Rheological study of mixed cyclopentane + CO2 hydrate slurry in a dynamic loop for refrigeration systems

Nada Chami, Yasmine Salehy, Dennis Burgner, Pascal Clain, Didier Dalmazzone, Anthony Delahaye, L. Fournaison

To cite this version:

Nada Chami, Yasmine Salehy, Dennis Burgner, Pascal Clain, Didier Dalmazzone, et al.. Rheological study of mixed cyclopentane + CO2 hydrate slurry in a dynamic loop for refrigeration systems. Energy, 2023, 263, pp.125661. 10.1016/j.energy.2022.125661 . hal-04086801

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

Nada CHAMI[1, 2, *], Yasmine SALEHY[2], Pascal CLAIN[3, 2], Véronique OSSWALD[2], Didier DALMAZZONE[1], Anthony DELAHAYE[2], Laurence FOURNAISON[2].

1 UCP/ENSTA Paris, Institut Polytechnique de Paris, Palaiseau, France

2 Université Paris-Saclay, INRAE, FRISE, 92761, Antony, France

3 Léonard de Vinci Pôle Universitaire, Research Center, 92916 Paris la Défense, France

* Corresponding author: nadachami65@gmail.com

Abstract

The use of CO_2 hydrates as phase change materials is promising for secondary 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. A comparison of rheological parameters (viscosity, flow behavior...) was made between these two different hydrate formers: CP and mixed CP + CO_2 hydrate slurries. 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 12 mPa.s-1 at [100 – 1200 s^{-1}] for CP + CO_2 hydrates slurries. Moreover, mixed CP + CO_2 have shown a time-evolution of the rheological behavior.

Keywords: Gas hydrates, Emulsion, Rheology, Viscosity, Cyclopentane

1. Introduction

Air conditioning in commercial buildings is known as the most significant contributor to total energy consumption [1]. Air conditioner systems are continuously improved to render them more efficient. Secondary refrigeration involves cooling a secondary fluid using a primary system with primary refrigerants like hydrofluorocarbons (HFCs) (which are generally considered as "harmful" for the environment) and have the secondary fluid supply cooling where necessary. Usually, secondary refrigeration is less effective than primary refrigeration. Currently, the use of phase change materials (PCM) in secondary refrigeration (to form PCM slurry) is an innovative design in development. They improve the process by increasing the energy density of the fluid [2].

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 to 0.4 MPa). Gas hydrates have the advantage of being produced by non-mechanical methods by simple gas injection in a pre-cooled solution [3]. One of the most studied gas hydrates in the refrigeration field is carbon dioxide. The latent heat of CO_2 hydrate is 500 $kJ.kg^{-1}{}_{water}$, which is higher than that of ice (333 $kJ.\ kg^{-1}{}_{water}$) [4]. The phase change temperatures of CO_2 hydrate range of 273 to 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 secondary refrigeration applications, several studies have been developed to evaluate the 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 [5], tetrabutylammonium bromide (TBAB) [6], tetra-n-butylphosphonium bromide (TBPB) [7] and cyclopentane C_5H_{10} (CP) [8]. These additives are themselves able to form hydrate slurries at atmospheric pressures and low temperatures contrary to gas hydrates [9]. 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 to 285 K at formation pressures between 0.01 to 0.02 MPa, which is well within the operating conditions of conventional air conditioners. However, the latent heat of CP hydrate is 252.2 $kJ.kg^{-1}{}_{water,}$ half the value of CO_2 hydrate, which reduces the cold storage density. Zhang *et al*. [10] 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 the refrigeration 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 [15]. These studies have shown that CP + CO_2 hydrate slurry form in the temperature range of 279 to 285 K at formation pressures between 0.01 to 0.45 MPa and have a high dissociation enthalpy (462.5 ±1.5 $kJ^{-1}{}_{water}$) and an heat capacity value not too much further away from that of ice slurries (1479.09 ± 137.43 $J.K^{-1}.kg^{-1}{}_{hydrate}$ at 0.25 MPa) [11]. Nevertheless, in order to be implemented as phase change material slurries in secondary 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 [16], [17]. 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.* [18] 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.* [17] 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.* [19] 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.* [21] 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.* [22] 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.* [23] 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.* [24] 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.

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.* [22]	Water-in-oil emulsion	Stress-control-type rheometer	40	Viscoelasticity	1-100
Ahuja *et al.* [21]	Water-in-Kerosene	Stress-control-type rheometer	40	Viscoelasticity	1-100

	emulsion				
Ahuja *et al.* [18]	Water-in-oil emulsion	Stress-control-type rheometer	18	Thixotropic	1-100
Karanjkar *et al.* [19]	Water-in-oil emulsion	Stress-control-type rheometer	10-45	Shear thinning	1-100
Majid *et al.* [17]	Water-in-oil emulsions & non-emulsified system	Stress-control-type rheometer	10 excess of cyclopentane	Thixotropic	1000
Chen *et al.* [16]	Waxy water-in-oil emulsion	Stress-control-type rheometer	20-30	Shear thinning	1-300
Sandoval *et al.* [20]	Water-in-oil emulsion	Stress-controlled rheometer	20-30	Shear thinning	0.1-10
Liu *et al.* [23]	Waxy water in oil emulsion	Stress-controlled rheometer + Flow loop	20	Thixotropic	50-600
Chen *et al.* [24]	Waxy and wax-free emulsion	Stress Controlled rheometer	20-35		100-600

In this work, we present the rheological characteristics of oil-in-water CP hydrate slurries that forms at atmospheric pressure and measured for the first time with a capillary viscometer, unlike previous studies where the authors always use rotative rheometer and very often studied water-in-oil emulsion mixture. In addition, we will also study the rheological behavior of mixed CP + CO_2 hydrate slurry that has never been characterized before.

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). All materials were used without further purification.

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

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 ± 0.04 %) from Sensit and Transintruments (0 - 5 MPa, ± 0.05 %), an electromagnetic flowmeter (IFM6080K-type Vatiflux, 0.5%) (0 - 1800 l h^{-1} ± 2.5%), and a pump (220-type, Maximum flow rate = 0.17 $m^3.h^{-1}$). 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).

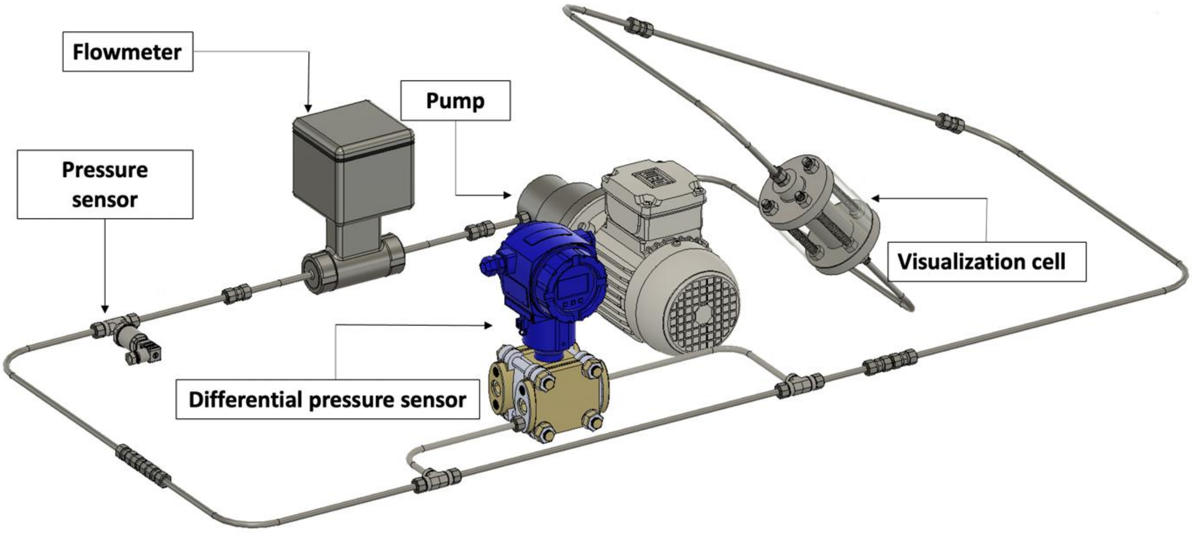

Fig. 1: Experimental loop

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 18000 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 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) [9], 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 [25], [26]. 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 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 [27], 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 equation resulting from this force balance then expresses the flow rate as a function of the shear stress and the shear rate:

$$ {}^{Q}/_{\pi R^3} = {}^{1}/_{4}\left({}^{8u}/_{D}\right) = {}^{1}/_{\tau_w^3}\int_0^{\tau_w} \tau^2 \dot{\gamma}\, d\tau \qquad \text{(Eq. 1)} $$

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:

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

After derivation of the (Eq. **1**), the Rabinowitsch-Mooney equation, expressing shear rate at the wall, can be deduced [28]:

$$ \dot{\gamma}_w = \left({}^{8u}/_{D}\right)\ 3n + {}^{1}/_{4n} \qquad \text{(Eq. 3)} $$

With *n* the behavior index defined as:

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

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.

