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Startup Flow of Gelled Crude Oils in Pipelines: the Roles of Shrinkage and Irreversible Time Dependence

Tese de Doutorado

Thesis presented to the Programa de Pós-graduação em Engenharia Mecânica of PUC-Rio in partial fulfillment of the requirements for the degree of Doutor em Engenharia Mecânica.

Advisor: Prof. Paulo R. de Souza Mendes

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Abstract

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Throughout the wax gelation, the network of paraffin crystals modifies the behavior of waxy crude oil. It changes from a low viscosity Newtonian to a high viscosity time-dependent material with yield strength. Now, it is totally challenging to find out the restart pressure for gelled crude oil flow with such a complex microstructure. Through my Master's dissertation, we investigated two viscoplastic materials, namely a hair gel with a negligible thixotropy and a quite thixotropic 2% aqueous suspension of Laponite to mimic the startup flow of waxy crude oils. For both materials, the minimum axial pressure gradient required for the onset of flow was measured, and the measured values were in good agreement with the prediction of a conventional force balance. On the other hand, industry cases have exhibited that the just mentioned force balance leads to an overestimation of the minimum startup pressure gradient. In some studies, an elicited explanation is the thixotropic behavior of the gelled crude, but our results above-mentioned served to falsify it. Over the first part of my PhD thesis, we aimed to verify in the laboratory that why the force balance does not hold for gelled crude oil and then we sought a physically proper explanation for this discrepancy and also a reliable way to predict the minimum startup pressure gradient. Along these lines, we show the role of gelled crude oil's shrinkage in the discordance between static yield strength and required minimum pressure gradient to onset the flow, through rheometry and fluid flow in a tube. Then, we introduce a modified force balance equation with the role of shrinkage included to best estimate the minimum restart pressure gradient. Another essential element through the restart flow of gelled waxy crude is to find out a reliable strategy to mathematically model the material's rheology. In most models that aim at predicting the rheological behavior of gelled waxy crude oil, the microstructure changes during flow are assumed to be thixotropic (reversible time dependent). But, we observed in our experiments with well-controlled flow and thermal histories that the irreversible character of time dependence is quite evident. Thus, in the second part of thesis we propose a model based on previous developments by Souza Mendes and co-workers that accounts for the irreversible time dependence observed experimentally in a waxy crude oil. The predictive capability of the proposed model is then assessed via comparisons with experimental data.

Keywords

Gelled Waxy Crude Oil; Startup Flow; Volume Shrinkage; Time-dependent; Irreversibility; Constitutive Model; Fluidity.

Resumo

Abedi, Behbood; de Souza Mendes, Paulo R. Inicio Escoamento de Óleos Gelificados de em **Oleodutos:** os Efeitos do Encolhimento e da Dependência Temporal Irreversível. Rio de Janeiro, 2020.83p. Tese Departamento de Doutorado de Engenharia Mecânica, Pontifícia Universidade Católica do Rio de Janeiro.

Durante a gelificação por parafina, a rede de cristais de parafina modifica o comportamento do óleo cru. Ele muda de um material newtoniano de baixa viscosidade para um material com dependencia temporal e de alta viscosidade com tensão limite do escoamento. Com isto, é totalmente desafiador descobrir a pressão minima de início do fluxo de petróleo gelificado com uma microestrutura tão complexa. Através da minha dissertação de mestrado, investigamos dois materiais viscoplásticos: um gel de cabelo com uma tixotropia desprezível e uma suspensão aquosa tixotrópica 2 % de laponita para imitar o início de fluxo de óleos gelificados. Para ambos os materiais, o gradiente de pressão axial mínimo necessário para o início do fluxo foi medido e os valores medidos estavam de acordo com a previsão do balanço de força convencional. Por outro lado, os casos da indústria exibiram que o balanço de força mencionado acima leva a uma superestimação da pressão mínima inicial. Em alguns estudos, uma explicação elicitada é o comportamento tixotrópico do petróleo gelificado, mas nossos resultados acima mencionados serviram para refutá-lo. Durante a primeira parte da minha tese de doutorado, buscamos verificar por laboratório porque o balanço de força não se aplica ao petróleo gelificado, em seguida, buscamos uma explicação fisicamente adequada para essa discrepância e também uma maneira confiável de prever a pressão mínima de início do escoamento. Nesta linha, mostramos o efeito do encolhimento do petróleo gelificado na discordância entre a tensão limite estática de escoamento e o gradiente de pressão mínimo necessário para iniciar o fluxo, através da reometria e do fluxo de fluido em um tubo. Em seguida, introduzimos uma equação de balanço de força modificada com o efeito de encolhimento incluído para obter o melhor estimação da pressão minima de início de escoamento. Outro elemento essencial sobre o início de escoamento de petróleo gelificado é descobrir uma estratégia confiável para modelar matematicamente a reologia do material. Na maioria dos modelos que visam prever o comportamento reológico de petróleo gelificado, as mudanças da microestrutura durante o fluxo são consideradas tixotrópicas; dependencia temporal reversivel. Porém, observamos em nossos experimentos com histórias de fluxo e térmicas bem controladas que o caráter irreversível da dependência temporal é bastante evidente. Assim, na segunda parte da tese, propomos um modelo baseado no desenvolvimentos anteriores de Souza Mendes e colaboradores que considera a dependência temporal irreversível observada experimentalmente para petróleo gelificado. A capacidade preditiva do modelo proposto é então avaliada através de comparações com dados experimentais.

Palavras-Chave

Óleo cru gelificado; Inicio de escoamento; Encolhimento; Dependência temporal; Irreversibilidade; Modelo constitutivo; Fluidez.

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1 Introduction

Flow assurance issues associated with deepwater flowlines and pipelines remain central to cost-effective field developments. Wax, asphaltene and hydrate plug formation comprise the key concerns [67]. Among them, wax deposition and gelation are two potentially catastrophic issues in both crude oil and gas condensate systems. The deposition of n-paraffin will commonly occur along the pipe walls when the temperature of produced fluids falls below the Wax Appearance Temperature (WAT), at which the first wax crystals start to precipitate out of solution [27]. Wax gelation is less common in steady-state than wax deposition, but it can have even greater impact. If during production the system shutdowns, fluid temperature drops below the fluid pour point, it allows the formation of a solid wax column. This situation can completely block the pipeline [58, 59]. Throughout the wax gelation, the network of paraffin crystals modifies the behavior of waxy crude oil [57]. It changes from a low viscosity Newtonian to a high viscosity time-dependent material with yield strength [19, 61]. There is a critical or range of stresses, below which no flow occurs, but above which the viscosity of a gelled system decreases drastically. Thus, in order to restart a gelled crude flow, a pressure larger than the typical operating one should be applied to exceed the static yield strength of the fluid at wall [4, 27, 50]. The usual solution to displace the gelled crude is to pump another fluid (typically water or light oil) into the pipeline at high pressure [9, 65]. Then, the main challange is to determine the minimum pressure at the tube entrance to generate a stress higher than its static yielding through gelled crude [1, 19]. Through my Master's dissertation (Abedi et al.[1]), we investigated two viscoplastic materials, namely a hair gel with a negligible thixotropy and a quite thixotropic 2% aqueous suspension of Laponite to mimic the startup flow of waxy crude oils. For both materials, the minimum axial pressure gradient required for the onset of flow was measured, and the measured values were in good agreement with the prediction of a conventional force balance

$$\sigma_w = \frac{R}{2} \frac{\Delta P_{\min}}{L} \tag{1-1}$$

On the other hand, industry cases have exhibited that the just mentioned force balance for predicting restart pressure leads to an overestimation of the minimum axial pressure gradient [1, 7]. In some studies the thixotropic effects are reported as an elicited explanation for this behavior [62], our results presented in [1] served to falsify it.

Over the first part of my PhD thesis, we aimed to verify in the laboratory that why the conservative equation does not hold for gelled crude oil and then we sought a physically proper explanation for this discrepancy and a reliable way to predict the minimum pressure gradient.

Multiple works in the literature point out the volume shrinkage of waxy crude oil during gelation process as a reason behind this discrepancy. Magda et al. affirms that a waxy crude oil under cooling experiences thermal shrinkage. Thermal shrinkage mainly causes waxy crude oil to shrink, and voids would then be formed in a gel, which would make the actual restart pressure in a pump to be much lower than what was predicted from the theoretical equations [7]. Ahmadpour et al.[2] discussed theoretically the weakly compressible nature of gelled waxy crude oil due to thermal shrinkage and asserts that the assumption of incompressible of the gel in the theoretical equation is no longer valid [7]. Vieira et al.[60] also reported that the voids formed in a gel, particularly around pipe wall, would reduce the stress between the wall and gel and consequently reduce the restart pressure at a significant level [7]. Chala et al.[6] indicates that the conventional force balance implemented in the industry with the assumption of constant yield stress and single phase crude oil needs to be modified to account for the gas voids effect and contributions.

Thus, we put our focus on the effect of gelled crude oil's volume shrinkage on the static yield strength and the minimum pressure gradient to onset the flow, through rheometry and fluid flow in a tube. The goal is to identify its influence qualitatively and quantitatively, and to determine that how it alters the established assumptions for the conventional force balance. When all is said and done, we need a tool, maybe a modified force balance, being able to translate a critical stress from rheometry to a minimum restart pressure in tube flow.

Another essential element through the restart flow of gelled waxy crude is to find out a reliable strategy to mathematically model the material's rheology.

Numerous studies have been published about the rheology of gelled waxy crude oils [3, 8, 9, 13, 19, 25, 34, 36, 38, 47, 62, 66]. Wardhaugh and Boger (1988)[66] identified three distinct characteristics of the yielding process, namely,

a solid (elastic) behavior, slow deformation, and a sudden failure of the sample that closely resembles the brittle or ductile fracture of solids. Houwink et al. (1971) [30] described a transition from elastic to plastic and then to viscous behavior [3].

The rheological behavior of gelled waxy crude oils as described in the literature and also observed in the tests presented in this work is rather complex, not falling into any category of materials that obey one of the traditional constitutive equations[40].

Modeling such a behavior remains a challenge, despite the existence of various modeling approaches [5, 19, 48, 63]. Most models found in the literature involve a large number of parameters, many of which having no obvious physical meaning. In addition, due to the high complexity of waxy crude oils, it is not simple to obtain rheological data that would allow model validation [21, 41].

The classic thixotropic model proposed by Houska [29] is frequently used to describe waxy crude oils [54], as in the works by Sestak et al. [52], Cawkwell and Charles [5], Wachs et al. [64] and Ahmadpour et al. [2], just to name a few. Models based on different approaches were also employed [19, 45, 54, 55, 56].

