encit 2020

ABCM
Associação Brasileira de Engenharia e Ciências Mecânicas

18th Brazilian Congress of Thermal Sciences and Engineering
November 16–20, 2020 (Online)

ENC-2020-0569

RHEOLOGICAL MEASUREMENTS OF TETRAHYDROFURAN HYDRATE SLURRIES

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Abstract. *Blockage of pipelines due to hydrate formation are one of the main concerns in flow assurance of the oil industry. The re-start problem is intrinsically dependent on the rheology of these slurries. In the present work we measure material functions of hydrate slurries formed from a mixture of Tetrahydrofuran (THF) in water. Rigid protocols are needed for hydrate formation and rheological measurements. We perform different tests in a Taylor—Couette geometry and measured the viscosity as a function of time for different conditions. Our results demonstrated the low level of time dependency for the volume fractions tested in the present work, namely 30%, 35%, and 40%. The higher the THF content, the lower is the final level of viscosity. The effects of pre-shearing level, rest waiting time, and total test time lead to small discrepancies in the flow curve, mainly concentrated in the lower range of shear rate values, for the parameters tested in the present work.*

Keywords: *Flow assurance, hydrates, rheological measurements*

1. INTRODUCTION

Hydrate formation is one of the main problems in flow assurance of the oil industry. Gas hydrates are crystalline solids formed by water and light molecules when specific thermodynamic conditions of high pressure and low temperature are attained. These conditions are common in deep and ultra–deep water This phenomenon is responsible for the blockage of pipelines causing the interruption in production what in turn has an enormous cost impact. Once the hydrates were formed and blockage had occurred, the conditions for the re-start of the production become significantly different. These materials resemble ice and this solid-like structure is associated to a yield stress, i.e. to a minimum stress state for the material to flow. Therefore, flow would start after the achievement of a pressure drop much higher than the one used in standard conditions. For the reasons described, the rheological characterization of hydrates is of paramount importance for flow assurance in the oil industry. The in lab studies involving hydrates can be performed employing a pressure cell in order to impose very high levels of pressure, such as the ones found in environmental conditions (Sandoval *et al.*, 2018, 2019) or can be done in ambient pressure conditions Lima Silva *et al.* (2018). It is worthy to notice that the final structure achieved by the material is a function of the method employed to reach the hydrate formation. In this regard, the protocol associated with the achievement of hydrate formation and the measurements conditions need to be strictly followed. In addition, due to the intrinsic complexity of the hydrate structure, rheological measurements are challenging. Hence, the evolution of certain material functions with respect to time is an important tool to understand this material behaviour.

In the case of ambient pressure conditions, the main hydrate forming agents employed are cyclopentane and tetrahydrofuran (THF). This second agent is more related to the present work. A mixture of THF and water was employed by Kalbus *et al.* (1995) to analyze the role of different chemical additives in their capacity to inhibit hydrate formation from rheometrical measurements,. This same kind of mixture was used by Wang *et al.* (2010) to obtain a hydrate slurry for the analysis of the flow and blockage in tubes. They have shown that turbulence can accelerate the process of hydrate formation. Yao *et al.* (2007) analyzed the rheology obtained from condensate oil and THF with different water cuts. The shear thinning behavior found in these compounds were associated to a breakage of agglomerates and a viscoplastic character was also identified, leading to a flow curve well fitted by a Herschel–Bulkley equation.

The objective of this work is to obtain reliable measurements of the flow curve of hydrate slurries formed from mixtures of tetrahydrofuran. To this end, we developed a protocol for these measurements and tested different conditions, such as time–dependency, pre-shearing level, rest waiting time, and total test time.

2. MATERIALS AND METHODS

2.1 Material and rheometric geometry

We investigate hydrate slurries formed from a mixture of water and tetrahydrofuran with different volume fractions: 30%, 35%, and 40% of the hydrocarbon. This compound is miscible in water and forms hydrates at ambient pressure in temperatures above 0^0C. We employed a Taylor—Couette geometry [1] to do the hydrate formation procedure and to perform the rheological measurements.