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 [29]:

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

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, $\frac{8U}{D}$), based on previous equations. Then the behavior index n, as described by (Eq. **4**), corresponds to the slope of the representative curve of the function $\tau_w = f\left(\frac{8U}{D}\right)$. Likewise, the consistency index k and the yield stress τ_0, as described by (Eq. **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.

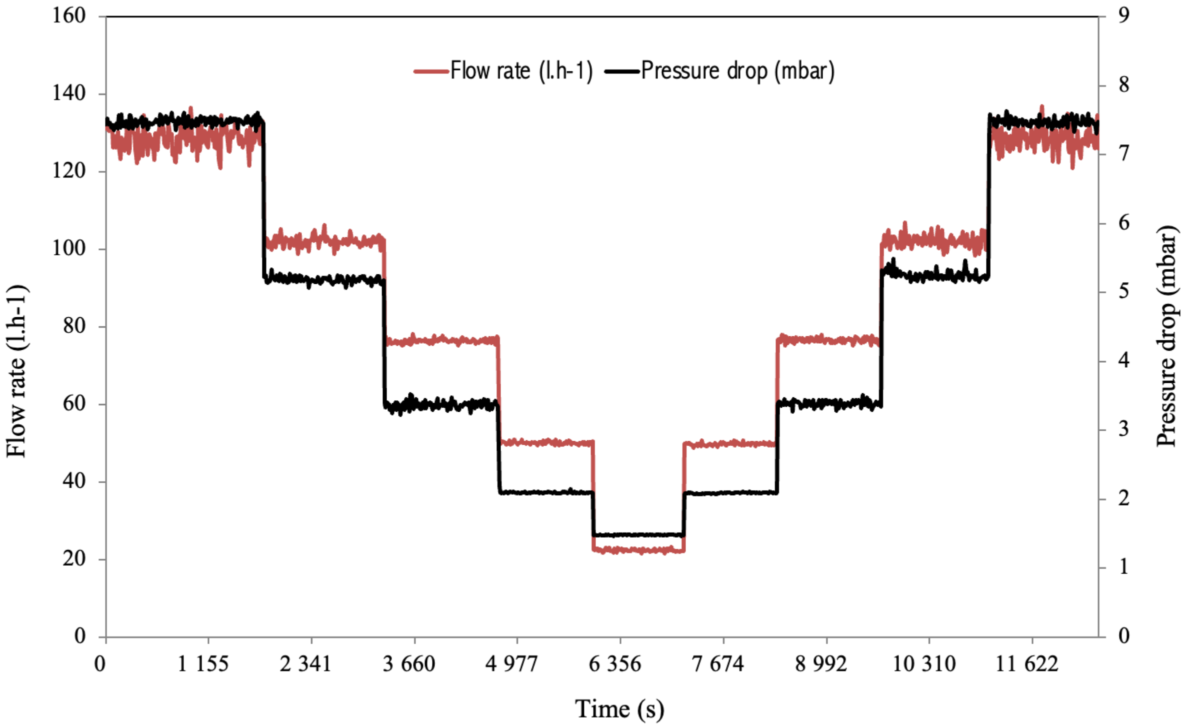

Fig. 2: Experimental protocol

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 simple CP hydrate and mixed CP + CO_2 hydrate slurries of cyclopentane 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.

The loop was loaded with various CP fractions: 3, 5, 7, 10, 12, and 15wt %. 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 [9], 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 when we focus on the rheological properties as in the current study. 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 [30], [31]. 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.

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. **3**, 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. **3** shows also that the behavior index value above 1 for cyclopentane fraction below 5 wt%. The behavior index was approximated by (Eq. **7**) for CP hydrate slurry and by (Eq. **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 5wt% 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. (Eq. **9**) and (Eq. **10**) represent the consistency index k for CP hydrate slurry and mixed CP + CO_2 hydrate slurry respectively:

$$k = 0.0011\, e^{28.24 x_{CP}} \qquad \text{(Eq. 9)}$$

$$k = 0.0004 e^{31.714 x_{CP}} \qquad \text{(Eq. 10)}$$

In addition, the yield stress can be neglected. As shown in Fig. **4**, 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).

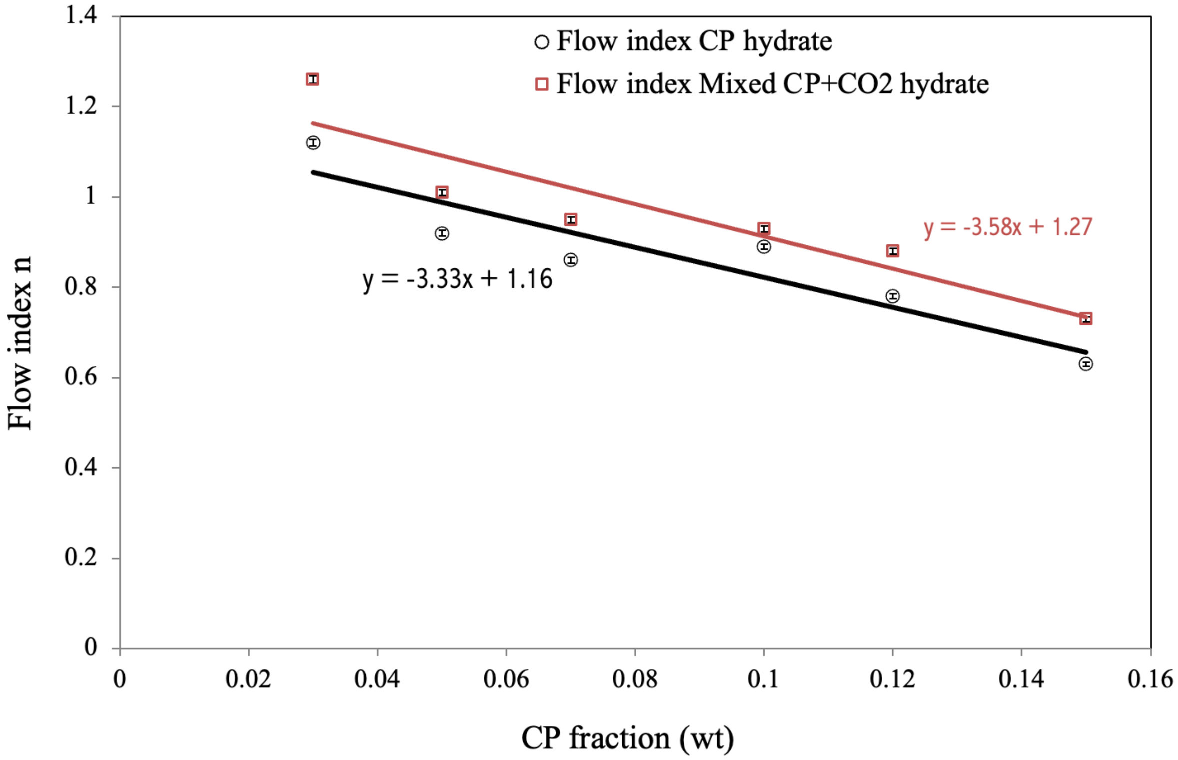

Fig. 3: Behavior index *n* as a function of CP fraction for CP hydrate and mixed CP + CO_2 hydrate slurry

