Research Square

Preprints are preliminary reports that have not undergone peer review.
They should not be considered conclusive, used to inform clinical practice,
or referenced by the media as validated information.

Prolonged Static Aging of Olefin-Based Inverse Emulsion Drilling Fluids: Temperature–Time Effects on Rheology, Stability, and Filtration

Gabriel Reis Simplício de Souza
Universidade Federal de Uberlândia
Heitor Otacílio Nogueira Altino
Universidade Federal de Uberlândia
Elessandre Alves de Souza
Petrobras (Brazil)
Marcos Antônio de Souza Barrozo
Universidade Federal de Uberlândia
Marina Seixas Pereira
Universidade Federal de Uberlândia
Claudio Roberto Duarte
claudioduarte@ufu.br

Universidade Federal de Uberlândia

Research Article

Keywords: Synthetic drilling fluid, olefin-based inverse emulsion, thermal aging, rheology, emulsion stability, filtration

Posted Date: July 24th, 2026

DOI: https://doi.org/10.21203/rs.3.rs-10295093/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License

Additional Declarations: No competing interests reported.

Prolonged Static Aging of Olefin-Based Inverse Emulsion Drilling Fluids: Temperature–Time Effects on Rheology, Stability, and Filtration

Gabriel Reis Simplício de Souza[a], Heitor Otacílio Nogueira Altino[a], Elessandre Alves de Souza[b], Marcos Antônio de Souza Barrozo[a], Marina Seixas Pereira[a], Claudio Roberto Duarte[a]*.

[a]*Faculty of Chemical Engineering, Federal University of Uberlândia, Uberlândia, MG, Brazil.*

[b]*Petrobras and Leopoldo Américo Miguez de Mello Research and Development Center, Brazil.*

***Corresponding author:** Claudio Roberto Duarte*

***E-mail address:** claudioduarte@ufu.br*

***ORCID:** https://orcid.org/0000-0001-7539-3054*

Abstract

Synthetic-based drilling fluids (SBFs) formulated as olefin-based inverse emulsions are widely used in deepwater operations, where static intervals during BOP tests, equipment failures, and maintenance can expose the fluid to high temperatures without shear, accelerating interfacial degradation and structural changes. The role of aging time as a governing factor remains underexplored, since previous studies have mainly emphasized temperature effects and conventional aging durations of up to 16 h. This study investigates the coupled effects of aging temperature (100–150 °C) and prolonged static exposure (24–168 h) on the rheological behavior, emulsion stability, and filtration performance of an olefin-based synthetic drilling fluid stabilized by low-HLB amide/amidoamine-type emulsifiers, using a Central Composite Design. Results reveal nonlinear temperature–time domains in which physicochemical rearrangements progressively transition into irreversible degradation, evidenced by changes in yield stress, increases in consistency index and apparent viscosity, and reduction in flow behavior index. These responses indicate enhanced pseudoplasticity and structural reorganization of the multicomponent fluid. Thermal aging promoted interfacial destabilization, brine manifestation, and droplet coalescence, consistent with partial emulsifier degradation indicated by thermogravimetric analysis. Filtration showed a nonlinear response, with reduced filtrate volume at higher temperatures attributed to physical transformation of the filtration control additive and formation of a denser filter cake. These findings demonstrate that aging time is a critical and previously overlooked factor governing performance loss in olefin-based synthetic drilling fluids, with direct implications for fluid integrity management during prolonged static intervals in deepwater operations.

Keywords: Synthetic drilling fluid; olefin-based inverse emulsion; thermal aging; rheology; emulsion stability; filtration.