2.2 Constant shear rate measurements protocol

The standard protocol followed for the tests imposing constant shear rate is described next

1. Bath temperature is adjusted to 0^0C
2. Peltier temperature is adjusted to 10^0C
3. Gap is adjusted in the Rheometer system
4. Mixture sample is poured into the cup.
5. After the cylinder is in contact with the mixture, we let 10 minutes until the whole system reaches temperature equilibrium
6. The test is initiated and the viscosity is measured before hydrate formation for 5 minutes
7. With the aid of a steel spatula, a tiny perturbation is introduced in the mixture surface for 20 seconds, after which hydrates are formed
8. Viscosity continuous to be captured after hydrate formation

2.3 Flow curve measurements protocol

The standard protocol followed for the tests to measure the flow curve is described next

1. Bath temperature is adjusted to 0^0C
2. Peltier temperature is adjusted to 10^0C
3. Gap is adjusted in the Rheometer system
4. Mixture sample is poured into the cup.
5. After the cylinder is in contact with the mixture, we let 10 minutes until the whole system reaches temperature equilibrium
6. A pre-shear is imposed at the rate of $\dot{\gamma} = 200\mathrm{s}^{-1}$
7. With the aid of a steel spatula, a tiny perturbation is introduced in the mixture surface for 20 seconds, after which hydrates are formed
8. The shear rate is kept at this level for 10 minutes for the sample to be homogenised
9. The rheometer is stopped and the material stays at rest for 5 minutes
10. A shear rate ramp is imposed to the material and the viscosity is captured

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[1] Cup diameter: 27mm; Bulb diameter: 25.0775mm, height: 37.5983 mm; Cone angle: 120^o; Gap: 3mm; Sample volume: 16.3 mL

3. RESULTS

3.1 Constant shear rate measurements

Figure 1 shows the viscosity as a function of time in constant shear rate experiments. The shear rate values belong to the interval $\dot{\gamma} \in [1, 500]\mathrm{s}^{-1}$. In each subfigure we can see the influence of the THF volume fraction. For the lowest shear rate value employed, $\dot{\gamma} = 1\mathrm{s}^{-1}$ the results are quite scattered. Even though, we can identify a more constant viscosity value for longer times, after a viscosity overshoot, for volume fractions of THF of 35% and 40%. For higher values of shear rate we can identify a viscosity plateau value in the first 5 minutes of the test, before hydrate formation (see the followed protocol in the previous section). After that, we notice a viscosity increase after which it evolves to a state where, even not being constant, it does not exhibit a significant variation. We can notice that the higher the THF volume fraction, the lower is the average viscosity value. This fact was consistent in the whole range of shear rates. In addition, this lower average value has a lower variance for high shear rate values. These results can be rearranged as in Fig. 2, where they are separated by THF volume fraction. There, we can notice that the results obtained for the 40% volume fraction of THF are more stratified and in a monotonic disposition, except for the $\dot{\gamma} = 300\mathrm{s}^{-1}$.

3.2 Flow curves

In this subsection we show flow curve results represented by the viscosity as a function of the shear rate. The flow curves are obtained by imposing a shear rate sweep. The standard protocol included a pre–shear treatment The cases shown in the figures below tested different conditions experienced by the materials.

In Fig. 3, the flow curve for the hydrate formed from a 30% THF mixture with water is shown together with some steady–state results obtained from constant shear rate experiments. We can observe an excellent agreement for this points, with the exception of the $\dot{\gamma} = 25\mathrm{s}^{-1}$ and $\dot{\gamma} = 50\mathrm{s}^{-1}$. Even in these cases, the discrepancy was not significant. These results reveal the low level of time–dependency, since the regular time of acquisition was able to capture the same value as a long time of exposition to the same shear rate. We can observe in Fig. 3 a shear–thinning effect. It is important to notice that, since the final hydrate slurry is a suspension of hydrate in which the continuous (liquid) phase is THF, the increase in the concentration of this compound yields to a reduction in the final viscosity of the slurry.

We tested the influence of the level of the shear rate imposed in the pre–shear stage. Figure 4 shows that imposing $\dot{\gamma} = 50\mathrm{s}^{-1}$ or $\dot{\gamma} = 100\mathrm{s}^{-1}$ no significant changes are observed. However, in the case of a pre–shear of $\dot{\gamma} = 200\mathrm{s}^{-1}$ notice that agreement is reached only after a certain level of shear rate. Further tests are need for a more conclusive study of this effect, since it is expected that a higher shear rate would induce a more intense breaking down and, consequently, a lower viscosity level.

The influence of the resting time, after the hydrate was formed and before the flow curve measurements are performed, is shown in Fig. 5. We notice some discrepancy for lower values of the shear rate, with some organization with the lower viscosity corresponding to the highest resting time. However, for higher values of the shear rate the fluctuations are more random and no significant differences are detected.