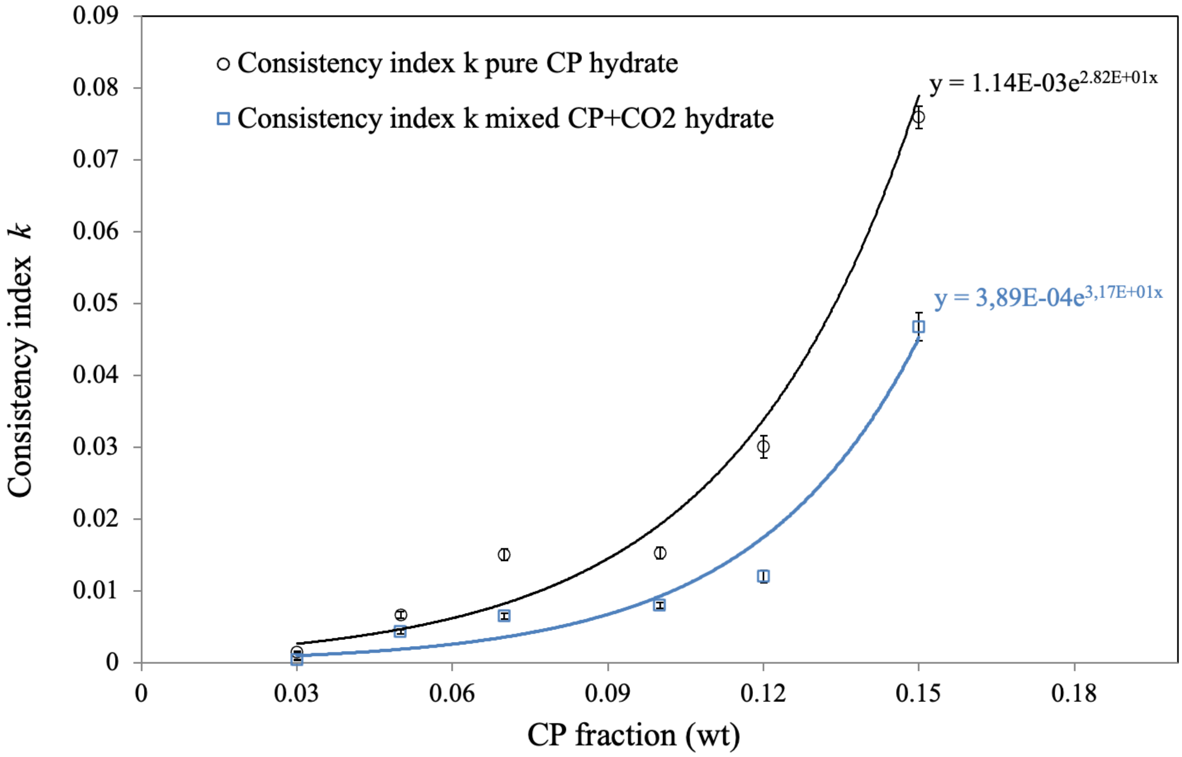

Fig. 4: Consistency index *k* as a function of CP fraction for CP hydrate and mixed CP + CO_2 hydrate slurry

3.2 Effects of CP fraction on viscosity values of hydrate slurries

Karanjkar *et al.* [19] have shown that shear-thinning behavior of CP hydrate slurry, (Chen et al., Majid et al.) [17], [19] pointed out a thixotropic behavior, and Ahuja et al. [21] 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 [32], the data of apparent viscosity can be represented as a function of CP fraction. Fig. 5 and Fig. 6 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 modelled using Herschel-Bulkley's (HB) model (Eq. **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:

$$\boldsymbol{\tau_w = k\,\dot{\gamma}_w^{n}} \qquad \text{(Eq. 11)}$$

$$\tau_w = (0.0011e^{28.24x_{CP}}).\dot{\gamma}_w^{-3.33x_{CP}+1.16} \qquad \text{(Eq. 12)}$$

$$\boldsymbol{\tau_w = \left(0.0004e^{31.71x_{CP}}\right).\dot{\gamma}_w^{-3.58x_{CP}+1.27}} \qquad \text{(Eq. 13)}$$

A good agreement between experimental data and model fittings (cf.(Eq. **12**) and (Eq. **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%.