1. Introduction

Global oil demand is projected to increase by 6% between 2022 and 2028 (IEA 2023). In this context, Brazil has intensified exploration activities in deep and ultra-deepwater reservoirs, driving the development of drilling technologies capable of operating under high-pressure and high-temperature (HPHT) conditions (Petrobras 2025). Drilling in such complex environments frequently faces severe operational challenges, resulting in Non-Productive Time (NPT) that costs the petroleum industry billions of dollars annually and poses significant safety risks (Assi et al. 2021). Therefore, maintaining wellbore stability and operational safety during these extended operations is a critical priority that serves the needs of a broad audience, including operators, service companies, and environmental agencies.

Drilling fluids play a central role in well construction by stabilizing the wellbore, maintaining hydrostatic pressure, transporting cuttings, and cooling and lubricating the drill string (IOGP 2016; Caenn et al. 2016). Among the available systems, synthetic-based drilling fluids (SBFs) are widely used in Brazilian offshore operations, particularly in pre-salt fields, due to their superior performance under HPHT conditions and compliance with environmental regulations (Stout and Payne 2017). These fluids are typically formulated as water-in-oil (W/O) emulsions based on olefins, stabilized by surfactants that govern both rheological behavior and interfacial integrity (ASME 2005; Hassan et al. 2023).

Although emulsification requires high shear to generate small droplets, the resulting emulsions are inherently thermodynamically unstable. Destabilization mechanisms such as flocculation, coalescence, sedimentation, and creaming may occur simultaneously, making emulsion stability a complex and time-dependent phenomenon (Goodwin 2004; Tian et al. 2022). Under high-pressure and high-temperature (HPHT) drilling conditions, thermal stress accelerates additive degradation and weakens interfacial films. Previous research demonstrates that the heat stress history significantly alters the rheological behavior of invert emulsion drilling fluids, leading to structural thermal modifications and potentially severe phase separation under extended high-temperature and high-pressure exposure (Lee et al. 2012).

This thermal degradation scenario becomes particularly critical during static intervals encountered in deepwater drilling operations, including connections, BOP tests, bit replacement, logging, casing running, maintenance operations, wiper trips, and cementing, when circulation is interrupted and the fluid remains confined without shear (API 2016; Caenn et al. 2016; Friaça et al. 2023). These events may individually impose static conditions lasting from 8 to 12 hours, while more severe situations such as equipment failures, well control interventions, and the accumulation of NPT can extend static exposure to several days, reaching or exceeding 168 hours (Assi et al. 2021).

Under these conditions, the absence of shear combined with high temperatures accelerates emulsion degradation by weakening interfacial films and reducing emulsifier effectiveness through increased solubility in the oil phase (Binks and Rocher 2009; Jiang et al. 2024). As a result, emulsion integrity deteriorates, increasing the risk of barite sag, loss of hydrostatic pressure, wellbore instability, and formation influx (Lee et al. 2012).

Despite its operational relevance, static aging remains underexplored. Most studies on SBFs have focused on dynamic aging or short-term thermal exposure, typically limited to 16 hours following standard American Petroleum Institute (API) protocols (Razali et al. 2018; Peixoto et al. 2021; Kania et al. 2021;

Celino et al. 2022; Vasconcelos et al. 2022). Although some studies have evaluated static aging, they remain restricted to standard durations and specific additive effects (Arain and Ridha 2025). As a result, the role of aging time as a governing factor in emulsion degradation remains a critical scientific and operational gap.

Prolonged exposure to high temperatures under static confinement can activate nonlinear and irreversible degradation pathways that are not captured by short-term tests, directly affecting long-term fluid reliability during operational pauses. This issue is particularly relevant in deepwater wells, where extended static intervals combined with high temperatures create favorable conditions for emulsifier degradation, droplet growth, and structural reorganization, potentially progressing unnoticed until operational failure occurs (Apostolidou et al. 2022; He et al. 2024; Fookes et al. 2024; Zhao et al. 2024; Shi et al. 2025; Arain and Ridha 2025).