In most models that aim at predicting the rheological behavior of gelled waxy crude oils, the microstructure changes during flow are assumed to fall within the frame of thixotropy [32, 33, 43, 44], that is, the time dependence is assumed to be reversible [41].

By reversibility it is meant here that the equilibrium structuring level is a sole function of stress [16, 20]. For example, suppose the material is at equilibrium (or steady state), and hence at a structuring level λ_A that corresponds to a stress σ_A . The stress is then changed to another stress $\sigma_B > \sigma_A$ and held constant until equilibrium and hence another structuring level $\lambda_B < \lambda_A$ is attained. If the material is reversible from the time-dependence viewpoint, then when the stress is changed back to σ_A , the structuring level eventually gets back to λ_A (when equilibrium is attained). The waxy crude studied here is not reversible in this sense. We observed in our experiments with well-controlled flow and thermal histories that the irreversible character of time dependence is quite evident, since once the microstructure is broken due to a high stress, it will not fully rebuild after the stress is withdrawn.

In the literature, several authors have reported at least certain degree of "partial reversibility/irreversibility" in waxy crude oils [21, 22, 31, 40, 41, 53, 63]. Visintin et al. [63] and Sun et al. [54] argue that there are different views in academia on what conditions the "partial reversible/irreversible" behavior of gelled waxy crude oil could be classified as thixotropic.

Although most constitutive models available in the literature for time-dependent materials are restricted to reversible (thixotropic) behavior, some models for irreversible behavior have been published recently. Mendes et al. [40] proposed a model based on their experimental results. The kinetic equation is based on viscosity, which includes a term to predict irreversible instantaneous changes. It was shown that their model predicts the flow characteristics of sweep test and sudden shear rate decrease. Yuan et al. [68] introduced a multi-parameter model with two kinetic equations to take into account irreversible effects of waxy crude oils. Dimitrou and Mckinley [21] introduced irreversibility in their model from plastic deformation and the "back stress" concept, and the predictions were compared with results of LAOS experiments. Based on the ideas of Dimitrou and Mckinley [21], Geri et al. [26] incorporated fractal aggregate theory to develop a model with thermal history.

Marchesini et al. [39], adapted the thixotropic elastoviscoplastic model of de Souza Mendes [15] to account for irreversible effects of a cement paste. The final model is based on a single structure parameter able to describe effects of chemical reactions and irreversible shear degradation. Rodrigues and de Souza Mendes [51] used another approach to develop a model accounting for irreversible time dependence of cement slurries. The model is fully based on rheological experiments and the fluidity concept [20].

In the second part of my thesis, we propose a model that accounts for the irreversible time dependence observed experimentally in a waxy crude oil. We present an alternate viewpoint about the irreversible character of gelled crude oils, introducing two flow curves, one obtained from initially fully-structured samples and the other from initially fully unstructured samples. Then we incorporate these ideas in a constitutive model that evolved from previous developments [20, 51]. The structuring level of the microstructure is given by an evolution equation for the fluidity instead of the classical λ structure parameter. All parameters of the model arise in mathematical functions selected by their ability to predict the same qualitative behavior of previously obtained experimental data. The predictive capability of the proposed model is then assessed via comparisons with experimental data.

We developed a novel evolution equation for the fluidity that involves no postulated functions or parameters. Rather, it involves measurable material functions only. To relate the stress with the kinematics we employ a tensorial Oldroyd-B-like differential equation whose relaxation and retardation times are also measurable functions of the fluidity. The material functions needed in the model are shown to be obtainable from data of standard experiments, and a relatively simple procedure to obtain these material functions is described. This procedure is employed to an aqueous suspension of laponite to obtain the material functions that arise in the model [20].

1.1 Objectives

In the firs part, we investigate the effect of gelled crude oil's morphology on the static yield strength and the required minimum pressure gradient to onset the flow, through rheometry and fluid flow in a tube. And then, we aim to introduce a modified force balance equation with the role of shrinkage included to best estimate the minimum restart pressure.

And the second part, we present our view on the time-dependent irreversible behavior of gelled crude oils flow and then intend to integrate this comportment in a constitutive model based on preceding works by de Souza Mendes et al., Rodrigues and de Souza Mendes which as mentioned mainly differs from the ones present in the literature. The validity of model also will be checked with the experimental data.

2 Experimental configurations

2.1 Rheometry

An important component of the study of gelled crude oil is rheometry, which broadly encompasses the development of specific experimental techniques and quantitative measurements for characterizing the rheology of a particular material.

2.1.1 The AR-G2 Magnetic Bearing Rheometer

TA Instruments rheometer, the AR-G2, was launched in February 2005. Two features were introduced for this instrument to provide a low torque performance never previously obtainable on a commercial rheometer. Good low torque performance is important for the rheological characterization of soft materials. The broader a rheometer torque range, and the better its operation at the low torque end of the range, more fully and accurately the rheological properties of these materials can be measured.

The AR-G2 is a combined motor and transducer (CMT) instrument. This design has traditionally been used for rheometers like the AR-G2 that operate in controlled stress in their native mode. The lower component of the measuring system is fixed, the upper is attached to a shaft, that can rotated by a torque produced by an induction motor (See Fig.**2.1**).



Figure 2.1: Rheometer AR-G2

The constraint on low torque performance of such an instrument is the friction between rotating and stationary components. An induction motor is therefore used not only because the rapidity and stability of its response, but more specifically to minimize the friction.

But the rotating shaft has to be supported in some way, and this requires a bearing: another source of friction. Until now, all high performance commercial CMT rheometers have used air bearings, either of the jet or the diffusion type, and for progress to made, a new technology had to be found : a magnetic bearing, which had previously been used for research instruments used only in creep [49]. The move from air to magnetic technology greatly reduced the friction from the bearing itself, but to make full use of this improvement, it was also necessary to make changes to the motor, to reduce the friction due to that component of the rheometer. To do this, the gap between the stationary and the rotating component was increased. It was important that the improvements in the low torque performance produced by the changes to the motor and bearing should not have been achieved at the expense of performance elsewhere, in particular by reducing the instrument stiffness or substantially increasing the inertia. But checkout process demonstrate that the improvements have been made without compromising on the rheometer's mechanical stiffness or its inertia [10].

2.1.2 The ARES-G2

The ARES-G2 is the most advanced rotational rheometer for research and material development (See Fig.2.2). It remains the only commercially available rheometer with a dedicated actuator for deformation control, Torque Rebalance Transducer (TRT), and Force Rebalance Transducer (FRT) for independent shear stress and normal stress measurements. It is recognized by the rheological community as the industry standard to which all other rheometer measurements are compared for accuracy [11].

An accurate mechanical measurement is based on the fundamental assumption of a controlled variable (stimulation) and a measured variable (response). The separation of these key experimental quantities guarantees the greatest accuracy. Moreover, the analytical components dedicated to each task should be optimized to their assigned role. In the case of a modulus measurement, the application of strain and the measurement of stress should be separated, or in the case of a viscosity measurement, the application of strain rate and the measurement of stress are to be decoupled. This is the approach taken by the TA Instruments ARES-G2, leading to measurements free of instrument artifacts over wide ranges of stress, strain, and frequency.



Figure 2.2: Rheometer ARES-G2

2.1.3 Geometries

Peltier Plate Geometries

Peltier Plate geometries come in 8 mm, 20 mm, 25 mm, 40 mm, 50 mm, and 60 mm diameters. Upper Cone geometries are available in 0.5° , 1° , 2° , and 4° cone angles. By changing diameter and cone angle, the measurable range of stress and strain or shear rate can be varied to capture the widest range of material properties [23, 24].

Standard Peltier Plate The Standard Peltier Plate is the most common selection, offering an 80 mm diameter hardened surface to accommodate up to 60 mm upper plates for maximum sensitivity [23, 24].

Materials of Construction and Surfaces Peltier Plate geometries come standard in the following materials:

- Stainless Steel: Rugged, very good chemical resistance for highly basic or acidic materials
- Stainless Steel with Composite Heat Break: Same properties as stainless steel with added benefit of composite heat break, which insulates upper geometry when controlling temperatures away from ambient

- Hard Anodized Aluminum: Excellent thermal conductivity, low mass, fair chemical resistance
- Titanium: Low mass, excellent chemical resistance

Geometries are available in multiple surface finishes, including smooth, sandblasted, and crosshatched [23, 24].

Crosshatched

About characteristics of Crosshatched geometry notice Table. 2.1.

Diameter	Roughness	Gap
60 mm	500 microns	1000 microns

 Table 2.1:
 Crosshatched chart

See figures (2.3, 2.4) for more on this.



Figure 2.3: Crosshatched plate



Figure 2.4: Crosshatched roughness

Sandblasted

About characteristics of Sandblasted geometry notice Table. 2.2.

Diameter	Roughness	Gap
$60 \mathrm{mm}$	1.25 microns	500 microns

 Table 2.2:
 Sandblasted chart

See figures (2.5, 2.6) for more on this.



Figure 2.5: Sandblasted plate



Figure 2.6: Sandblasted roughness

Cup and Rotor Geometeries

The standard Peltier Concentric Cylinder geometries include a cup radius of 15 mm, configured with either a Recessed End or DIN Rotor. Both rotors have a height of 42 mm. The double gap concentric cylinder has an additional shearing surface over single gap providing lower stress and higher sensitivity for extremely low viscosity solutions [23, 24].

Grooved Recessed-End Rotor and Grooved Cup

About characteristics of Grooved Recessed-End Rotor and Grooved Cup geometry notice Table. **2.3**.

Table 2.3: Grooved Recessed-End Rotor and Grooved Cup chart

Rotor Diameter	Cup diameter	Operating Gap
$27.66~\mathrm{mm}$	$30 \mathrm{mm}$	3600 microns

See figures (2.7, 2.8) for more on this.



Figure 2.7: Grooved Recessed-End Rotor



Figure 2.8: Grooved Recessed-End Rotor and Grooved Cup

2.2 Fluid Transport in Tube

2.2.1 Experimental Setup

The experimental setup is designed to investigate and characterize fluid flow in a tube. The setup consists of a reservoir with maximum volume of 4.7 liter, a roughened snake-like tube with length of 2.5 meter and diameter of 1 cm, two

water bathes to reproduce a temperature above WAT (resembling an oil reservoir) and cold sea bed temperature, manometers and some connections.