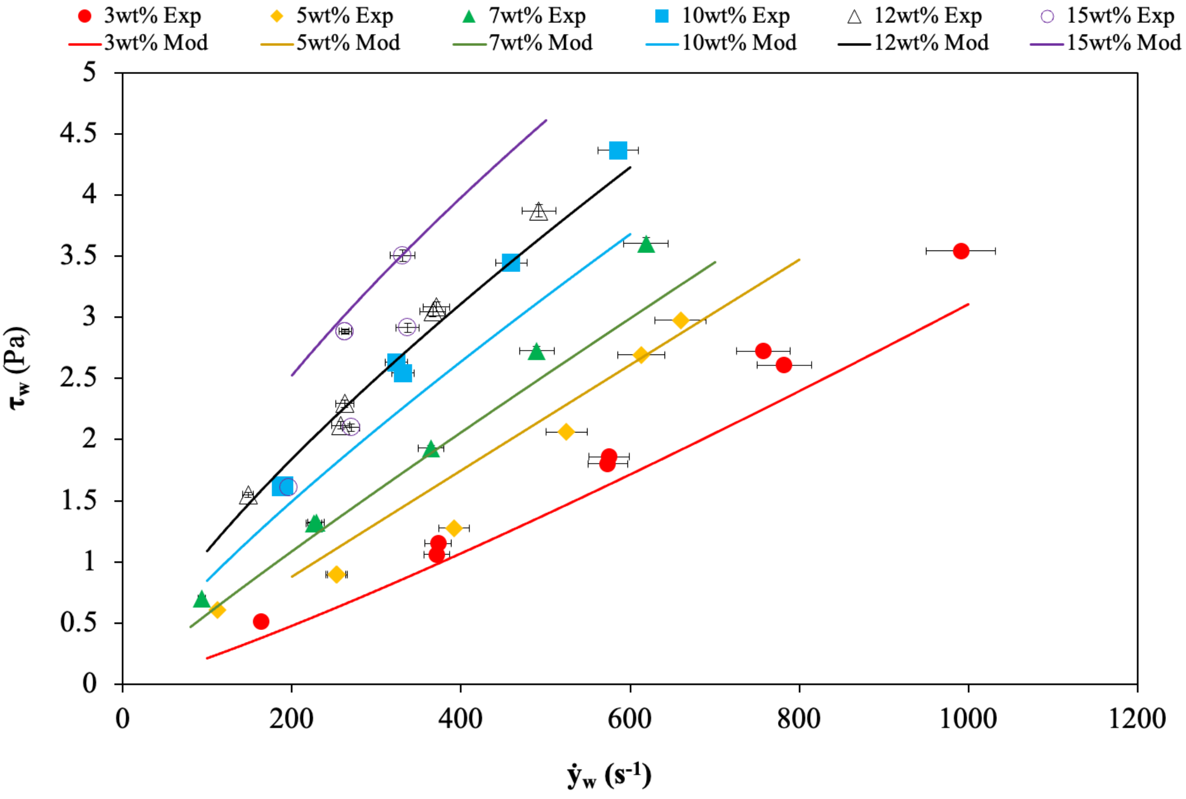

Fig. 5: CP hydrate slurry rheograms for CP fraction between 3 and 15 wt%

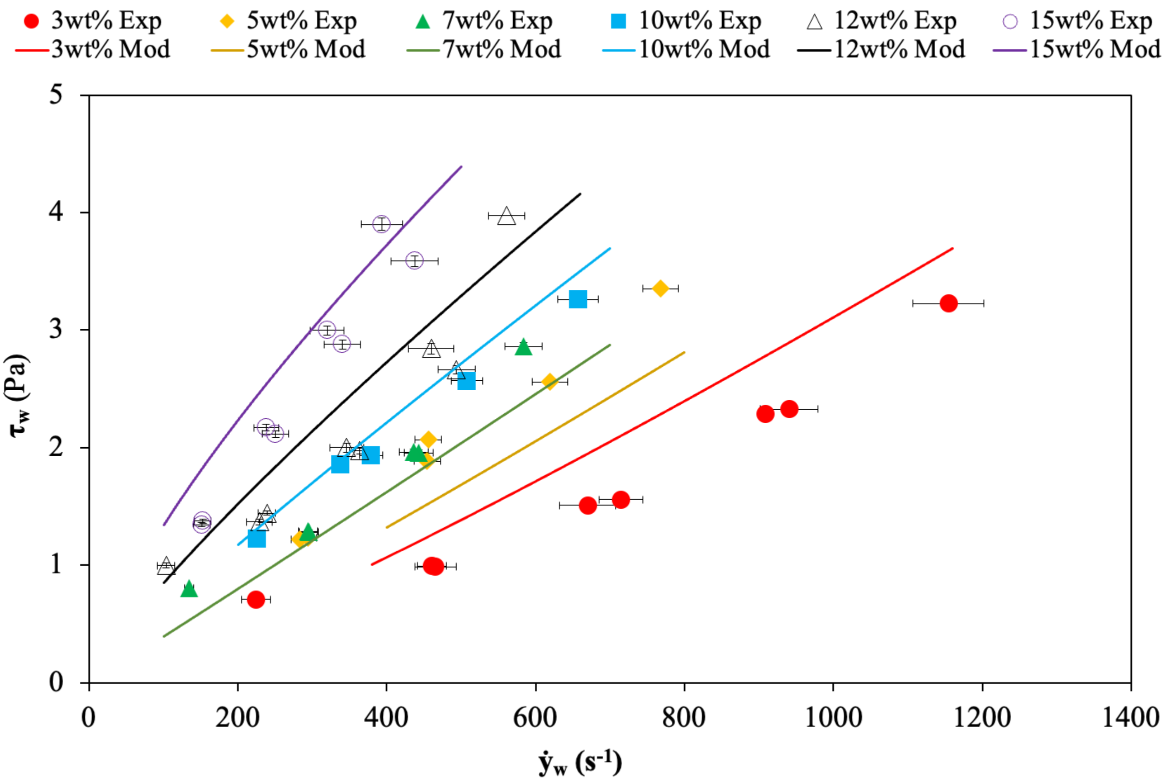

Fig. 6: Mixed CP + CO_2 hydrate slurry rheograms for CP fraction between 3 and 15wt%

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. 7 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. 8). 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 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.

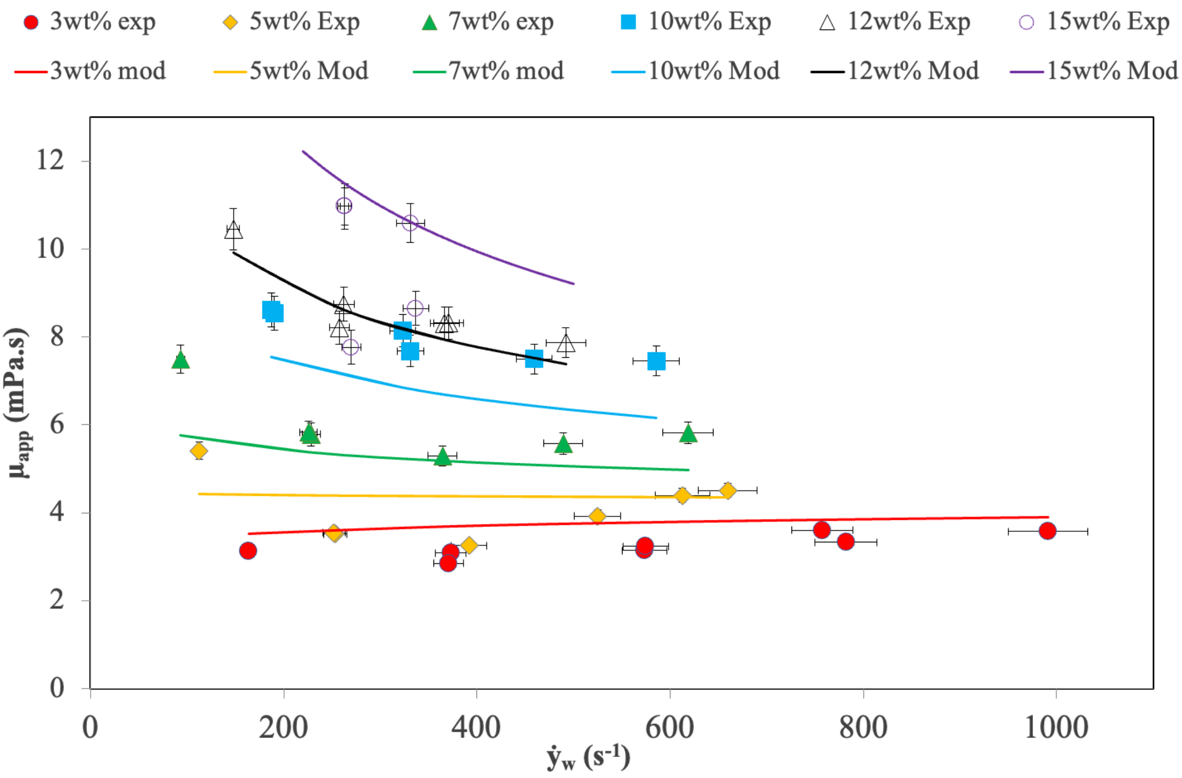

Fig. 7: Apparent viscosity of CP hydrate slurry for CP fraction between 3 and 15wt %

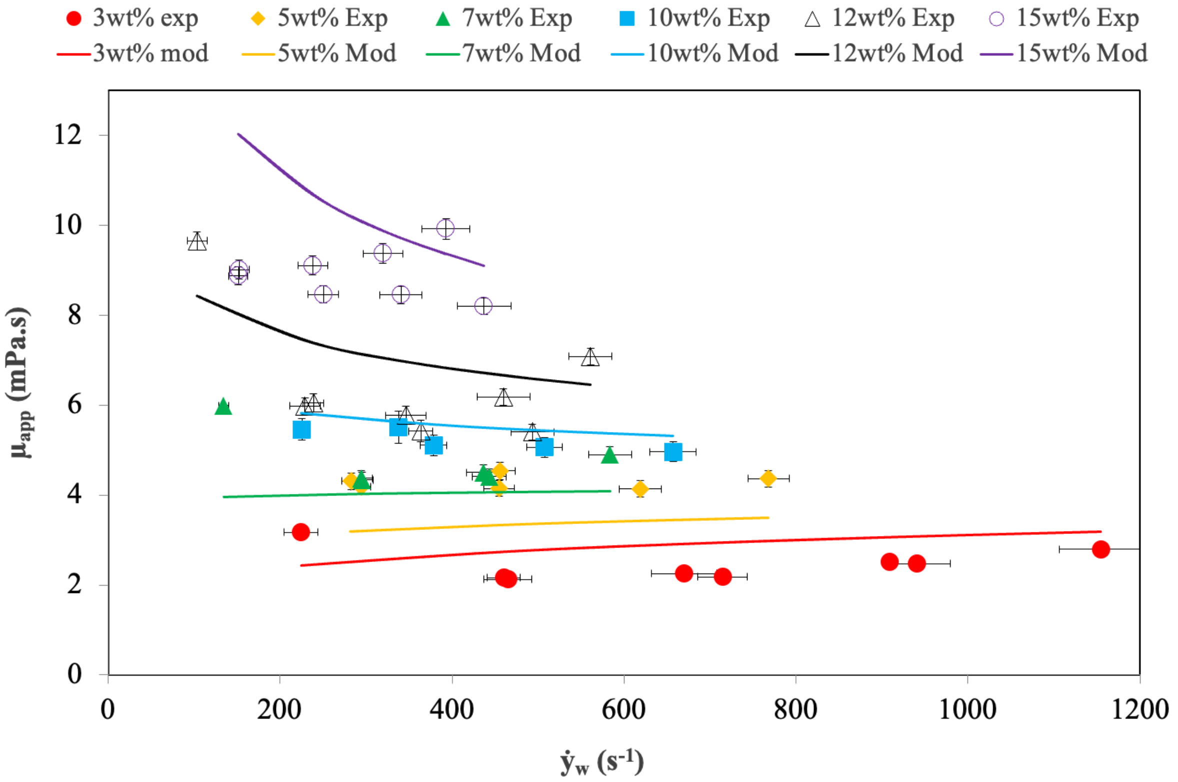

Fig. 8: Apparent viscosity of mixed CP + CO_2 hydrate slurry for CP fraction between 3 and 15wt%