4. CONCLUSIONS

In the present work we measured material functions of hydrate slurries formed from a mixture of Tetrahydrofuran (THF) in water for different values of volume fractions: 30%, 35%, and 40%. We followed rigid protocols to induce hydrate formation and rheological measurements. These measurements were performed for constant shear rate experiments and for flow curves where a shear rate sweep is imposed. We employed the Taylor—Couette geometry embedded with a Peltier system to control temperature and measured the viscosity for different conditions with respect to the protocol. Our results demonstrated the low level of time dependency for the volume fractions tested in the present work. The higher the THF content, the lower is the final level of viscosity. The effects of pre-shearing level, resting time, and total test time lead to small discrepancies in the flow curve, mainly concentrated in the lower range of shear rate values, for the parameters tested in the present work.

5. ACKNOWLEDGEMENTS

This research was partially funded by grants from CNPq (Conselho Nacional de Pesquisa e Desenvolvimento) and PETROBRAS.

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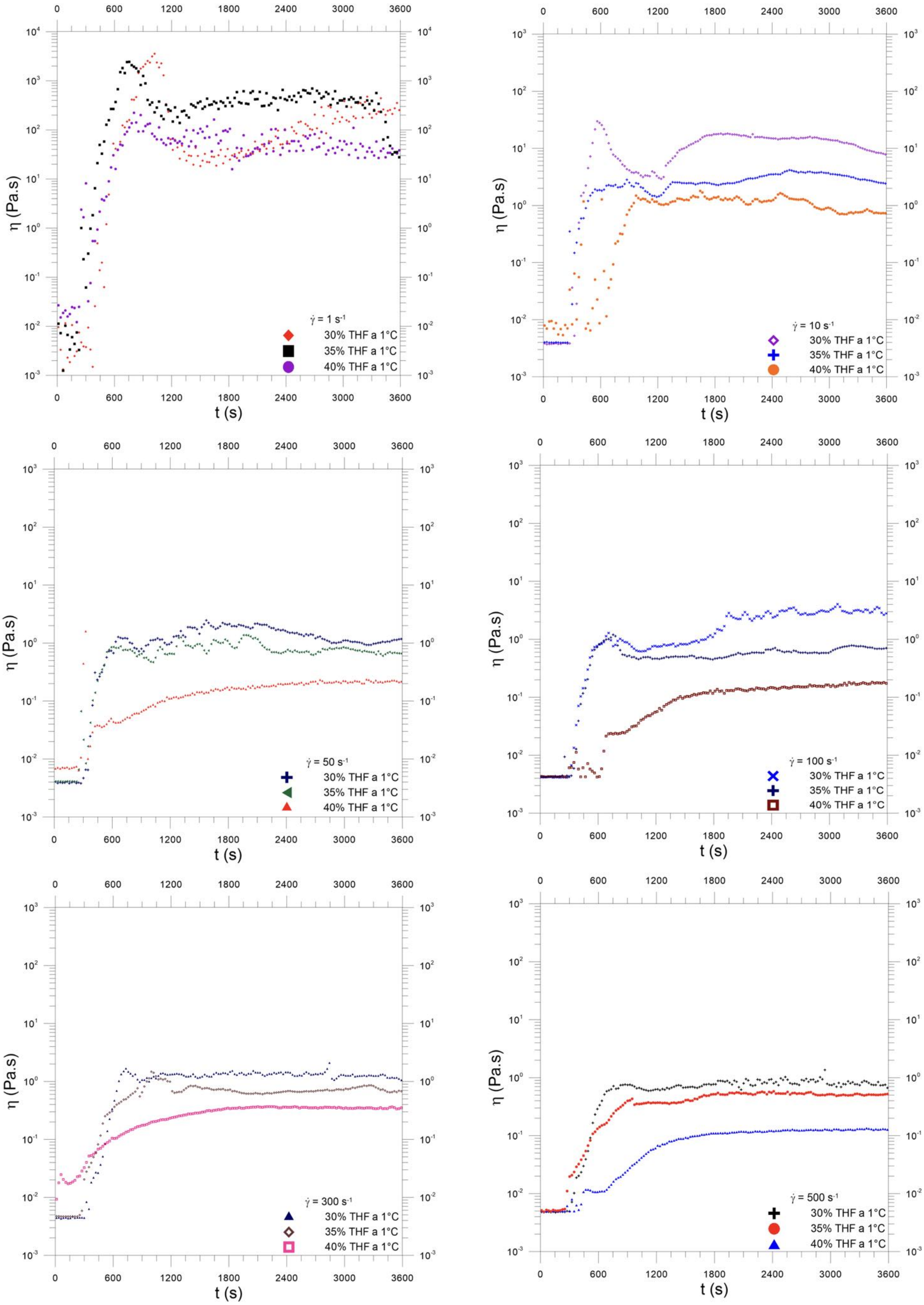