Tube

Two plates each containing snaked-like half round pipe together form the tube in this setup. The described structure provides an opportunity to have an access to the tube wall to alter the roughness if it is needed and also it guarantees perfect residual removal from the tube's wall. The structure is illustrated in figures (2.9, 2.10) in more details.



Figure 2.9: Bolted plates enclosing a snaked-like tube



Figure 2.10: Top and side view of single plate containing half round tube

Differential Pressure Measurement

Depending on a range of differential pressure, two different types of manometers were used.

WTPD-4010 Differential pressure transmitters For pressures below than 1 bar this transmitter was used (See Fig. **2.11**). WTPD-4010 differential pressure transmitters have resistive piezoelectric sensor element which convert a pressure difference between high and low side exerted by fluid to an electrical signal, the electrical signal is amplified, linearized and made available in standardized sign. For more technical data notice Table. **2.4**.

Table 2.4: Technical features, WTPD-4010

Feed	9-33 V DC
Accuracy	$\pm 0.25\%~\mathrm{FS}$
Temperature Limit	0 to 70° C



Figure 2.11: Manometer for pressures less than 1 bar

Series 490 Digital Manometers For pressures over 1 bar this type of manometer was used (see Fig. 2.12). Series 490 Digital Manometers are versatile, hand-held, battery operated manometers available in several basic ranges. All models measure either positive or negative differential pressures with $\pm 0.5\%$ of full scale accuracy. For more technical data notice Table. 2.5.

Table 2.5:Technical features, series 490

Feed	9 Volt alkaline battery
Accuracy	$\pm 0.5\%$ FS
Pressure Hysteresis	$\pm 0.1\%$ of FS
Temperature Limit	$0 \text{ to } 40^{\circ} \text{ C}$



Figure 2.12: Manometer for pressures larger than 1 bar

Anther component of the setup is connections which assemble the whole together.

Applying air pressure, fluid flows from reservoir through manometer and the tube, therefore the transport of fluid into tube could be examined. Figure (2.13) shows the whole experimental setup.



Figure 2.13: Experimental configuration of fluid transport in a tube - modified for the gelation process

About the wall roughness of tube, it should be mentioned that different tests were performed using a hair gel [1] until a sufficient roughness was achieved which consequently slip was totally eliminated. The roughness is not quite uniform through the whole tube and it varies in the range between 1 to 400 microns but the 100 microns is a totally acceptable average value as R_a of roughness at tube's wall. For more insight about shape of roughness at the tube's wall figure (2.14) is inserted here.



Figure 2.14: Wall roughness along tube

3 Volume shrinkage

3.1 Introduction

As mentioned earlier, in the industry is reported that the conventional force balance grossly overestimates the minimum axial pressure gradient required. Some works indicate that the occurrence of volume shrinkage through gelation process affects the gelled oil morphology and consequently the startup pressure. In this part, the gelled crude's volume shrinkage in rheometry and tube flow is investigated qualitatively and quantitatively. It is described that how the shrunk volume triggers the wall slippage. Then, it is striven to understand the relationship between the rheological properties and the minimum pressure gradient required for the onset of flow once the volume shrinkage has altered the formerly determined assumptions for the conservative equation. After all, a new term as the constant of shrinkage is introduced and incorporated in the conventional force balance to develop an approximate solution for predicting the minimum restart pressure.

3.2 Gelation procedure

To conduct the investigations, the gelation process of waxy crude oil must be reproduced. It could be from any temperature above the WAT - resembling the crude oil reservoir temperature - to the $4 \,^{\circ}$ C indicating the stagnant crude oil temperature through pipelines at seabed.

In my Master's dissertation, for experiments with Laponite suspension [1], the constant initial state for the all rheometry and flow in tube tests was established to ensure the reproducibility of the experiments. We controlled the shear history, aging[42] and time-dependency of materials alongside the wall slippage. There, each sample after being loaded was put at rest, for 3300 seconds obtained from a time sweep test[1], to rebuild the material's microstructure to the structured state. After the resting time, the test was ready to start. In this work to do the same with crude oil which is a challenging case, seeing that the gelation process is required to be conducted before each test, we capitalize on fixed temperature

periods, i.e., fixed gelation procedure instead of the resting time to implement the constant initial condition. Therefore, the thermal history as a new element should be controlled alongside the others mentioned above [40].

In this part, the experiments illustrated in Figures 3.1, 3.2, 3.3, 3.4, 3.12 and 3.15 were performed with the aid of ARES-G2 strain-controlled rheometer and the rest of them were conducted with AR-G2 stress-controlled rheometer. We utilized two types of geometries with roughened surface; the crosshatched parallel plates and a grooved couette geometry. For the crosshatched plates, an operating gap of 1 mm was applied. Later in the text, for each test is included specifically which one of the geometries is used.

All utilized crude oil samples were pristine ones which have undergone the gelation procedure before each test.

To comprehend the role of thermal history, we designed various experiments which start with a test to determine the WAT (see Fig.**3.1**). The viscosity as a function of temperature is measured in a temperature sweep from higher to lower ones till the dramatic change in the viscosity slope is observed which is due to the appearance of wax crystals indicating the WAT. The measurements were repeated using two different cooling rates; -0.2 and -0.1 °C/min. Petroleum #1 with the viscosity of 0.032 Pa.s at 25 °C was utilized.



Figure 3.1: WAT measurement by temperature sweep test – petroleum #1 – grooved couette geometry

Thus, for petroleum #1 the step change of temperature for gelation process

can be started from any degrees above the 20 $^{\circ}$ C.

In figure **3.2**, three identical samples of petroleum #1 undergo three distinct gelation processes. In the first gelation process, the crude oil is put for 3600 seconds under static heating (no shear) at 30 °C and then 10000 seconds at 4 °C under constant shear rate of $1 s^{-1}$ to evaluate the gelled crude viscosity. For the second and the third ones, the same procedure only with different step changes of temperature are taken; from 45 °C to 4 °C and from 60 °C to 4 °C, respectively. The results show that the viscosity of gelled crude for the third process is the highest (8.65 Pa.s) and for the second one (6.65 Pa.s) in higher than the first one (1.91 Pa.s). It means that a larger step change of temperature causes a stronger gelation and consequently a higher viscosity.



Figure 3.2: Effect of different step changes of temperature on gelled petroleum #1's viscosity; 1 : static heating at 30 °C for 1 hr, 2 : cooling at 4 °C for 10000 seconds while $\dot{\gamma} = 1$ (1/s) is applied, and similarly for other steps 3 : 45 °C, 4 : $\dot{\gamma} = 1$ (1/s) at 4 °C, 5 : 60 °C and 6 : $\dot{\gamma} = 1$ (1/s) at 4 °C – grooved couette geometry

The Figure **3.3** reports about the role of evaporation on the gelled crude oil's viscosity. The gelation procedures with the same step change of temperature from 30 °C to 4 °C, but with different heating periods were applied to two pristine samples of petroleum #1. The sample in the first test was put under static heating at 30 °C for half an hour. In the second test, the sample was subjected to static heating of one hour at 60 °C and then half an hour at 30 °C. Although the step changes of temperature are the same, the thermal history makes difference here. As the evaporation occurred in the second process is greater, the gelled crude viscosity for the second test is higher, too (7.59 Pa.s > 2.21 Pa.s).



Figure 3.3: Effect of thermal history on gelled petroleum #1's viscosity; 1 : static heating at 30 °C for 1/2 hr, 2 : cooling at 4 °C for 1 hr while $\dot{\gamma} = 1$ (1/s) is applied, 3 : 1 hr at 60 °C and 4 : 1/2 hr at 30 °C, 5 : $\dot{\gamma} = 1$ (1/s) at 4 °C for 1 hr – grooved couette geometry

In Figure **3.4**, a sample for three times experiences the same gelation process with the step change of temperature from 30 °C to 4 °C. It is shown that after each heating period, even with relatively low temperature of 30 °C, the gelled crude becomes more viscous; 1.89 Pa.s < 2.03 Pa.s < 2.21 Pa.s. This result asserts that the thermal memory of the waxy crude oil can not be erased.



Figure 3.4: Thermal memory (history) for gelled petroleum #1; 1 : static heating at 30 °C for 1 hr, 2 : cooling at 4 °C for 10000 seconds while $\dot{\gamma} = 1$ (1/s) is applied, and the same procedure is repeated through the other steps 3 : 30 °C, 4 : $\dot{\gamma} = 1$ (1/s) at 4 °C, 5 : 30 °C and 6 : $\dot{\gamma} = 1$ (1/s) at 4 °C – grooved couette geometry

Accordingly to establish the constant initial state, before each test starts, we put the pristine sample under static heating period; it can be $30 \,^{\circ}$ C or $45 \,^{\circ}$ C regarding the experimental circumstances. The heating duration is selected as 1 hour because we want to repeat the same process in the tube flow and the fluid volume in tube needs a long time to reach the thermodynamic equilibrium. Then, the temperature goes down abruptly to $4 \,^{\circ}$ C and the sample remains at static cooling for 1 hour. This way, all the samples for the experiments possess the same microstructure level and the same viscosity.

3.3 Gelled crude oil characterization

In this section, the static heating was conducted at 30 °C; to inflict minimum of alteration in crude oil's composition. First thing, we did some visualization tests. Figure **3.5** displays a drop of petroleum #1 before and after the gelation process in contact with air obtained with an Eclipse LV100N POL (Nikon) microscope. The crucial observation here is the free surface shrinkage which appears as rugosities altering the free surface form.



Figure 3.5: Drop of petroleum #1 (a) above WAT (b) at $4 \degree C$ – free surface volume shrinkage – border retreat observed

In another visualization test, Figure **3.6** shows a drop of petroleum #1 in Linkam shear cell (CSS450) mounted on the microscope during the static cooling; this time the sample has contact with air (free surface) and the geometry. The image in right side is inverted to help the comparison between border positions. The left side indicates the gelled crude's structure just reached at $4 \,^{\circ}$ C, the right side shows the same position only after more 15 minutes. The comparison illustrates the shrinkage as a heterogeneous border retreat at free surface. No sign of shrinkage is observed (from upside view) throughout the interface with geometry. The shrinkage at interfaces can cause the wall slippage in rheometry experiments.



Figure 3.6: Visualization of volume shrinkage for a sample of petroleum #1 loaded in parallel plates (Linkam shear cell) – (a) just reached at 4 °C and (b) at 4 °C for 15 min – heterogeneous border shrinkage at free surface

Now, the first rheometry experiment to be run is the creep test utilizing crosshatched parallel plates and grooved couette geometry to determine the static yield strength. It should be mentioned that the duration of creep tests is 1 hour;

alike the preceding work [1].