Table 2 : Comparison of viscosities of CP hydrate slurry

Reference	Water cut (%)	Shear rate(s^{-1})	Viscosity (Pa. s)
Chen et al. [24]	20	300	0.017±0.002
Liu et al. [23]	20	300	0.014
This work (CP hydrate)	85	300	0.012±0.0004
	88		0.009±0.0004
	90		0.007±0.0004
	93		0.005±0.0002
	95		0.004±0.0001
	97		0.004±0.0001

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 **2**) should be considered with caution. Yet, Table **2** 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. 9 shows the variation of viscosity as a function of shear rate for CP, CO_2, TBPB [32], SDS-CO_2 [33] and mixed CP + CO_2 hydrate slurries. This comparison shows that 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.

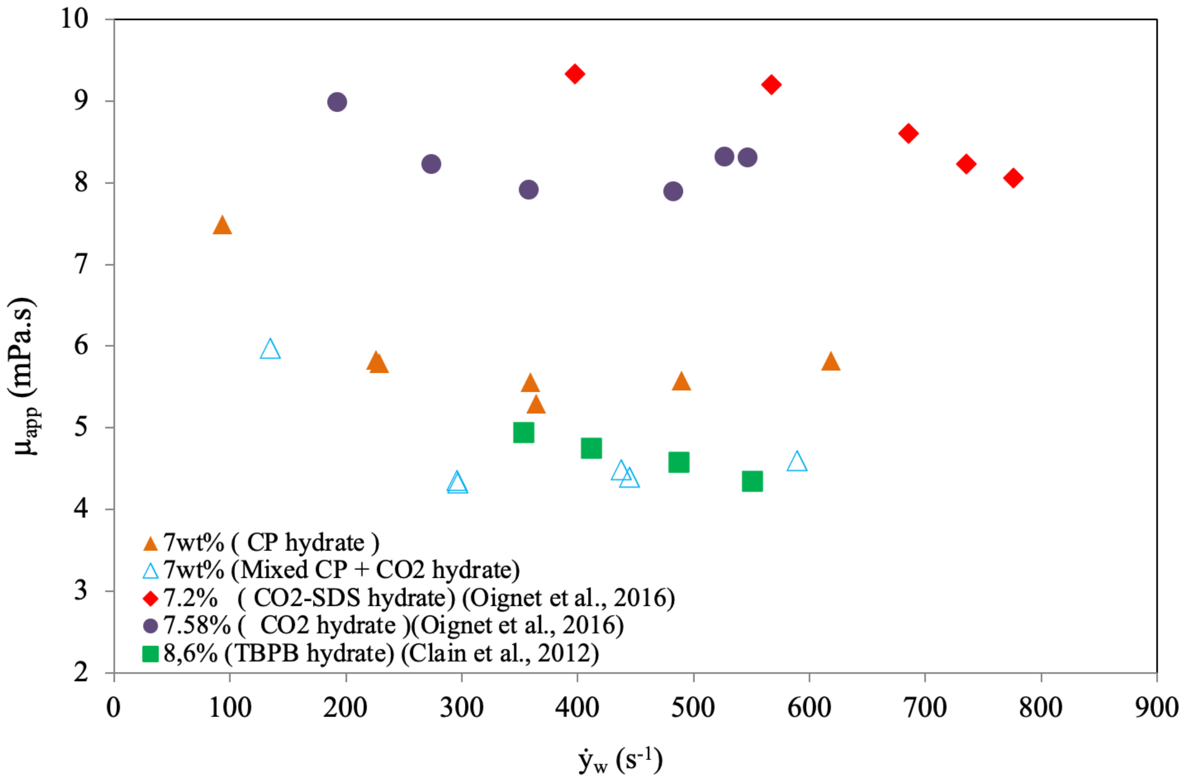

Fig. 9: Comparison between different types of hydrates

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 [17], [18]. 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 refrigeration. In this work, the rheological characterization of hydrate slurry was done at two different measurement times. The first one was done directly after the hydrate formation (t = 0 h). The second measurement was made 16 hours after the hydrate formation, (t = 16 h), and after the first rheological characterization at t = 0 h without changing any operating parameters.

This characterization at different times showed a change in behavior index *n* values when CP fraction varies from 3 to 12 wt% (lower than 1 at t = 0h, except the point at 3 wt%, and higher than 1 at t = 16h) (Fig. 11). 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 12wt % was presented in Fig. 13. The viscosity of mixed CP + CO_2 hydrate slurry shows an increase with the shear increase, contrary to what was found at t = 0h 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 specially at relatively low CP fraction.

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. [32], which allows the verification of the system regime, the Re $_{MR}$ number [28] 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.

The Fig. 12 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. Therefore, the changes in rheological behavior after 16 h of mixed CP + CO_2 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 lower at t = 16 h than at t = 0 h which becomes more obvious at the 12 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 100-240V. Fig. 10 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 [34]. Nevertheless, the number of cyclopentane drops was significantly lower after the hydrate dissociation, which was also reported by [20]. 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 and the increase of viscosity is limited, resulting in a change in behavior after 16 hours. Liu *et al.* [24] have found a similar behavior for hydrate slurry in the presence of wax. The authors explained that the viscosity decreases with the increase of the wax concentration used. The same behavior was observed even earlier by Karanjkar *et al.* [19] using a hysteresis loop for CP hydrate slurry.

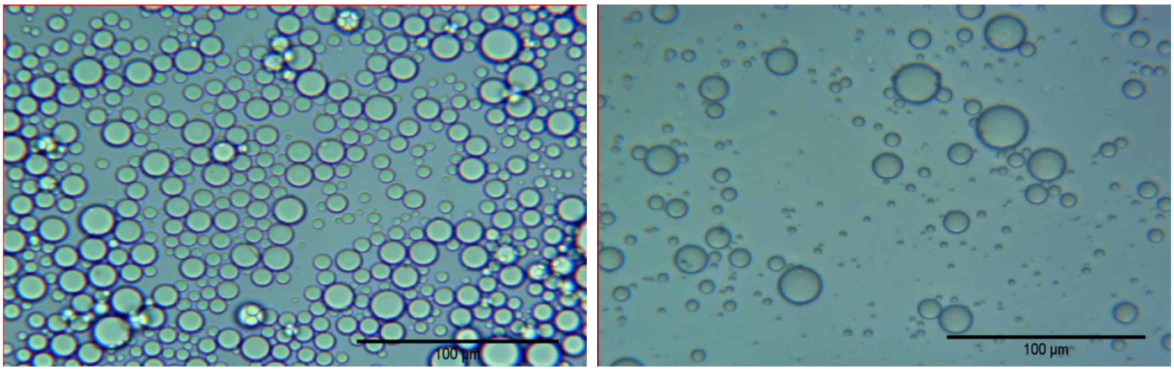

Fig. 10: Microphotographs of the 10wt % cyclopentane in water emulsion at different time periods: (a) before hydrate formation (b) after hydrate dissociation.