Figure 1. Viscosity as a function of time in constant shear rate experiments for three volume fractions of THF, 30%, 35%, and 40%. Each subfigure corresponds to a different level of shear rate.

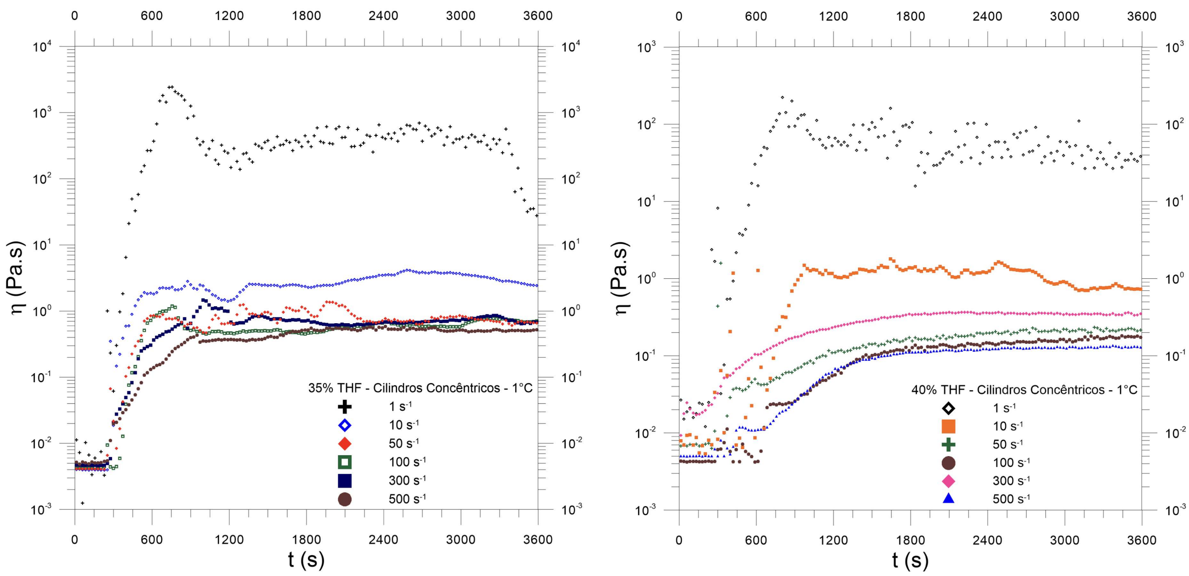

Figure 2. Viscosity as a function of time for different levels of shear rate. Left, 35% in volume fraction of THF. Right, 40% in volume fraction of THF.

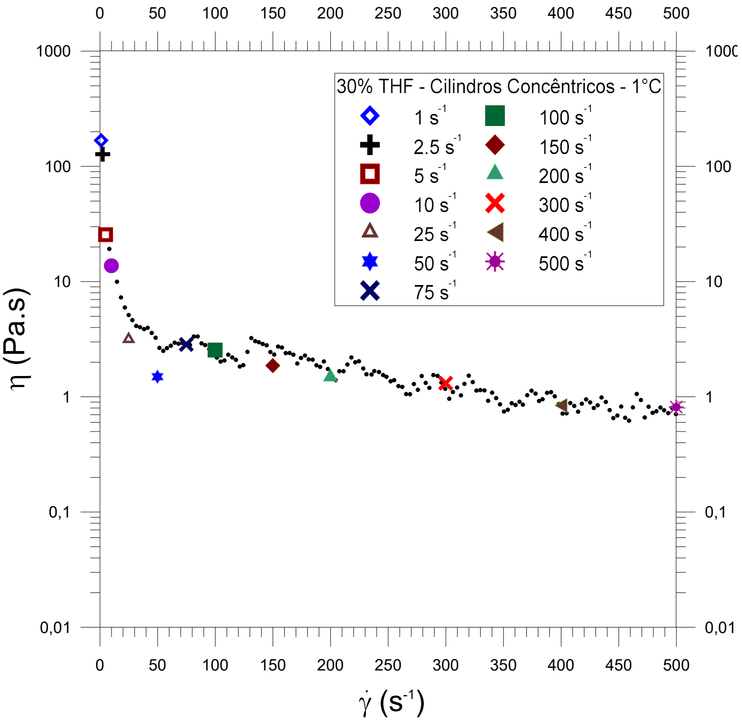

Figure 3. Flow curve of the 30% of volume fraction of THF with additional points obtained from the constant shear rate experiments.