For each rheometric flow, appropriate measures must be applied to mitigate the possible volume shrinkage related wall slip, along with we have implemented roughened surface geometries. For the crosshatched parallel plates, we divide the static cooling into pair of 30 min, after the first half, the gap is reduced slightly to force the all shrunk volume out [7, 28] and then the sample is let going through the second half of cooling period.



Figure 3.7: Creep test – crosshatched parallel plates – petroleum #1

For crosshatched parallel plates, the static yield strength lies between the 26 and 27 Pa.

About the gap reduction, we performed tests to ensure that the gap reduction does not alter the microstructure state. In these tests, we applied gap reductions of 10 and 100 microns and measured the viscosity at $\dot{\gamma} = 1 \ s^{-1}$, obtaining essentially the same value, except for a slight influence of wall slip observed after the gap reduction of 10 microns (Fig. **3.8**). We also applied a very small angular displacement to one of the plates, and then measured again the viscosity at $\dot{\gamma} = 1 \ s^{-1}$. In this case, the viscosity value was way less than the viscosity value obtained after the gap reductions (Fig. **3.8**).


Figure 3.8: Effect of the gap reduction and of a very small angular displacement on the microstructure state.

These results indicate that the influence of the gap reduction on the gelled crude microstructure is negligible, leading us to use a 100-micron gap reduction.

For the grooved couette geometry (concentric cylinders), we need a new scenario to eliminate the shrunk volume. In a simple test (Fig. **3.9**) the shrinkage in the cup of couette geometry was reproduced.



Figure 3.9: Reproduction of volume shrinkage in the cup of couette geometry - crosshatched parallel plates

The shrunk volume is observed at free surface in the neck of flask. Thus, to remove the similar shrunk volume in couette geometry, we fill the cup more than normal in a way that this shrinkage occurs above the bob, i.e., out of the couette

flow calculations. As it is illustrated in Fig. 3.10.



Figure 3.10: Removing the longitudinal free surface shrunk area from coette flow calculations – a) before the gelation b) after the gelation – petroleum #1





Figure 3.11: Creep test – grooved couette geometry – petroleum #1

The results show a disagreement with those of the parallel plates. It displays

the viscosity bifurcation between 16 and 17 Pa which means the lower static yield strength. And for applied stresses of 15 and 16 pa, it illustrates a kind of failed avalanche which is not a well-known comportment. These phenomena could be due to wall slippage.

Next, we performed the constant shear rate tests utilizing the both geometries, each was repeated minimum three times. The flow curve is then constructed with the averaged steady-state shear stress values obtained in the constant shear rate tests. This procedure is taken over common flow curve test considering the complexity and high time-dependency of material. The results in Fig. **4.11** ensures the occurrence of wall slippage, as the measured shear stresses at lower shear rates for couette flow are smaller compared to those for parallel plates .



Figure 3.12: Flow curve with crosshatched parallel plates and grooved couette geometry – slippage observed for couette flow – petroleum #1

It indicates that in addition to the free surface shrunk volume which is macroscopic and was eliminated, an another chunk of shrunk volume occurs at the interface between fluid and geometry. Some published works characterize this chunk of shrunk volume composed of voids, mostly the trapped gas-voids [6, 7]. The volume shrinkage due to voids at the rotor and cup's wall and also tube's wall can not be removed, besides it contributes significantly to the wall slip. As this chunk of the shrinkage affects the shear stress and pressure measurements most, we call it the effective shrinkage.

2. Volume shrinkage

A bi-dimensional quarter of five-spot model is constructed to quantify the shrunk volume. The physical Properties of model are as follows: $12 \text{ cm} \times 12 \text{ cm}$, single gap = 0.3 mm, double gap = 0.6 mm (see Fig. **3.13**).



Figure 3.13: Bi-dimensional quarter of five-spot model

We performed the gelation process on petroleum #1 in the model with single gap. We let an injection hole open in contact with air to reproduce the both forms of interfaces which a crude oil sample is subjected to; free surface and in contact with a geometry. A shrunk area around the injection hole (free surface contact) is observed, but nothing macroscopic in contact with geometry (the same as in Fig. **3.6**). When we doubled the gap, the free surface shrunk area enlarged and again nothing macroscopic at the interface with geometry was noticed (see Fig.**4.12**).



(a) Bi-dimensional model with single gap – gelation from 30 $^{\circ}\mathrm{C}$ to 4 $^{\circ}\mathrm{C}$ – shrunk area = 2.61%



(b) Bi-dimensional model with double gap – gelation from 30 °C to 4 °C – shrunk area = 3.56%



This finding is the key to the shrinkage behavior of waxy crude oil. It says that, although the overall shrunk volume is constant for the samples with the same paraffin content through the same gelation process, its morphology depends on geometry. So, it can be deduced that the shrunk volume by cause of the flow resistance, divides unproportionally into the free surface chunk which is observed during each test and the voids in the interface between fluid and geometry or maybe within the fluid. The flow resistance here is the resultant of the fluid viscosity, compressibility [35] and the restricting geometry. In this case, it is implied that either some voids are even smaller than the model's gap and can not be observed from upside view or for the small volume in the model, gas bubbles are able to escape to the free surface chunk; it could be both.

Thus, the bigger gap generates the less resistance which results in the higher free surface shrunk volume; that means the less effective shrunk volume.

It is difficult to measure an actual amount of effective shrinkage, but using this method we can quantify the free surface shrinkage. And as for the same sample through the same gelation process, the overall volume shrinkage is constant, this way we can compare the effective shrinkage values which is crucial for our investigations.

To generalize our observations and proposed arguments, we conduct the same creep tests, with the same measures implemented to eliminate the shrunk volume using another crude oil sample. Petroleum #2 with the viscosity of 0.028 Pa.s at 25 °C was used. The WAT for this petroleum is measured around 17 °C which



indicates that it contains less paraffin than petroleum #1 (see Fig.4.13).

Figure 3.15: WAT measurement by temperature sweep test - petroleum #2

Figure **3.16** reports the static yield strength between 14 and 14.2 Pa using the crosshatched parallel plates. And for the grooved couette geometry, figure **3.17** exhibits the viscosity bifurcation between 10 and 10.3 Pa.



Figure 3.16: Creep test - crosshatched parallel plates - petroleum #2



Figure 3.17: Creep test - grooved couette geometry - petroleum #2

The difference between the static yield strength values for the geometries are narrower which originates from the lower content of paraffin, consequently less effective shrinkage and lower impact of wall slip.

Again a failed avalanche is observed in the couette flow for applied shear stress of 10 Pa. Thus, it is an inherent behavior in presence of wall slip. We call this phenomenon a lazy avalanche.

We talked about the heating period in detail. For the cooling period, the most important element is the aging. In figure **3.18**, for peroleum #1, we increased the static cooling period of the gelation from 1 hour to 24 hours. It is shown that the static yield strength has raised by almost 5 times; from somewhere between 26 and 27 Pa to a stress between 50 Pa and 51 Pa.



Figure 3.18: Creep test - aging effect - static cooling for 24 hours instead of 1 hr - crosshatched parallel plates - petroleum #1

It exhibits the importance of early restart; the longer the gelation goes, the higher the minimum startup pressure becomes.

3.4 Gelled crude oil flow in a tube

After rheometry tests, we conducted the flow in tube experiments to measure the minimum startup axial pressure gradient. Here, the updated version of fluid flow setup is described in detail (see Fig.**3.19**).



Figure 3.19: Flow in the tube configuration -1 and 2: pressurized air above the crude oil and water containers to push them into the tube, 3 and 4: circulation of warm water at a temperature above the WAT from a bath into the jacket of crude oil container to maintain the crude oil at a desired temperature through the static heating, 5: crude oil injection into the entrance of tube, 6: the augmented transparent tube to the exit of tube, 7: after the static cooling, this tube is connected to inject the water exerting the pressure to find out the minimum startup pressure gradient, 8 and 9: circulation of water at 4 °C from a bath to maintain the plate at this temperature through the static cooling

In addition, steps should be taken to mitigate the volume shrinkage. The volume shrinkage in tube is similar to couette flow's shrinkage; longitudinal free surface and radial as voids at tube's wall.

The same gelation process is implemented for the each flow in tube test. First, the container is loaded with crude oil and is put under static heating at a desired temperature above the WAT for 1 hour ¹. Then, by exerting a high pressure of the air above the container, the crude oil sample is pushed rapidly into the tube[1]. We augmented a transparent tube to the exit of snake-like tube to atmosphere (tube #6 in Fig. **3.1**) and allow it to be filled. Once the whole tube is completely filled, at the same time the pressure in the container is brought back to ambient pressure and we immerse the plate in the water bath resembling the seabed at 4° C. The connection valve of tube entrance is closed while the exit

¹using water jacket of the container connected to a bath

(augmented part) is left open to the atmosphere pressure (free surface contact). The stagnant sample continues through static cooling at 4 °C for 1 hour.

With the aid of augmented tube, the longitudinal free surface shrinkage occurs in this part and not in the snake-like tube (alike the couette geometry). As this augmented part is placed after the manometer connection, that means the longitudinal shrinkage occurs out of the force balance calculations and this helps to measure the proper pressure gradient. But, it should be noticed that it is not possible to eliminate voids at the tube's wall, so the effective shrinkage will influence our pressure measurements.

Now, the test is ready to start. The water is injected into the tube from another container at some fixed pressure. If no flow occurs immediately after exerting the pressure, we wait up to one hour² to allow for possible delayed onset of flow as a consequence of thixotropic effects. If no flow is observed after one hour, the test is interrupted by bringing back the pressure to the ambient pressure[1].

We open the plate, clean it up, change the crude oil sample in the container and run the whole gelation process again. A new test begins by raising the pressure to a higher fixed value. we keep performing successive tests until we reach the minimum pressure gradient required for flow, $\Delta P_{\min}[1]$.

We conducted tests to discover the minimum startup pressure gradient with the step change of temperature from 30 °C to 4 °C. The obtained values are 9.1 Pa for the petroleum #1 and 5.5 Pa for the petroleum #2. These values are even less than those of the couette flow (between 16 and 17 Pa for petroleum #1; between 10 and 10.3 Pa for petroleum #2). It arises from the fact that the tube is way longer than couette geometry, the resistance is higher, the more trapped gas voids occurs, so the effective shrinkage is much larger. Therefore, the slippage effect grows and the minimum pressure required decreases.

3.5 Approximate solution

As follows, the no-slip condition is not established and the Eq. 1-1 is not applicable anymore. We need another tool to connect the static yield strength in a rheometer with the minimum startup pressure gradient in a tube.