In this context, the present study investigates the effects of temperature and prolonged static aging time on the physicochemical behavior of an olefin-based synthetic drilling fluid formulated as an inverse emulsion under confined conditions. Aging tests were conducted using a Central Composite Design to quantitatively evaluate coupled temperature–time effects on rheological behavior, emulsion stability, and filtrate volume, extending static exposure beyond the short-term conditions (≤16 h) commonly reported in the literature. High-temperature conditions in the range of 100–150 °C are commonly encountered in deepwater and HPHT drilling operations (Hossain and Al-Majed 2015; Caenn et al. 2016), where thermal stress can significantly affect emulsifier performance, solid-phase organization, additive integrity, and interfacial stability. Based on this operational context, the present study explores temperature–time domains representative of field conditions.

The main novelty of this study lies in the systematic evaluation of an olefin-based inverse-emulsion drilling fluid under confined static conditions, distinguished by three key contributions: (1) extension of aging duration up to 168 h to capture long-term degradation phenomena not observed in conventional short-duration protocols; (2) development of statistically significant empirical models describing the nonlinear evolution of rheological parameters as a function of temperature and time; and (3) identification of critical temperature–time thresholds (≥142.7 °C) associated with irreversible structural breakdown, while elucidating competing mechanisms involving emulsifier degradation, solid-phase reorganization, filtration control additive transformation, and filter cake sealing. Collectively, these

findings provide a quantitative framework for anticipating performance loss in olefin-based synthetic drilling fluids during extended operational pauses in deepwater scenarios.

2. Materials and Methods

The synthetic drilling fluid was formulated using 1-hexadecene (α-olefin) as the continuous oil phase and a sodium chloride brine as the dispersed aqueous phase, primary and secondary emulsifiers belonging to the amide/amidoamine class derived from tall-oil fatty acids and polyamines and characterized as low-HLB (≈3–6) lipophilic surfactants suitable for water-in-oil emulsion stabilization, calcium carbonate ($CaCO_3$, 2–44 μm) as a bridging agent, lime (CaO), a modified organophilic clay as viscosifier, barite ($BaSO_4$) as weighting agent, a fatty acid-based polymer as rheological modifier, and an acrylic-based copolymer as filtration control additive. All materials were provided by Petróleo Brasileiro S.A. (Petrobras).

The synthetic drilling fluid was formulated as an inverted emulsion composed of 60% (v/v) olefin as the continuous phase and 40% (v/v) saturated sodium chloride brine as the dispersed phase, with additives added according to the formulation described in Table 1. Fluid preparation was carried out using an Ultra-Turrax T25 (IKA) mixer, with temperature maintained at approximately 30 °C using a jacketed beaker. The order of addition and mixing times are reported in Table 1. At the end of preparation, the mixing speed was increased to 10,000 rpm for 15 min.

Table 1 Composition and preparation conditions.