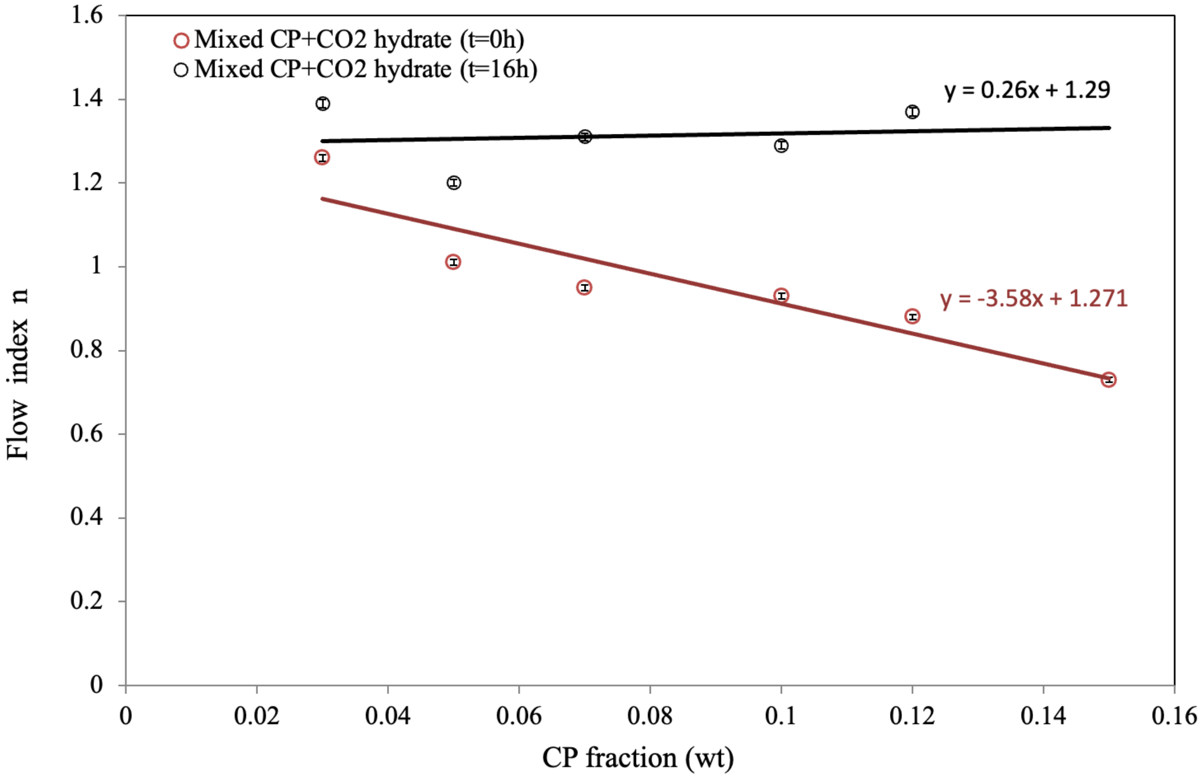

Fig. 11: Flow index as a function of CP fraction for mixed CP + CO_2 hydrate slurry at t=0 and after 16 h

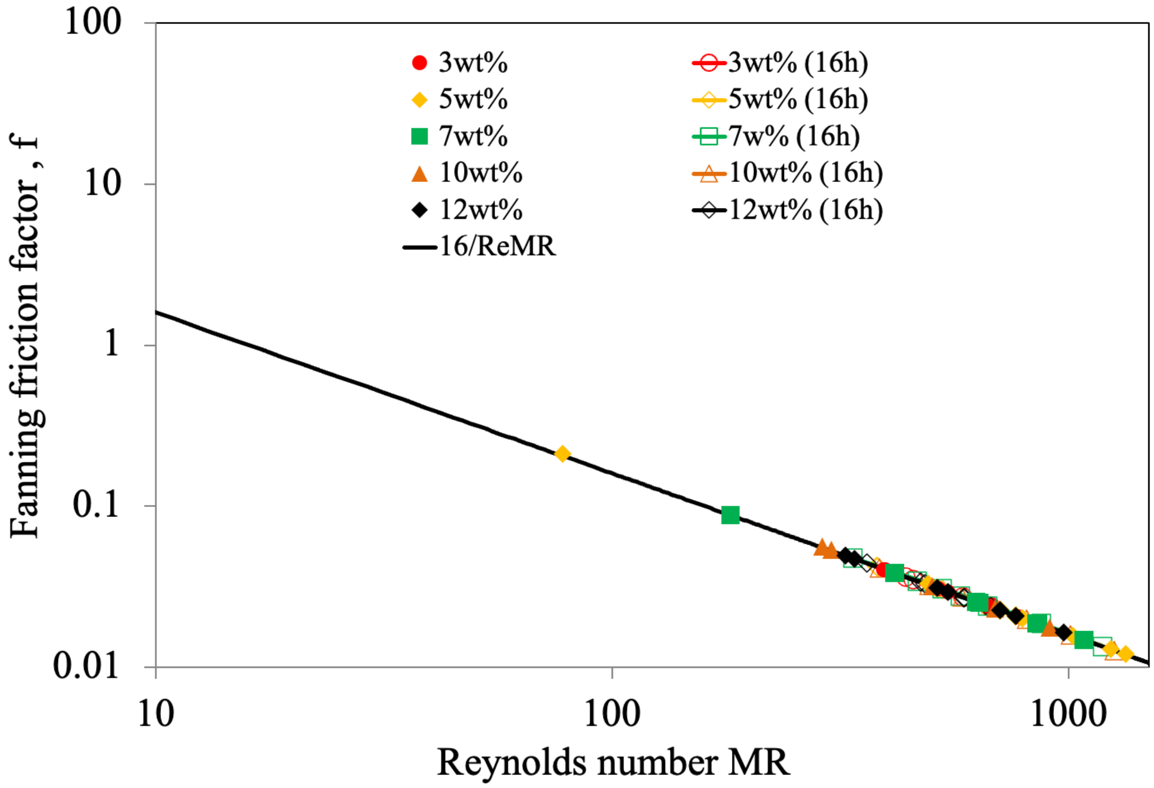

Fig. 12: Friction factor of CP + CO_2 hydrate slurry as a function of Reynolds number MR for various CP fractions after hydrate formation, and 16h after hydrate formation