We propose an approximate solution with the volume shrinkage as a leading actor. Let us assume the exaggerated graphic in Fig. **3.20** as representative for the situation of gelled waxy crude oil in a tube.

²This waiting time was chosen to be equal to the time duration of the rheological creep tests, to ensure that the measured yield strength be consistent with the conditions of the tube flow experiment.

2. Volume shrinkage



Figure 3.20: Exaggerated schematic of gelled crude oil morphology in a tube

The assumptions for the right-hand side of the Eq. 1-1 are still in place, but for the left-hand side the stress now is applied on the shrunk area.

$$\sigma_w 2\pi R_{sh} L = \Delta P_{min} \pi R^2 \tag{3-1}$$

Where R_{sh} is the shrunk radius. In this case, the longitudinal free surface shrinkage is eliminated from the calculations, so there is no contraction in the axial direction. The relevant equation for the general cases is as follows:

$$\sigma_w 2\pi R_{sh} L_{sh} = \Delta P_{min} \pi R^2 \tag{3-2}$$

Where L_{sh} is the shrunk length.

We introduce a new parameter called the constant of shrinkage (C_{sh}) in the equation. This constant holds for the percentage of tube wall's area which due to the shrinkage has lost its contact with the gelled crude oil. So, when this value is larger, the discordance between the static yield strength and the minimum restart pressure gradient is greater. We recalculate the inner area of cylinder as $2\pi RL(1 - C_{sh})$ which $(1 - C_{sh})$ means the approximated area percentage where still there is a contact between the material and the tube wall.

Thus, the new face of force balance equation applicable to the gelled crude flow in a tube becomes as:

$$\sigma_w = \frac{\Delta P_{min} \pi R^2}{2\pi R L (1 - C_{sh})} \tag{3-3}$$

$$\sigma_w(1 - C_{sh}) = \frac{R}{2} \frac{\Delta P_{min}}{L} \tag{3-4}$$

As the next step, we aim to evaluate the correlation between the paraffin content and the constant of shrinkage. With adding pure paraffin to petroleum #1, four new samples were made. Their compositions are listed in table **3.1**.

	sample 1	sample 2	sample 3	sample 4
composition	pet1 + 0%	pet1 + 0.5%	pet1 + 1%	pet1 + 2%

Table 3.1: Four new samples were made by adding pure paraffin to the petroleum # 1 – the added paraffin is in mass percentage

For all the samples, we conducted the same gelation process only with a step change of temperature from 45 °C to 4 °C, because 30 °C was too close to the WAT of sample 4.

Figure **3.21** shows the measured free surface shrinkage for these 4 samples, each test is repeated three times.



Figure 3.21: Free surface shrunk area of 4 samples with different paraffin content - single gap model - 3 repetitions

It is known that the higher paraffin content yields to a higher overall shrinkage. Therefore, the effective shrinkage is the highest for sample 4 as it has higher paraffin content and the lowest free surface shrinkage, and then for 3 > 2 > 1 respectively.

The static yield strength was measured at the non-slippage condition using crosshatched parallel plates. The required minimum pressure gradient to onset the flow in tube was measured as the wall slip exists. In agreement with the results obtained using the bi-dimensional model, the longitudinal free surface shrinkage observed in the augmented outlet of the tube was larger for sample 1 than the others. After all, the C_{sh} was calculated using the approximate solution. The whole results are inserted in table **3.2**.

	sample 1		sample 2		sample 3		sample 4
σ_w	31.5 Pa		207 Pa		344 Pa		914 Pa
ΔP_{min}	11 Pa		27 Pa		29 Pa		41 Pa
$C_{sh}\%$	66	<	87	<	91	<	95

 Table 3.2: The constant of shrinkage measured for 4 samples with different paraffin content

Theses results seal all we postulated earlier. The higher the paraffin content, the higher the effective shrinkage and the higher the constant of shrinkage.

3.6 Final remarks

We sought a reliable explanation for the discordance between the static yield strength from rheometry and the minimum restart pressure gradient in a tube; why the conventional force balance overestimates the predicted minimum restart pressure. We found the explanation in the morphology of gelled crude oil, where the volume shrinkage was observed through rheometry and a flow in tube. It is demonstrated that how the volume shrinkage incites the wall slippage and causes this discordance. Next, we tried to modify the conventional force balance with incorporating a new term as the constant of shrinkage into it. The modified equation is an approximated solution providing the best estimate for the minimum restart pressure gradient from static yield strength at no-slippage condition.

Regarding our experience in the industry, we were aiming for a practical solution for on-field applications. That is why we introduced the approximate solution. From the generated correlation between paraffin content and constant of shrinkage, for any petroleum knowing its paraffin content, the minimum restart pressure in a tube can be estimated from its static yield strength at no-slip condition.

It is worth noting that the experts require some knowledge on the effect of tube radius on gelled crude oil morphology to upscale the estimated value for a pipeline in real case. For example, as a future work, the same flow in tube experiments can be conducted using tubes with different radii to compare the related minimum restart pressure gradients. Learning about the effect of tube size serves in estimations with minimum error for the real cases.

4 Irreversible time dependence

4.1 Introduction

Next, we aim to mathematically model the gelled waxy crude oil's rheology. We introduce a constitutive model to describe the rheological behavior of gelled waxy crude oil. The irreversible time-dependence effects were experimentally characterized and incorporated into the model. The model is developed with basis on the data of standard rheological tests to determine the parameters of novel material functions that arise in the model development procedure, namely flow curve, destruction, and construction tests. The fluidity is directly employed as the indicator of the structuring level of the material. Good agreement is observed between the model predictions and the data, corroborating its potential as a useful tool in the study of start-up flows of gelled crudes in pipelines.

4.2 Sample preparation

A waxy crude oil sample (petroleum #3) with (Newtonian) viscosity of 0.028 Pa.s at 30 °C from the pre-salt field in southeastern Brazil was selected for the experimentations.

First, the WAT is determined by measuring the viscosity as a function of temperature in temperature sweep experiments whose results are given in Fig. **4.1**. The measurements were repeated using two different cooling rates, and an excellent repeatability was observed. The observed dramatic departure from the Arrhenius viscosity slope is due to the appearance of wax crystals, indicating that the WAT is $\simeq 19^{\circ}$ C. The test is conducted using a strain-controlled rheometer (ARES-G2) with a grooved couette geometry.



Figure 4.1: Temperature sweep of the crude oil viscosity used to determine the wax appearance temperature (WAT). The viscosity/temperature slope changes dramatically at the WAT due to precipitation of wax crystals.

This time to simulate the crude oil gelling process, the temperature of 45° C was chosen as the heating temperature for the subsequent experiments, considering the summertime temperatures. The same as the previous part, for all tests a petroleum sample was held at 45° C for an hour and then submitted to a step change to 4° C. The sample was then held for half an hour at 4° C and the gap between plates was reduced to compensate for paraffin shrinkage. After this adjustment the sample was kept at 4° C for another half hour, totalling one hour at 4° C.

The just described pre-treatment of the sample ensured a fixed initial state that was needed to obtain repeatability in the rheometrical and flow experiments. This pre-treatment was employed to all samples studied in this part.

4.3 Rheological experiments

As mentioned before, the rheological behavior of the gelled waxy crude oil is modelled here according to the method proposed by de Souza Mendes and co-workers ([20, 51]). This method requires data obtained from a set of rheological experiments which assess the mechanical behavior of the time-dependent material. These include the flow curve experiment and the construction and destruction experiments, described later in this text.

The experiments illustrated in Figures 4.2, 4.11, 4.14, 4.15 and 4.19 were performed with the aid of an ARES-G2 strain-controlled rheometer with crosshatched parallel plates. For the crosshatched plates the operating gap of 1 mm was implemented. All the other experiments were conducted with an AR-G2 stress-controlled rheometer with cross-hatched parallel plates, except for the results given in Fig. 4.5, for which a grooved Couette geometry was utilized.

Prior to each experiment, all crude oil samples employed were subjected to the aforementioned pre-treatment. This procedure was followed to ensure that all experiments started with pristine, identical samples.

4.3.1 Flow curve

In order to obtain the flow curve of the gelled waxy crude, we performed constant shear rate tests with initially fully-structured samples. The flow curve is then constructed with the steady-state shear stress values measured in the constant shear rate tests. Due to the complexity of the crude oil, we have repeated various times the constant shear rate tests to attain a representative flow curve. The full points shown in Fig. **4.2** are average values.



Figure 4.2: The flow curve of the gelled waxy crude oil. The empty datapoints are the steady-state values obtained in constant shear rate experiments using initially fully-structured samples. The full points are the average values for each shear rate.

From Fig. **4.2** it is seen that the dynamic yield strength obtained when the flow curve datapoints are acquired with initially fully-structured samples is about 7.5 Pa.

4.3.2 Creep tests

The creep experiment provides the static yield strength of the material, which is the maximum stress that the material (at 4° C) resists when fully structured. The results of this experiment are given in Fig. **4.3**, where the shear rate evolution is shown for different values of the imposed shear stress. Following the same protocol adopted in our investigations with a commercial hair gel and Laponite suspensions [1], we set at 3600 s the total time of these creep tests, and hence the yield strength obtained is representative of a process whose characteristic time is one hour.



Figure 4.3: Results of the creep experiments to determine the static yield strength of the gelled waxy crude oil.

The dramatic shear rate bifurcation observed in Fig. **4.3** indicates that the static yield strength (1 h) lies between 31 and 32 Pa.

4.3.3 Characterization of the time-dependent irreversible behavior

Upon observation of the sample after the creep tests (Figs. **4.4**a and **4.4**b), we noticed that it remains in a gel-like state when previously sheared at a constant

shear stress below the static yield strength (Fig. **4.4**b), but becomes permanently fluid-like when the previously imposed stress was above the static yield strength (Fig. **4.4**a). This characterizes an irreversible behavior [41].



Figure 4.4: Appearance of the gelled waxy crude oil sample after the creep test. For an imposed shear stress (a) above the static yield strength, and (b) below the static yield strength.

To better characterize this irreversible (time-dependent non-thixotropic) behavior of the gelled waxy crude oil and confront it with the thixotropic (time-dependent reversible) behavior of a Laponite suspension, we performed experiments whose results are given in Figs. **4.5** (Laponite suspension) and **4.6** (gelled waxy crude). The rheological properties of the Laponite suspension are described in my Master's dissertation in detail (Abedi et al. [1]). In these tests, the initially fully structured sample is alternately subjected to a constant shear rate for a short period and a constant shear stress below the yield strength for increasingly longer times. The idea of these tests is to assess the extent of microstructure rebuilding as a function of the time period in which the stress is kept below the yield strength, thus allowing construction of the microstructure .

