doi.org/10.1021/ie800949k.

[11] Zhang Y, et al. Phase equilibrium of cyclopentane + carbon dioxide binary hydrates in aqueous sodium chloride solutions. J Chem Eng Data 2017;62(8):2461–5. https://doi.org/10.1021/acs.jced.7b00404. août.

[12] Chami N, et al. Thermodynamic characterization of mixed gas hydrates in the presence of cyclopentane as guest molecule for an application in secondary refrigeration. Chem Eng Sci 2021;116790. https://doi.org/10.1016/j.ces.2021.116790.

[16] Lee J, Kim K-S, Seo Y. Thermodynamic, structural, and kinetic studies of cyclopentane + CO2 hydrates: applications for desalination and CO2 capture. Chem Eng J 2019;375:121974. https://doi.org/10.1016/j.cej.2019.121974. nov.

[17] Chen Y, et al. In situ viscosity measurements of a cyclopentane hydrate slurry in waxy water-in-oil emulsions. Energy Fuel 2019;33(4):2915–25. https://doi.org/10.1021/acs.energyfuels.8b04268. avr.

[18] Majid AAA, Tanner B, Koh CA. Cyclopentane hydrate slurry viscosity measurements coupled with visualisation. Mol Phys 2019;117(23–24):3860–70. https://doi.org/10.1080/00268976.2019.1670877.

[19] Ahuja A, Zylyftari G, Morris JF. Yield stress measurements of cyclopentane hydrate slurry. J Non-Newtonian Fluid Mech 2015;220:116–25. https://doi.org/10.1016/j.jnnfm.2014.11.007.

[20] Karanjkar PU, Ahuja A, Zylyftari G, Lee JW, Morris JF. Rheology of cyclopentane hydrate slurry in a model oil-continuous emulsion. Rheol Acta 2016;55(3):235–43. https://doi.org/10.1007/s00397-016-0911-1. mars.

[21] Sandoval GAB, et al. A rheological study of parameters that influence the formation of cyclopentane hydrates. Energy Fuel 2021;35(22):18467–77. https://doi.org/10.1021/acs.energyfuels.1c02726.

[22] Ahuja A, Zylyftari G, Morris JF. Calorimetric and rheological studies on cyclopentane hydrate-forming water-in-kerosene emulsions. J Chem Eng Data 2015;60(2):362–8. https://doi.org/10.1021/je500609q. févr.

[23] Zylyftari G, Ahuja A, Morris JF. Modeling oilfield emulsions: comparison of cyclopentane hydrate and ice. Energy Fuels oct. 2015;29(10):6286–95. https://doi.org/10.1021/acs.energyfuels.5b01431.

[24] Liu Y, et al. Rheological study of low wax content hydrate slurries considering phase interactions. J Nat Gas Sci Eng 2021;94:104106. https://doi.org/10.1016/j.jngse.2021.104106.

[25] Y. Chen et al., « Kinetic and rheological investigation of cyclopentane hydrate formation in waxy water-in-oil emulsions », Fuel, vol. 287, p. 119568, mars 2021, doi: 10.1016/j.fuel.2020.119568.

[26] Delahaye A, Fournaison L, Jerbi S, Mayoufi N. Rheological properties of CO2 hydrate slurry flow in the presence of additives. Ind Eng Chem Res 2011;50(13):8344–53. https://doi.org/10.1021/ie200185q. juill.

[27] Oignet J, et al. Rheological study of CO2 hydrate slurry in the presence of Sodium Dodecyl Sulfate in a secondary refrigeration loop. Chem Eng Sci 2017;158:294–303. https://doi.org/10.1016/j.ces.2016.10.018.

[28] Steffe JF. Rheological methods in food process engineering. Freeman press; 1996.

[29] Metzner A, Reed J. Flow of non-Newtonian fluids—correlation of the laminar, transition, and turbulent-flow regions. AIChE J 1955;1(4):434–40.

[30] Andersson V, Gudmundsson JS. Flow properties of hydrate-in-water slurries. Ann N Y Acad Sci 2000;912(1):322–9.

[31] Rouaud M. Calcul d'incertitudes: application aux sciences expérimentales. Mathieu Rouaud; 2014 [En ligne]. Disponible sur: https://books.google.fr/books?id=cPN MMQAACAAJ.

[32] Marinhas S, Delahaye A, Fournaison L. Solid fraction modelling for CO2 and CO2–THF hydrate slurries used as secondary refrigerants. Int J Refrig 2007;30(5):758–66. https://doi.org/10.1016/j.ijrefrig.2006.12.010.

[33] Marinhas S, Delahaye A, Fournaison L, Dalmazzone D, Fürst W, Petitet J-P. Modelling of the available latent heat of a CO2 hydrate slurry in an experimental loop applied to secondary refrigeration. Chem Eng Process: Process Intensif 2006;45(3):184–92. https://doi.org/10.1016/j.cep.2005.08.002. mars.

[34] Clain P, Delahaye A, Fournaison L, Mayoufi N, Dalmazzone D, Fürst W. Rheological properties of tetra-n-butylphosphonium bromide hydrate slurry flow. Chem Eng J 2012;112–22. https://doi.org/10.1016/j.cej.2012.04.027. 193-194.

[35] Oignet J, et al. Rheological study of CO2 hydrate slurry in the presence of Sodium Dodecyl Sulfate in a secondary refrigeration loop. Chem Eng Sci 2017;158:294–303. https://doi.org/10.1016/j.ces.2016.10.018.

[36] McClements DJ. Food emulsions: principles, practices, and techniques. CRC press; 2004.

[37] Webb EB, Rensing PJ, Koh CA, Sloan ED, Sum AK, Liberatore MW. High-pressure rheology of hydrate slurries formed from water-in-oil emulsions. Energy Fuel 2012;26(6):3504–9. https://doi.org/10.1021/ef300163y. juin.