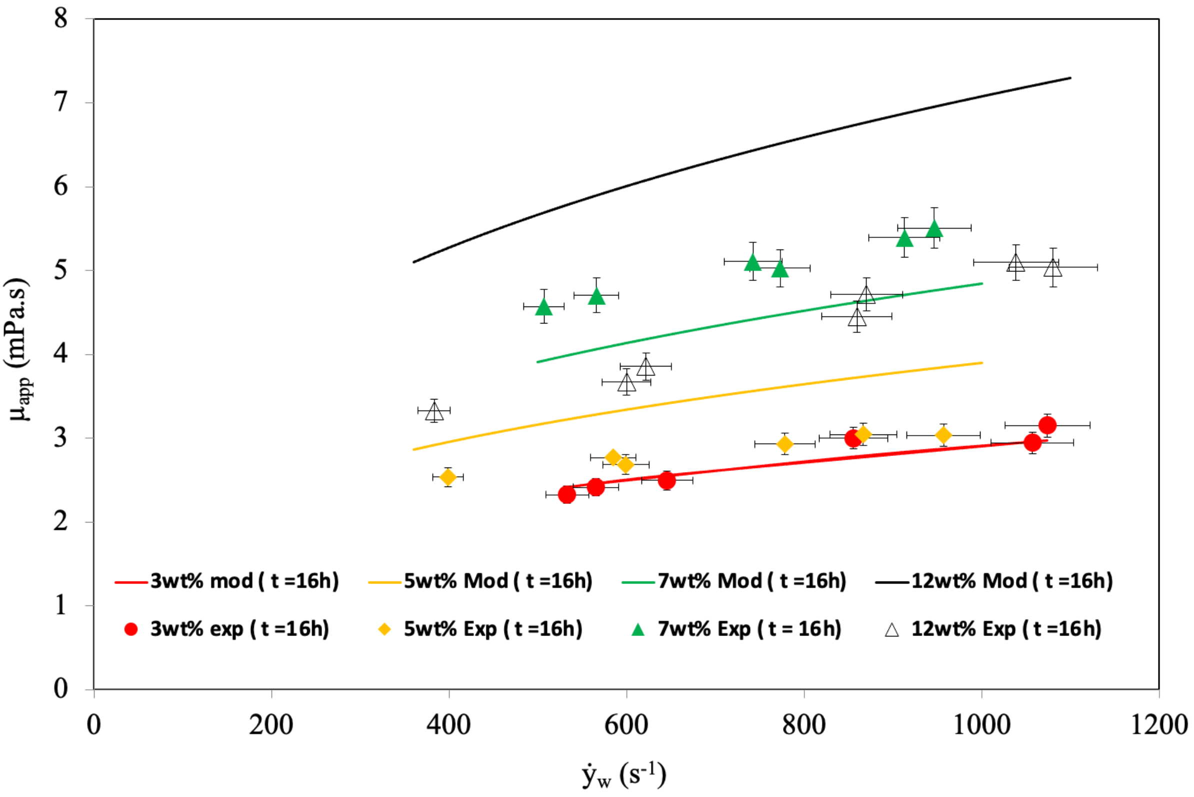

Fig. 13: Apparent viscosity of mixed CP + CO_2 hydrate slurry for CP fraction between 3 and 12 wt% 16 h after hydrate formation

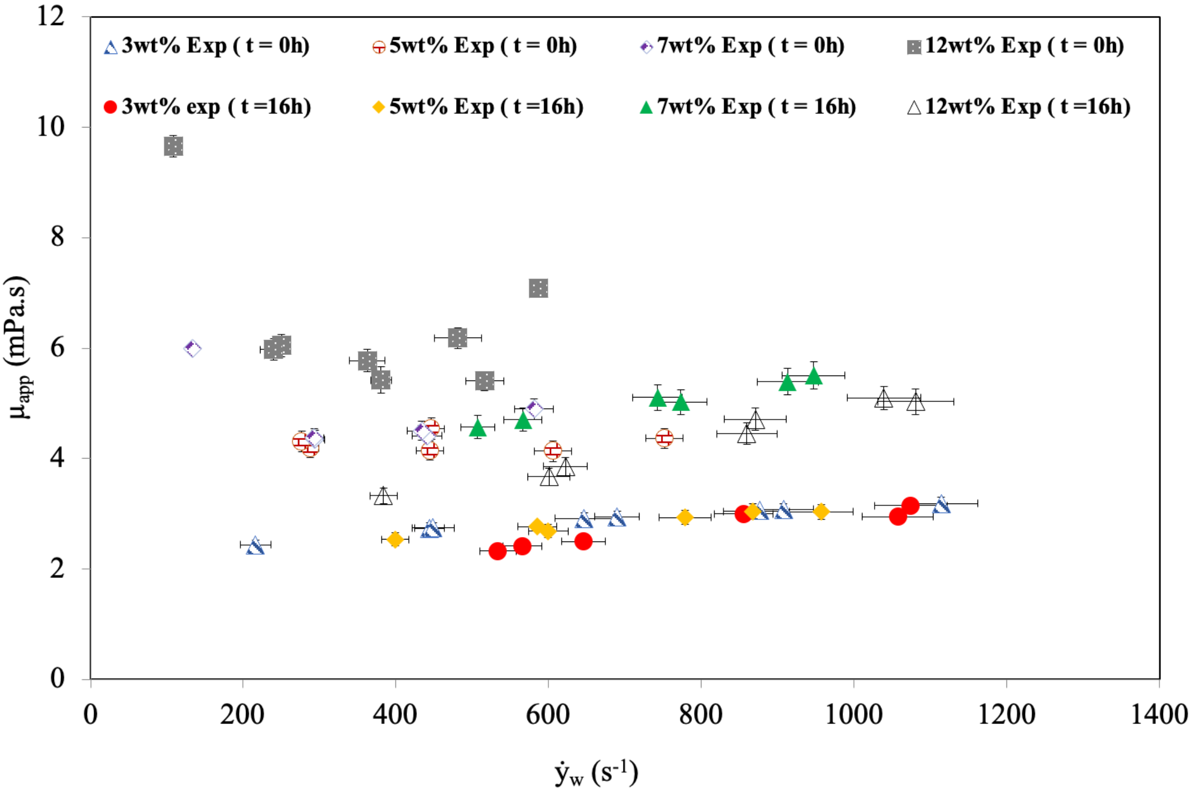

Fig. 14: Comparison between the viscosity of mixed CP + CO_2 hydrate slurry at 0 h and the viscosity after 16 h

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 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 7wt%.
- 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 refrigeration applications.
- The measurement at different times indicates the mixed CP + CO_2 hydrate slurry exhibit a behavior change.
- 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 verification of this data with complementary characterization methods in the loop will be presented in a further work.

Acknowledgements

This work was supported by the French National Research Agency under the program MUSCOFI (ANR-18-CE0-0028) and undertaken in the frame of the US Partnership for International Research and Education program (National Science Foundation Award Number 1743794) and of the French Research Consortium “GDR-2026 Hydrates de gaz”.

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

References

[1] A. Mathur, S. A. Muthukumaraswamy, et L. Varela, « Investigation and Analyses of Energy-Efficient Technologies for HVAC and Lighting Systems via Energy Auditing Processes », in *2018 International Conference on Smart Grid and Clean Energy Technologies (ICSGCE)*, 2018, p. 186‑ 190. doi: 10.1109/ICSGCE.2018.8556644.

[2] I. Tanasawa et S. Takao, « Low-Temperature Thermal Storage Using ClathrateHydrate Slurries of Tetra-n-butylammonium Bromide: Thermophysical Properties and Morphology of ClathrateHydrate Crystals », présenté à International Heat Transfer Conference Digital Library, 2002.

[3] I. Chatti, A. Delahaye, L. Fournaison, et J.-P. Petitet, « Benefits and drawbacks of clathrate hydrates: a review of their areas of interest », *Energy Conversion and Management*, vol. 46, n° 9, p. 1333‑ 1343, 2005, doi: https://doi.org/10.1016/j.enconman.2004.06.032.

[4] L. Fournaison, A. Delahaye, I. Chatti, et J.-P. Petitet, « CO2 Hydrates in Refrigeration Processes », *Ind. Eng. Chem. Res.*, vol. 43, n° 20, p. 6521‑ 6526, sept. 2004, doi: 10.1021/ie030861r.

[5] S.-P. Kang, H. Lee, et B.-J. Ryu, « Enthalpies of dissociation of clathrate hydrates of carbon dioxide, nitrogen, (carbon dioxide+ nitrogen), and (carbon dioxide + nitrogen+ tetrahydrofuran) », *The Journal of Chemical Thermodynamics*, vol. 33, n° 5, p. 513‑ 521, 2001, doi: https://doi.org/10.1006/jcht.2000.0765.

[6] M. Darbouret, M. Cournil, et J.-M. Herri, « Rheological study of TBAB hydrate slurries as secondary two-phase refrigerants », *International Journal of Refrigeration*, vol. 28, n° 5, p. 663‑ 671, 2005, doi: https://doi.org/10.1016/j.ijrefrig.2005.01.002.

[7] P. Clain, F. T. Ndoye, A. Delahaye, L. Fournaison, W. Lin, et D. Dalmazzone, « Particle size distribution of TBPB hydrates by focused beam reflectance measurement (FBRM) for secondary refrigeration application », *International Journal of Refrigeration*, vol. 50, p. 19‑ 31, févr. 2015, doi: 10.1016/j.ijrefrig.2014.10.016.