In the case of the Laponite suspension, the constant shear rate imposed was $200 \, s^{-1}$, and the constant shear stress imposed was $3 \, \text{Pa}$ (Fig. **4.5**). While all periods under constant shear rate lasted 120 s, the 5 periods under constant shear stress were progressively longer, lasting 5, 10, 20, 30 and 60 minutes, in this chronological order. It is seen in this figure that the longer the period at constant stress, the higher the initial shear stress of the subsequent constant shear rate period, which indicates that longer periods at a stress below the yield strength imply larger extents of microstrucure rebuilding.



Figure 4.5: The microstructure breakdown and rebuild test for the Laponite suspension.(a) Six 120 s periods of constant shear rate equal to $200 \,\mathrm{s}^{-1}$ are intercalated by five periods of a constant shear stress (3 Pa) below the dynamic yield strength ($\sigma_{y,d} = 6$ Pa from [20]). The resting times are progressively longer, namely 5, 10, 20, 30 and 60 minutes; (b) the data pertaining to the periods of constant shear rate.

In the case of the gelled waxy crude (Fig. **4.6**), the constant shear rate imposed was $\dot{\gamma} = 1 \, s^{-1}$, and the constant shear stress imposed was null (0 Pa). All periods under constant shear rate lasted 300 s, and the 5 periods under null shear stress were the same ones used in the test with the Laponite suspension

(namely 5, 10, 20, 30 and 60 minutes). It is seen in this figure that, in contrast to what was observed for the Laponite suspension, at the end of the first period at constant shear rate, the shear stress reaches a constant value around 0.155 Pa, and this same value is observed during all other values at constant shear rate. This means that no microstructure rebuilding whatsoever occurs during the null shear stress periods, regardless of their time duration.



Figure 4.6: The microstructure breakdown and rebuild test for the gelled waxy crude. Six 300s periods of constant shear rate equal to $1 \,\mathrm{s}^{-1}$ are intercalated by five periods of null constant shear stress (0 Pa). The resting times are progressively longer, namely 5, 10, 20, 30 and 60 minutes; (b) the data pertaining to the periods of constant shear rate.

The origin of this behavior is assessed via micrographs obtained with an Eclipse LV100N POL (Nikon) microscope, equipped with a QIClick (Q-Imaging) camera (See Fig. **4.7**).



Figure 4.7: Eclipse LV100N POL (Nikon) microscope, equipped with a QIClick (Q-Imaging) camera – the Linkam shear cell (CSS450) mounted on the microscope

The images were analyzed by the QCapture (Q-Imaging) software. The micrographs were taken during a cooling protocol identical to the one employed before the rheological measurements. Figure **4.8** shows the structuring of a sample at the WAT ($19^{\circ}C$) and below. It is seen that an organized network becomes clearly denser as the temperature is decreased.



Figure 4.8: Micrographs showing the structuring of the waxy crude oil during the cooling period.

After taking the micrographs shown in Fig. **4.8**, the temperature is kept at 4°C and the Linkam shear cell (CSS450) mounted on the microscope is turned on so that a shear rate of $\dot{\gamma} = 15 \text{ s}^{-1}$ is applied to the sample for 240 s, and then the sample is brought back to rest. Figure **4.9** illustrates that the network is broken by the action of the imposed shear rate. Furthermore, it is seen that this scenario does not change after half an hour at rest, i.e. there is no sign of network rebuilding and hence the structured state is not recovered. These observations are consistent with the irreversible time-dependent behavior illustrated above in Figs. **4.4** and **4.6**.



(a) Just after applying shear

(b) After 30 minutes at stagnant state

Figure 4.9: Irreversible destruction due to shear of the microstructure of the gelled waxy crude. The organized network is not recovered.

4.3.4 Implications of irreversibility to the flow curve and to modeling

The previous thixotropy models proposed by de Souza Mendes and co-workers [14, 15, 17, 20] explore the fact that the flow curve of thixotropic materials is unique, in the sense that the equilibrium (steady-state) viscosity is a sole function of stress (or shear rate). While this property is observed for thixotropic materials, the same is not true for other time-dependent materials like the present irreversible gelled waxy crude.

It is easy to see that irreversibility implies non-uniqueness of the flow curve, since we obtain different equilibrium viscosities at a given shear stress (or shear rate) depending on the initial structuring level of the microstructure [26, 40]. That is, if the sample is initially fully structured when we impose a constant stress (above the static yield strength), then the equilibrium viscosity at that stress will be higher than if the initial structuring level is low, since there will not be enough microstructure rebuilding once the microstructure has been destructed to a large extent.



Figure 4.10: Stress (left) and viscosity (right) time response to an imposed $1 \, \text{s}^{-1}$ shear rate, after a 1800 s constant-stress pre-shear. The blue and light green curves pertain to a pre-shear above the static yield strength, and the dark green curve pertains to a pre-shear below the static yield strength. Gelled waxy crude.

This fact is illustrated in Fig. **4.10**, which shows the results of the following test: we start with a fully structured sample, and first impose a constant shear stress for 1800s and then impose a constant shear rate of 1 s^{-1} for other 1800s. When the imposed stress is below the static yield strength (5 Pa in Fig. **4.10**), there is no microstructure breaking during the constant-stress period, but when the 1 s^{-1} shear rate is imposed, the stress must rise above the static yield strength to break the percolated network and reduce the structuring level. The final equilibrium shear stress in this case is observed to be higher than the previously imposed stress, but of course lower than the static yield strength, resulting in an equilibrium viscosity of about 10 Pa.s.

When the imposed shear stress is above the static yield strength (35 and 70 Pa in Fig. **4.10**), then the equilibrium shear stress at 1 s^{-1} is quite low, indicating a low equilibrium viscosity (about 1 Pa.s) and hence a low structuring level. In summary, for the same shear rate we have two different equilibrium viscosities, a higher one when the sample is initially fully structured and a lower one when the sample has been previously submitted to a stress higher than the static yield strength. Moreover, the lower equilibrium viscosity seems to be independent of the intensity of the previously imposed stress (provided it is above the static yield strength), indicating that after yielding the microstructure of the waxy crude acquires a single, very low equilibrium structuring level.



Figure 4.11: Stress (left) and viscosity (right) time response to an imposed $1 \,\mathrm{s}^{-1}$ shear rate, after a 2400 s constant-shear rate pre-shear. Each color corresponds to a different imposed shear rate during the pre-shear period. Gelled waxy crude.

If the applied pre-shear is at constant shear rate instead of constant shear stress, however, a different response is observed, as illustrated in Fig. **4.11**. During the pre-shear period, the shear stress initially raises very fast and attains a peak above the static yield strength. This cannot be seen in Fig. **4.11** because it occurs in a matter of just a few seconds, even for the 0.1 s^{-1} pre-shear case. Immediately after yielding, however, the stress level is reduced, at first sharply and then progressively more mildly.

For the pre-shear at low shear rate (Fig. **4.11**, curve for 0.1 s^{-1} pre-shear), the maximum shear stress attained is just slightly above the static yield strength, and persists for an extremely short period only. Hence the damage to the microstructure is quite low, comparable to the damage that occurs when a constant shear stress just below the static yield strength is used in the pre-shear period (no damage) and then a small shear rate is imposed (small damage) (Figs. **4.10**(a) and (b), dark green curves). Therefore, the viscosity evolution curves at 1 s^{-1} for the two types of pre-shear are nearly coincident (cf. dark green viscosity curves in Figs. **4.10**(b)).

For the pre-shear at high shear rate (Fig. **4.11**, curve for 100 s^{-1} pre-shear), the maximum shear stress attained is very large, reducing dramatically the structuring level, reaching the same level observed when a constant shear stress much higher than the static yield strength is used in the pre-shear period (Figs. **4.10**(a) and (b), blue curves). Therefore, the viscosity evolution curves at 1 s^{-1} for the two types of pre-shear are again nearly coincident (cf. blue viscosity curves in Figs. **4.10**(b) and **4.11**(b)).

For the pre-shear at an intermediate shear rate (Fig. 4.11, curve for $10 \, \text{s}^{-1}$ pre-shear), the sample is exposed to a stress higher than the static yield strength at the early stages of pre-shear for a short period. Consequently, the structuring level is not reduced as much as if a constant shear stress above the static yield strength were applied for a long period. Therefore, the viscosity evolution curves at $1 \, \text{s}^{-1}$ for the two types of pre-shear are rather different in this case (cf. light green viscosity curves in Figs. **4.10**(b) and **4.11**(b)). Note that in the case of constant-stress pre-shear at 35 Pa the equilibrium viscosity coincides with the one obtained with a 70 Pa pre-shear, suggesting that the structuring level for the 35 Pa pre-shear case has already reached a minimum. On the other hand, the equilibrium viscosity pertaining to a $10 \, \text{s}^{-1}$ pre-shear is much higher, indicating a larger structuring level. These results illustrate further that the equilibrium viscosity of time-dependent irreversible materials is a strong function of the shear history, and that intermediate levels of structuring level are attainable at constant shear rate but not at constant shear stresses.

The type of behavior illustrated in Figs. **4.10** and **4.11** precludes the direct application of the procedure proposed in [20] in the development of a constitutive model for the gelled waxy crude, i.e. the set of tests designed for the (thixotropic) Laponite suspension [20] had to be modified to accommodate the irreversibility observed in the gelled waxy crude.

4.3.5 Microstructure construction and destruction tests

In this section we describe two tests that provide crucial information for the development of the constitutive model.

The first one is called here the *microstructure construction test*, which probes the ability of the microstructure to rebuild after being broken down by action of a shear stress higher than the static yield strength (equal to 31.5 Pa for the present waxy crude). It starts with a fully-structured sample—prepared with the same heating/cooling protocol described above—and consists of imposing a constant shear stress above the static yield strength until steady state is achieved, and then abruptly reducing the shear stress to a value below the dynamic yield strength ($\sigma_{y,d} = 7.5 \text{ Pa}$).



Figure 4.12: Raw data of the construction test for the gelled waxy crude. Fully-structured samples are submitted to different levels of stress (σ_i), all above the static yield strength, until steady state is achieved. Subsequently, the stress is changed to $\sigma_f = 7$ Pa, which is below the static and dynamic yield strengths obtained with initially fully-structured samples.