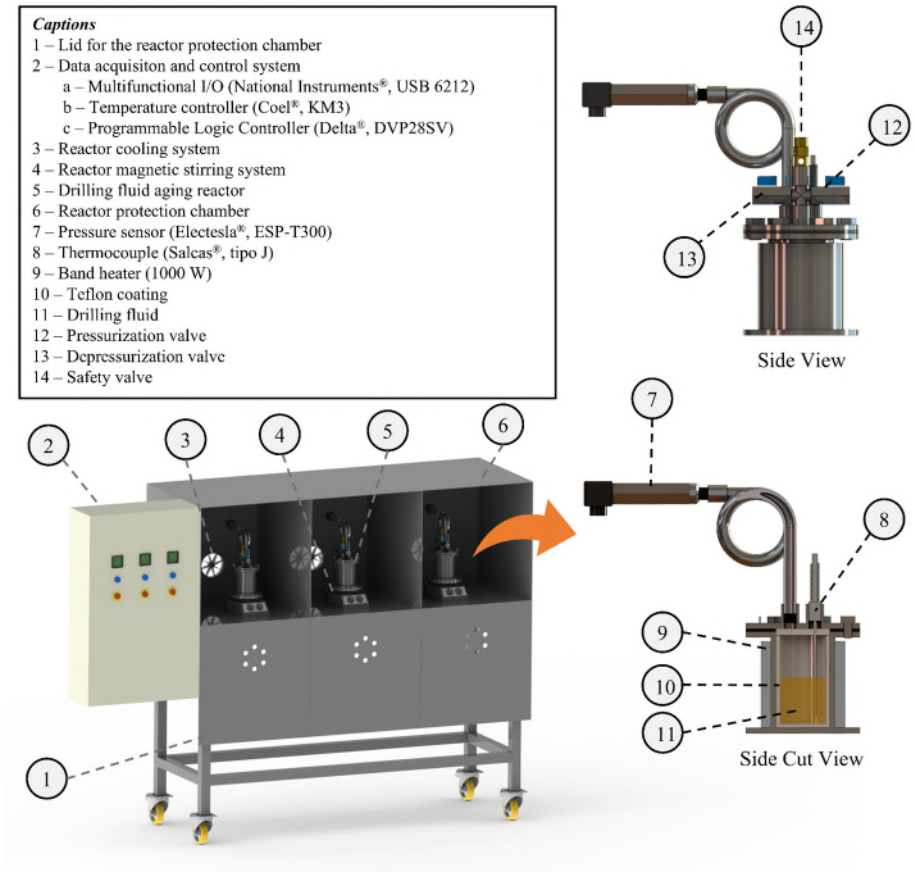
Addition order	Component	Composition		Stirring time (hour)
		Concentration	Unit	
1[a]	Olefin	0.58	bbl/bbl	1
2[a]	Primary emulsifier	7	lb/bbl	
3[a]	Secondary emulsifier	8	lb/bbl	
4[a]	Lime	5	lb/bbl	
5[b]	Brine	0.39	bbl/bbl	2
6[c]	Filtration control	2	lb/bbl	2
7[c]	Viscosifier	5	lb/bbl	
8[c]	Limestone	10	lb/bbl	
9[c]	Rheological modifier	2.75	lb/bbl	
10[c,d]	Barite	100	lb/bbl	

[a] The first step
[b] The second step
[c] The third step
[d] 15 min at 10,000 rpm after third step

Static aging tests were conducted using a custom-built system consisting of three jacketed stainless steel reactors (500 mL) internally coated with Teflon, in accordance with API RP 13I (API 2016), as illustrated in Fig. 1. Each reactor was equipped with a thermocouple in direct contact with the fluid, a PID-controlled heating system (1000 W band heater), and a high-temperature pressure sensor, allowing continuous monitoring of temperature and pressure.

For each experiment, 190 g (≈160 mL) of drilling fluid were loaded into the reactor, and aging temperature and duration were set according to the experimental design. After reaching the target temperature, the system was sealed and pressurized with nitrogen at 5 bar. This pressure level was applied exclusively to suppress water evaporation during high-temperature aging, as recommended by API RP 13I (API 2016), rather than to reproduce downhole pressure conditions. Temperature and pressure were continuously monitored throughout the experiments using a data acquisition system, and no pressure variations indicative of leakage or fluid loss were observed. At the end of each test, the fluid was cooled to ambient temperature before depressurization.

Fig. 1 Drilling fluid aging unit



After aging, the fluid was gently homogenized using a low-speed paddle mixer prior to characterization.

Thermogravimetric analysis (TGA) was performed on selected pure additives to assess their thermal stability and degradation behavior. Measurements were conducted using a Shimadzu® DTG-60H over a temperature range of 25–1000 °C, at a heating rate of 10 °C min^{-1} under nitrogen flow (50 mL min^{-1}), using sample masses between 6 and 10 mg, following standard procedures described in ASTM E1131. The analysis provided a qualitative reference for comparing the relative thermal robustness of individual components under inert conditions. Additionally, TGA and DrTGA analyses were performed on the formulated drilling fluid before aging (UDF) and after aging at 100, 125, and 150 °C for 48 h, using the same experimental conditions described above. These measurements were conducted to assess the thermal behavior of the fluid as a multi-component system and to compare it with the pure-additive results.