[8] J. S. Zhang et J. W. Lee, « Equilibrium of Hydrogen + Cyclopentane and Carbon Dioxide + Cyclopentane Binary Hydrates », *J. Chem. Eng. Data*, vol. 54, n° 2, p. 659‑ 661, févr. 2009, doi: 10.1021/je800219k.

[9] M. Nakajima, R. Ohmura, et Y. H. Mori, « Clathrate Hydrate Formation from Cyclopentane-in-Water Emulsions », *Ind. Eng. Chem. Res.*, vol. 47, n° 22, p. 8933‑ 8939, nov. 2008, doi: 10.1021/ie800949k.

[10] Y. Zhang *et al.*, « Phase Equilibrium of Cyclopentane + Carbon Dioxide Binary Hydrates in Aqueous Sodium Chloride Solutions », *J. Chem. Eng. Data*, vol. 62, n° 8, p. 2461‑ 2465, août 2017, doi: 10.1021/acs.jced.7b00404.

[11] N. Chami *et al.*, « Thermodynamic characterization of mixed gas hydrates in the presence of cyclopentane as guest molecule for an application in secondary refrigeration »,

Chemical Engineering Science, p. 116790, 2021, doi: https://doi.org/10.1016/j.ces.2021.116790.

[12] P. J. Herslund, N. Daraboina, K. Thomsen, J. Abildskov, et N. von Solms, « Measuring and modelling of the combined thermodynamic promoting effect of tetrahydrofuran and cyclopentane on carbon dioxide hydrates », *Fluid Phase Equilibria*, vol. 381, p. 20‑ 27, nov. 2014, doi: 10.1016/j.fluid.2014.08.015.

[13] Y. Matsumoto, T. Makino, T. Sugahara, et K. Ohgaki, « Phase equilibrium relations for binary mixed hydrate systems composed of carbon dioxide and cyclopentane derivatives », *Fluid Phase Equilibria*, vol. 362, p. 379‑ 382, janv. 2014, doi: 10.1016/j.fluid.2013.10.057.

[14] W.-L. Zhao, D.-L. Zhong, et C. Yang, « Prediction of phase equilibrium conditions for gas hydrates formed in the presence of cyclopentane or cyclohexane », *Fluid Phase Equilibria*, vol. 427, p. 82‑ 89, nov. 2016, doi: 10.1016/j.fluid.2016.06.044.

[15] J. Lee, K.-S. Kim, et Y. Seo, « Thermodynamic, structural, and kinetic studies of cyclopentane + CO2 hydrates: Applications for desalination and CO2 capture », *Chemical Engineering Journal*, vol. 375, p. 121974, nov. 2019, doi: 10.1016/j.cej.2019.121974.

[16] Y. Chen *et al.*, « In Situ Viscosity Measurements of a Cyclopentane Hydrate Slurry in Waxy Water-in-Oil Emulsions », *Energy Fuels*, vol. 33, n^{o} 4, p. 2915‑ 2925, avr. 2019, doi: 10.1021/acs.energyfuels.8b04268.

[17] A. A. A. Majid, B. Tanner, et C. A. Koh, « Cyclopentane hydrate slurry viscosity measurements coupled with visualisation », *Molecular Physics*, vol. 117, n^{o} 23‑ 24, p. 3860‑ 3870, 2019, doi: 10.1080/00268976.2019.1670877.

[18] A. Ahuja, G. Zylyftari, et J. F. Morris, « Yield stress measurements of cyclopentane hydrate slurry », *Journal of Non-Newtonian Fluid Mechanics*, vol. 220, p. 116‑ 125, 2015, doi: https://doi.org/10.1016/j.jnnfm.2014.11.007.

[19] P. U. Karanjkar, A. Ahuja, G. Zylyftari, J. W. Lee, et J. F. Morris, « Rheology of cyclopentane hydrate slurry in a model oil-continuous emulsion », *Rheologica Acta*, vol. 55, n^{o} 3, p. 235‑ 243, mars 2016, doi: 10.1007/s00397-016-0911-1.

[20] G. A. B. Sandoval *et al.*, « A Rheological Study of Parameters That Influence the Formation of Cyclopentane Hydrates », *Energy and Fuels*, vol. 35, n^{o} 22, p. 18467‑ 18477, 2021, doi: 10.1021/acs.energyfuels.1c02726.

[21] A. Ahuja, G. Zylyftari, et J. F. Morris, « Calorimetric and Rheological Studies on Cyclopentane Hydrate-Forming Water-in-Kerosene Emulsions », *J. Chem. Eng. Data*, vol. 60, n^{o} 2, p. 362‑ 368, févr. 2015, doi: 10.1021/je500609q.

[22] G. Zylyftari, A. Ahuja, et J. F. Morris, « Modeling Oilfield Emulsions: Comparison of Cyclopentane Hydrate and Ice », *Energy Fuels*, vol. 29, n^{o} 10, p. 6286‑ 6295, oct. 2015, doi: 10.1021/acs.energyfuels.5b01431.

[23] Y. Liu *et al.*, « Rheological study of low wax content hydrate slurries considering phase interactions », *Journal of Natural Gas Science and Engineering*, vol. 94, p. 104106, 2021, doi: https://doi.org/10.1016/j.jngse.2021.104106.

[24] 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.

[25] A. Delahaye, L. Fournaison, S. Jerbi, et N. Mayoufi, « Rheological Properties of CO2 Hydrate Slurry Flow in the Presence of Additives », *Ind. Eng. Chem. Res.*, vol. 50, n° 13, p. 8344‑ 8353, juill. 2011, doi: 10.1021/ie200185q.

[26] J. Oignet *et al.*, « Rheological study of CO2 hydrate slurry in the presence of Sodium Dodecyl Sulfate in a secondary refrigeration loop », *Chemical Engineering Science*, vol. 158, p. 294‑ 303, 2017, doi: https://doi.org/10.1016/j.ces.2016.10.018.

[27] J. F. Steffe, *Rheological methods in food process engineering*. Freeman press, 1996.

[28] A. Metzner et J. Reed, « Flow of non‐ newtonian fluids—correlation of the laminar, transition, and turbulent‐ flow regions », *Aiche journal*, vol. 1, n° 4, p. 434‑ 440, 1955.

[29] V. Andersson et J. S. Gudmundsson, « Flow properties of hydrate-in-water slurries », *Annals of the New York Academy of Sciences*, vol. 912, n° 1, p. 322‑ 329, 2000.

[30] S. Marinhas, A. Delahaye, et L. Fournaison, « Solid fraction modelling for CO2 and CO2–THF hydrate slurries used as secondary refrigerants », *International Journal of Refrigeration*, vol. 30, n° 5, p. 758‑ 766, 2007, doi: https://doi.org/10.1016/j.ijrefrig.2006.12.010.

[31] S. Marinhas, A. Delahaye, L. Fournaison, D. Dalmazzone, W. Fürst, et J.-P. Petitet, « Modelling of the available latent heat of a CO2 hydrate slurry in an experimental loop applied to secondary refrigeration », *Chemical Engineering and Processing: Process Intensification*, vol. 45, n° 3, p. 184‑ 192, mars 2006, doi: 10.1016/j.cep.2005.08.002.

[32] P. Clain, A. Delahaye, L. Fournaison, N. Mayoufi, D. Dalmazzone, et W. Fürst, « Rheological properties of tetra-n-butylphosphonium bromide hydrate slurry flow », *Chemical Engineering Journal*, vol. 193‑ 194, p. 112‑ 122, 2012, doi: https://doi.org/10.1016/j.cej.2012.04.027.

[33] J. Oignet *et al.*, « Rheological study of CO2 hydrate slurry in the presence of Sodium Dodecyl Sulfate in a secondary refrigeration loop », *Chemical Engineering Science*, vol. 158, p. 294‑ 303, 2017, doi: https://doi.org/10.1016/j.ces.2016.10.018.

[34] D. J. McClements, *Food emulsions: principles, practices, and techniques*. CRC press, 2004.