The results of the microstructure construction test for the waxy crude are shown in Fig. 4.12, where the shear rate is plotted as a function of time. It can be seen from this figure that the yielded waxy crude possesses negligible elasticity, because of the discontinuous decrease in shear rate that occurs in response to the imposed step reduction in stress. It also illustrates that for initial stresses σ_i ranging from a value just above the static yield strength (35 Pa) to a much higher value (55 Pa), the shear rate always drops to nearly the same value when the stress is changed to $\sigma_f = 7 \text{ Pa}$, meaning that the instantaneous structuring level just after the collapse of the initially percolated microstructure is nearly independent of the shear stress that causes the breakdown. Moreover, there is just a little increase in the structuring level after the stress reduction, as indicated by the rather small decrease in shear rate along the period in which the stress is kept at a low value (namely 7 Pa). It is also worthy of note the fact that the final structuring level (and hence the equilibrium viscosity) is a function of the imposed stress σ_f only, i.e. it does not depend on the value σ_i of the stress used to cause yielding. Moreover, the steady state value corresponding to σ_f is still quite high, indicating a rather low structuring level. This means that there is no intermediate structuring level, i.e. the material is either fully structured or at very low structuring levels that vary within a narrow range during a weak rebuilding. It is important to keep in mind that if the material were thixotropic (reversible), the shear rate would eventually go to zero when subjected to a stress below the yield strength, because at this low level of stress the microstructure would rebuild completely. And correspondingly, as another sign of irreversibility, the measured shear rates at the shear stress applied (namely 7 Pa) are higher than the flow curve ones, indicating that the related steady-state viscosities have decreased after the microstructure breakdown.



Figure 4.13: Raw data of the destruction test for the gelled waxy crude. Fully-structured samples are submitted to a constant shear stress of $\sigma_i = 7$ Pa (thus below the static and dynamic yield strengths) during 600 s. Subsequently, the stress is suddenly raised to different σ_f values above the static yield strength.

The other rheological test that is central to the development of the constitutive model is the here called *microstructure destruction test*. It consists of imposing on a fully-structured sample a constant shear stress above the static yield strength, and observe the shear rate (or viscosity) evolution. After the pre-treatment the crude oil is at the fully structured condition, but in order to follow the same procedure adopted for the Laponite suspension in [20], each sample was first kept for 600 s under stress of $\sigma_i = 7 \text{ Pa}$ (thus below the static and dynamic yield strength). Subsequently, the stress is increased to a σ_f value above the static yield strength. Figure **4.13** shows the results of the microstructure destruction test for the waxy crude investigated. Interesting features of this material can be observed in this figure. Within the time interval during which $\sigma_i = 7 \text{ Pa}$, the measured shear rate decreases continuously to very low values,

up to a point below the rheometer resolution, beyond which the data are no longer plotted. At time t = 600 s a sharp rise of the shear rate is observed for all the imposed shear stresses (σ_f), certainly due to to a dramatic collapse of the initially percolated microstructure. After yielding, the shear rate eventually reaches a plateau, indicating equilibrium (or steady-state) conditions. The higher the imposed stress the sooner equilibrium is reached; as for instance, the steady state is achieved sooner for 55 Pa than 37 Pa.

4.4 The constitutive model

4.4.1 Fluidity

The constitutive model for the waxy crude proposed here is based on a method described in [20]. This method was successfully applied for a Laponite suspension (thixotropic) and adapted for a cement slurry (time-dependent irreversible) [20, 51].

Instead of using the classical structure parameter (usually denoted by λ), we use the fluidity ϕ_v (reciprocal of viscosity) to indicate the structuring level of the microstructure. The dimensionless fluidity ϕ_v^* is defined as

$$\phi_v^* \equiv \frac{\phi_v - \phi_0}{\phi_\infty - \phi_0} \qquad \Rightarrow \qquad \phi_v \equiv \phi_v^*(\phi_\infty - \phi_0) + \phi_0 \tag{4-1}$$

where ϕ_0 is the zero shear rate fluidity and ϕ_{∞} is the infinite shear rate fluidity. From its definition, it becomes clear that ϕ_v^* is a normalized quantity, $0 \le \phi_v^* \le 1$. For yield strength materials the viscosity diverges as $\dot{\gamma} \to 0$ and hence $\phi_0 = 0$. Therefore,

$$\phi_v^* \equiv \frac{\phi_v}{\phi_\infty} \tag{4-2}$$

for yield strength materials, which is the case for most materials of interest such as the waxy crude investigated here.

4.4.2 Stress/kinematics relation

The differential equation that characterizes the relationship between stress and the kinematics is an adaptation of the classic Oldroyd-B model to accommodate structuring-level-dependent relaxation and retardation times [14, 15, 17, 20]. Following the reasoning described in [15] by de Souza Mendes et al., the following tensorial differential equation is obtained:

$$\dot{\boldsymbol{\gamma}} + \theta_{\infty}(\phi_{v}^{*}) \overline{\dot{\boldsymbol{\gamma}}} = \phi_{v} \left[\boldsymbol{\sigma} + \theta_{s}(\phi_{v}^{*}) \overline{\boldsymbol{\sigma}} \right]$$
(4-3)

In this equation, $\theta_s(\phi_v^*)$ is the relaxation time; $\theta_{\infty}(\phi_v^*)$ is the retardation time; $\dot{\gamma} \equiv \nabla v + \nabla v^T$ is the rate of strain tensor field (v is the velocity vector field); $\sigma \equiv T + (p + \mathrm{tr}\sigma/3)I$ is the extra-stress tensor field (T is the Cauchy stress tensor field, $p \equiv -(1/3)\mathrm{tr}T$ is the mechanical pressure, and I is the identity tensor); and $\ddot{\dot{\gamma}}$ and $\ddot{\sigma}$ are the upper-convected time derivatives of $\dot{\gamma}$ and σ respectively.

However, since no elasticity effect was observed in the waxy crude, then the relaxation and retardation times are both null, and hence Eq. (4-3) reduces to the Generalized Newtonian Liquid equation:

$$\dot{\boldsymbol{\gamma}} = \phi_{\infty} \phi_v^* \boldsymbol{\sigma} \tag{4-4}$$

4.4.3 The evolution equation for ϕ_v^*

For thixotropic materials, the equilibrium viscosity is not a function of shear history [43, 44, 46]. In the present case of the waxy crude, the equilibrium viscosity is a function of shear history, and hence the material does not possess a unique flow curve that could be used in the model to characterize a material in equilibrium condition [18]. For time-dependent materials in general, there is a one-to-one correspondence between the viscosity (or fluidity) and the the structuring level, but in the case of irreversible time-dependent materials like the waxy crude under study, the structuring level itself is a function of the shear history, in contrast to thixotropic materials such as Laponite suspensions.

In this work the dimensionless fluidity (ϕ_v^*) itself is employed as a measure of the structuring level, and we use the fact that the shear stress is the breaking agent of the material microstructure[20, 51].

The rate of change of ϕ_v^* is assumed to depend on both the current fluidity ϕ_v^* and the equilibrium fluidity evaluated at the current stress as discussed in [20]. However, due to irreversibility, the rate of change of the fluidity depends also on whether the current microstructure change is construction $(d\phi_v^*/dt < 0)$ or destruction $(d\phi_v^*/dt > 0)$:

$$\frac{d\phi_v^*}{dt} = \begin{cases} f_c(\phi_{eq,c}^*(\sigma), \phi_v^*) & \text{when } d\phi_v^*/dt < 0\\ f_d(\phi_{eq,d}^*(\sigma), \phi_v^*) & \text{when } d\phi_v^*/dt > 0 \end{cases}$$

$$\tag{4-5}$$

The functions f_c and f_d appearing in Eq.(4-5) are determined from the construction and destruction experiments, and $\phi_{eq,c}^*(\sigma)$ and $\phi_{eq,d}^*(\sigma)$ are the *construction* and *destruction flow curves*, respectively. All these material functions are defined and described in detail in the following sections.

4.4.4 Flow Curves

As we have already adumbrated, due to its irreversible time dependence the waxy crude possesses two flow curves. One of them corresponds to an initially fully structured microstate, i.e. each point of this flow curve is obtained with a fresh, fully structured sample, submitted just before the test to the pre-treatment described earlier in this text. Because in this procedure microstructure destruction occurs while the steady state is approached, we call this the "destruction flow curve" $\phi_{eq,d}^*$, given in Fig. **4.14** for the waxy crude under investigation.



Figure 4.14: The destruction flow curve, given in terms of the dimensionless equilibrium fluidity as a function of the dimensionless shear stress. Obtained from initially fully structured waxy crude samples.

It is worth mentioning that, in the rheometrical experiments, we first obtain

the equilibrium stress as a function of the shear rate, and then, using the definition of equilibrium fluidity, we transform the data to the form dimensionless equilibrium fluidity versus shear stress given in Fig. **4.14**, which is the form needed in the model formulation. We use the equation proposed by Souza Mendes and co-workers [20] to express the flow curve in this form:

$$\phi_{eq,d}^*(\sigma/\sigma_{y,d}) = \frac{\frac{\sigma_{y,d}}{\sigma} \left(|\sigma/\sigma_{y,d} - 1| \right)^{1/n_d}}{\frac{\sigma_{y,d}\phi_{\infty,d}}{\gamma_{1,d}} + \left[\frac{\sigma_{y,d}}{\sigma} \left(|\sigma/\sigma_{y,d} - 1| \right)^{1/n_d} \right]} H\left(\sigma/\sigma_{y,d} - 1 \right)$$
(4-6)

where H is the Heaviside step function; $\sigma_{y,d}$ is the dynamic yield strength; K_d is the consistency index; n_d is the power-law index; $\dot{\gamma}_{1,d}$ is the shear-rate that characterizes the beginning of the power-law region; and $\phi_{\infty,d}$ is the infinite-shear-stress fluidity. Due to the complex nature of the crude oil, we obtained non-negligible data scattering. For this reason, we repeated at least three times each datapoint, and plotted average values in Fig. **4.14**. The dashed curve in this figure is a least-squares fit of Eq. (4-6) to the data, and the equation parameters thus obtained are given in the legend of Fig. **4.14**. It is remarkable the large difference between the static ($\simeq 31.5$ Pa) and the dynamic (7.5 Pa) yield strength values, indicating an extensive (and partially irreversible) breakdown of the microstructure at the yielding point.