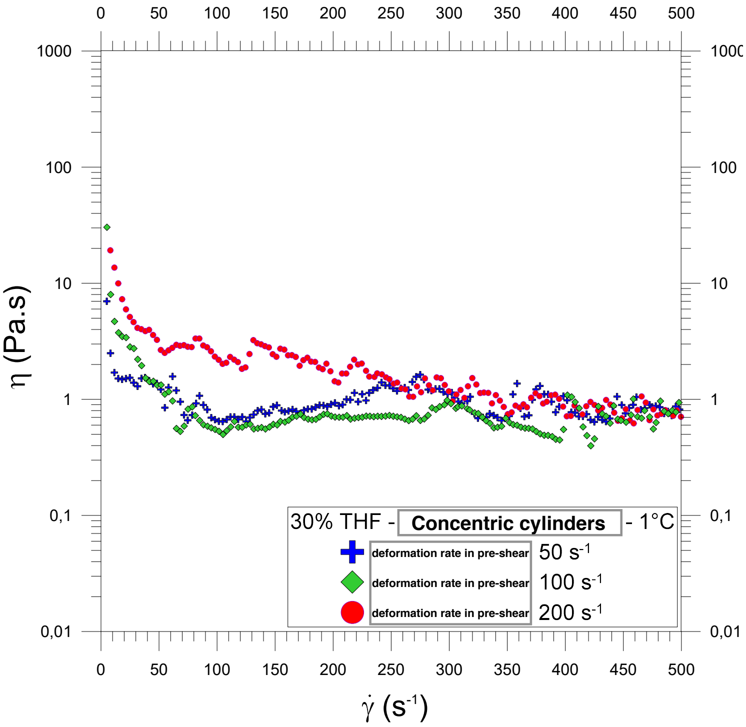

Figure 4. Flow curves of the 30% of volume fraction of THF obtained after different pre-shear conditions.

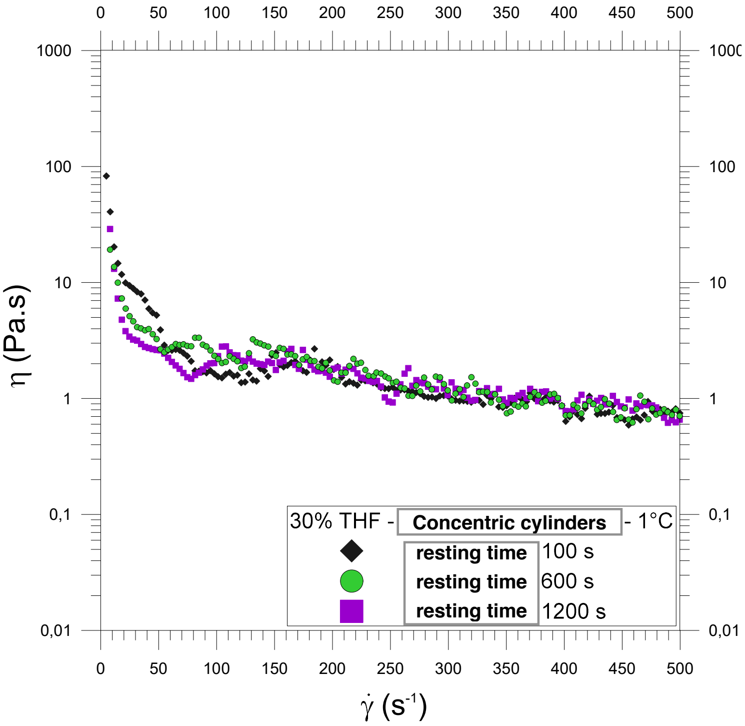

Figure 5. Flow curves of the 30% of volume fraction of THF obtained after different values of waiting time.