On the other hand, the second flow curve corresponds to an initially unstructured microstate. That is, as in the case of the destruction flow curve, the procedure to obtain each point of this flow curve starts with a fresh, fully structured sample, submitted just before the test to the heating/cooling protocol described earlier in this text. Then the sample is pre-sheared with a constant shear stress until steady state is achieved. This stress is higher than all stresses corresponding to the flow curve datapoints, to ensure that during the test corresponding to each datapoint the steady state is approached from above, i.e. the equilibrium fluidity is lower than the fluidity transient values along the test. Therefore, in this procedure microstructure construction occurs while the steady state is approached. Due to this reason, we call this the "construction flow curve" $\phi_{eq,c'}^*$ given in Fig. **4.15** for the waxy crude under investigation.



Figure 4.15: The construction flow curve, given in terms of the dimensionless equilibrium fluidity as a function of the dimensionless shear stress. Obtained from pre-sheared gelled waxy crude samples.

Thus, except for the pre-shear applied to the samples, the procedure, data reduction and curve fitting procedures are exactly equal to the ones described above to obtain the destruction flow curve. The fitting equation is also given by Eq. (4-6), except that the subscripts "d" are replaced with "c" standing for "construction," and the corresponding parameters, obtained via least squares fit, are given in the legend of Fig. **4.15**.

4.4.5 Determining the functions f_c and f_d

In contrast to the vast majority of thixotropy models found in the literature, we do not postulate *a priori* the form of the function that appears on the right-hand side of the evolution equation. Instead, the determination of this function is dictated by the results of the construction and destruction experiments presented in section 3. In this manner, we expect an enhanced predictive capability.

To this end, first the results of the construction and destruction experiments are recast in terms of fluidity using the 21-component of Eq. (4-4):

$$\phi_v^* = \frac{\dot{\gamma}/\sigma_f}{\phi_\infty} \tag{4-7}$$

Figure **4.16** gives the (transient) dimensionless fluidity as a function of a dimensionless time, for different initial structuring levels ϕ_i^* (that correspond to

different initial stresses σ_i) and a final stress of $\sigma_f = 7$ Pa. In this figure, we shifted the experiment times to present the data with respect to a single reference time scale that corresponds to an experiment starting at the lowest possible structuring level, i.e. $\phi_i^* = 1$. A detailed discussion of this procedure is found in [20].



Figure 4.16: The construction experiment results, given in terms of the dimensionless fluidity of the gelled waxy crude.

These results show that the equilibrium fluidity reaches a value around $\phi_{eq}^* = 0.53$ when a step-change to $\sigma_f = 7 \text{ Pa}$ was applied, regardless of the value of the initial stress σ_i . It is worth noting that this value of σ_f is lower than the static yield strength (equal to 31.5 Pa) and also of the dynamic yield strength of the destruction flow curve ($\sigma_{y,d} = 7.5 \text{ Pa}$), but higher than the dynamic yield strength of the construction flow curve ($\sigma_{y,d} = 0.75 \text{ Pa}$).

The following equation provides a good fitting for the construction data:

$$\phi_v^* = \phi_{ea.c}^* + (1 - \phi_{ea.c}^*)e^{-(t/t_c)^s} \tag{4-8}$$

where t_c is the *construction time*, s is a dimensionless fitting parameter. For the waxy crude investigated here their values were taken as constant and equal to s = 0.73 and $t_c = 13746$ s.

Differentiating Eq. (4-8) with respect to time and then eliminating the exponential term by using Eq. (4-8) itself, we obtain, after some algebra, an equation for f_c that carries the information of microstructure construction that

is experimentally observed:

$$f_{c} = -s \left[\frac{\phi_{v}^{*} - \phi_{eq,c}^{*}}{t_{c}} \right] \left[\ln \left(\frac{1 - \phi_{eq,c}^{*}}{\phi_{v}^{*} - \phi_{eq,c}^{*}} \right) \right]^{\frac{S}{s-1}}$$
(4-9)

Analogously to the above procedure, we derive the function f_d for the microstructure destruction process from the results of the destruction experiment, recast in terms of $\phi_v^*(t)$ in Fig. **4.17**:



Figure 4.17: The destruction experiment results, given in terms of the dimensionless fluidity of the gelled waxy crude.

From the trends observed in this figure, we observed that the following expression fits reasonably the destruction data:

$$\phi_v^* = \frac{\phi_{eq,d}^* t^{s_1 s_2}}{(t_a^{s_1} + t^{s_1})^{s_2}} \tag{4-10}$$



Figure 4.18: The avalanche time t_a as a function of $\phi_{eq,d}^*$ for the gelled waxy crude.

In this equation, t_a is the avalanche time [12] and s_1 and s_2 are dimensionless fitting parameters, taken as 1.5 and 0.2 respectively for the waxy crude investigated.

It is our experience with yield strength materials that the avalanche time t_a has the following properties: it decreases monotonically as the imposed stress σ is increased; it becomes very large as the imposed stress approaches the yield strength, and becomes negligibly small as the imposed stress becomes much larger than the yield strength.

Figure **4.18** presents t_a as a function of $\phi_{eq,d}^*$ for different values of s_1 and s_2 . The curve shown is a fit to the data of the following equation, which observes the correct trends:

$$t_a(\phi_{eq,d}^*) = 15000 - \frac{15000}{\left[1 + \left(\frac{\phi_{eq,d}^*}{0.69}\right)^{-14}\right]^{0.07}}$$
(4-11)

Following the same procedure used to determine f_c , we differentiate Eq.(4-10) with respect to time and then eliminate time using Eq.(4-10) itself.
After some algebra, we obtain the following expression for f_d :

$$f_d = \frac{s_1 s_2 \phi_v^*}{t_a \left(\frac{\phi_v^*}{\phi_{eq,d}^*}\right)^{1/s_1 s_2}} \left[1 - \left(\frac{\phi_v^*}{\phi_{eq,d}^*}\right)^{1/s_2} \right]^{(s_1+1)/s_1}$$
(4-12)

Therefore, the evolution equation assumes the following form:

$$\frac{d\phi_v^*}{dt} = \begin{cases}
-s \left[\frac{\phi_v^* - \phi_{eq,c}^*}{t_c}\right] \left[\ln\left(\frac{1 - \phi_{eq,c}^*}{\phi_v^* - \phi_{eq,c}^*}\right)\right]^{s/s-1}; & \frac{d\phi_v^*}{dt} \le 0 \\
\frac{s_1 s_2 \phi_v^*}{t_a \left(\frac{\phi_v^*}{\phi_{eq,d}^*}\right)^{1/s_1 s_2}} \left[1 - \left(\frac{\phi_v^*}{\phi_{eq,d}^*}\right)^{1/s_2}\right]^{(s_1+1)/s_1}; & \frac{d\phi_v^*}{dt} \ge 0
\end{cases}$$
(4-13)

It is important to emphasize that his equation is only applicable to the waxy crude oil under investigation. However, the method employed in its derivation can be used to develop models to describe the mechanical behavior of other time-dependent irreversible materials.

4.4.6 Application of the model to shear flow

Therefore, the constitutive model developed here for the waxy crude is composed of the 21-component of Eq. (4-4), Eq. (4-6), another equation identical to Eq. (4-6) for the construction flow curve, and Eq. (4-13). This set of equations involves several parameters, but all of them have already been determined from the above described experiments.



Figure 4.19: Comparison between data (blue circles) and the model predictions (line), for initially fully structured gelled waxy crude samples.

To assess the performance of the proposed model, we performed additional tests in which we measured the evolution of the fluidity when a constant shear rate is imposed. In these tests, the same pre-treatment was applied to the samples, which were initially fully structured. The results of these tests are shown in Fig. **4.19**, where we also plotted the model predictions, given by the continuous black lines. It is seen that the predictive capability of the model is excellent in this case. It is worth noting that, at the relatively high shear rate values shown, no stress overshoot was observed, essentially because in this case the stress raises very fast, and hence the "residence time" in which the stress remains close to the static yield strength is rather small. Therefore, the avalanche time is never significant, eliminating the possibility of stress overshoots. For low enough shear rate values (not explored), however, stress overshoots are expected to occur, due both to the possibly existing elasticity of the unyielded sample and to the large avalanche times observed when the current stress is above but very close to the static yield strength.

Comparisons for other situations are being carried out to better evaluate the predictive capability of this model.

4.5 Final remarks

A constitutive model capable of predicting irreversible effects was developed to describe the rheological behavior of a gelled waxy crude oil. Like in our previous works, the fluidity was employed as a measure of the structuring level, and an evolution equation for this quantity that only involves measurable material functions was developed. Irreversible effects were included by means of the usage of two flow curves, one obtained from initially fully structured samples and the other to highly unstructured ones. A good agreement between the model predictions and the results of constant shear rate experiment were obtained. Research is under way to provide comparisons between predictions and experimental results for other flow situations, such as the startup flow of initially unstructured gelled crudes in a tube.

The model described above is able to predict the startup flow of fully structured crude oils as long as elasticity does not play an important role, since it was neglected. For the waxy crude studied, elasticity is present when the oil is gelled, and is negligible after yielding. To verify the existence of elasticity of the fully structured crude as well as its importance in the startup flow problem, further experiments would be needed. It is worth noticing that the method proposed by de Souza Mendes et al. [20] can accommodate elasticity, and hence in principle a more complete model including this effect could be developed for the crude using the same method.

A last remark refers to the non-uniqueness of the flow curve. In this work, for simplicity we chose to work with two flow curves, one obtained with initially fully structured samples and another obtained with initially highly pre-sheared samples. Further investigation would be required to obtain other flow curves with samples whose initial structuring level were different from the two extremes already explored, and then to assess the importance of including a more elaborate description in the modeling.

5 The finale

As brought to your consideration, the conventional force balance was accommodated with the shrinkage constant and became a tool to connect the static yield strength measured at no-slip condition with the minimum restart pressure obtained in a tube flow tests. This manner, better estimations can be made for the restart pressure of gelled crude oil in pipelines.

Next, a constitutive model was presented for gelled crude oil comportment, incorporating the irreversible time-dependent characteristic. We modified our afore-introduced model for reversible time-dependent materials based on aqueous Laponite suspension. Our wider objective is that beside the startup flows, using different flow curves representing distinct microstructure states, be able to predict also creep-recovery tests for irreversible materials.

As a future and last step, the experiments to measure flow rates (mass rates) at various pressures above the minimum restart one were conducted. Then, we aim to compare the experimental results with the simulation results of gelled crude flow in a tube, as we did for a hair gel and the Laponite suspension, since the shrinkage and time-dependent irreversible effects now are integrated (see Fig. **5.1**).



Figure 5.1: Startup flow in a tube – measured mass (flow) at a exerted pressure above the minimum critical one

When it is done, for any desired flow rate, the required restart pressure is known. This could be *the finale* for this extensive work.

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