Rheological tests were carried out using a Brookfield R/S Plus rheometer equipped with a CC-40 coaxial cylinder geometry and coupled to a thermal bath to maintain a constant temperature of 30 °C. Flow curves were obtained under controlled shear rate conditions, with shear rates ranging from 0.1 to 1000 s^{-1}. All measurements were performed at 30 °C after cooling to standardize post-aging comparisons and isolate irreversible structural changes induced by thermal exposure, eliminating the influence of temperature-dependent viscosity variations between samples aged under different conditions.

The experimental data were fitted to the Herschel–Bulkley model using nonlinear regression:

$$\tau = K\gamma^{n} + \tau_0 \quad (1)$$

where τ is the shear stress (Pa), K is the consistency index ($Pa.s^n$), τ_0 is the yield stress (Pa), γ is the shear rate (s^{-1}), and n is the flow behavior index (-).

Emulsion stability was evaluated by transferring 60 mL of aged fluid into a graduated cylinder and monitoring phase separation at room temperature over 12 h. In addition, a parallel long-term monitoring test was conducted with the unaged drilling fluid (UDF) for 30 days to establish a reference separation trend. Olefin (supernatant) separation was quantified using an automated image analysis procedure based on a Python 3 script developed with the OpenCV library (Bradski 2000), which calculated phase height in pixels and converted it to volume.

Filtration tests were performed using a High Temperature and High Pressure (HTHP) filter press (OFITE) at 150 °F (65.6 °C) under a differential pressure of 500 psi (34.5 bar), with the filtrate volume recorded after 30 min, in accordance with API Recommended Practice 13B-2 (OFITE 2019; API 2023), ensuring comparability with standard protocols.

A central composite design (CCD) with two replicates at the central point, totaling ten experiments, was employed to evaluate the main effects and interaction between temperature and aging time on rheological properties. A rotational α value of 1.41 was adopted, resulting in an intermediate temperature level of 142.7 °C (coded level +1), with temperature ranging from 100 to 150 °C and aging time from 24 to 168 h. This axial point is inherent to the rotatable CCD, ensuring rotatability and uniform prediction variance, and is widely used in response surface methodology to identify nonlinear behavior and transition regions between stable and unstable regimes (Montgomery 2017). The upper temperature limit (150 °C) was defined by the operational capacity of the aging unit, while the lower bound (100 °C) was selected to investigate thermal aging above the onset of emulsifier degradation identified by TGA. Nitrogen pressure of 5 bar was applied during aging to prevent water evaporation, following API RP 13I (API 2016).

The selected aging time range (24 to 168 h) was defined to represent static exposure intervals encountered during deepwater drilling operations. In such environments, fluid circulation is interrupted during events such as BOP pressure tests, casing running, wiper trips, waiting-on-cement periods, and well control interventions. These conditions may extend static exposure to several days, reaching or exceeding 168 hours, as reported in field data associated with non-productive time events (Assi et al. 2021). The lower bound of 24 h was chosen as a condition beyond conventional aging protocols, which typically employ static durations of 16 h, while the upper bound was selected to capture extended static conditions relevant to field operations. The complete design matrix is presented in Table 2.

The independent variables were coded as dimensionless parameters according to:

$$X_T = \frac{T - T_0}{\Delta T} \tag{2}$$

$$X_t = \frac{t - t_0}{\Delta t} \tag{3}$$

where T and t are the actual values of temperature and aging time, and T_0 and t_0 and are the central values of each factor. ΔT and Δt represent the corresponding step sizes.

Response surface models were developed by fitting second-order polynomial equations. Model validity was assessed by analysis of variance (ANOVA) at a 5% significance level ($p \leq 0.05$). The

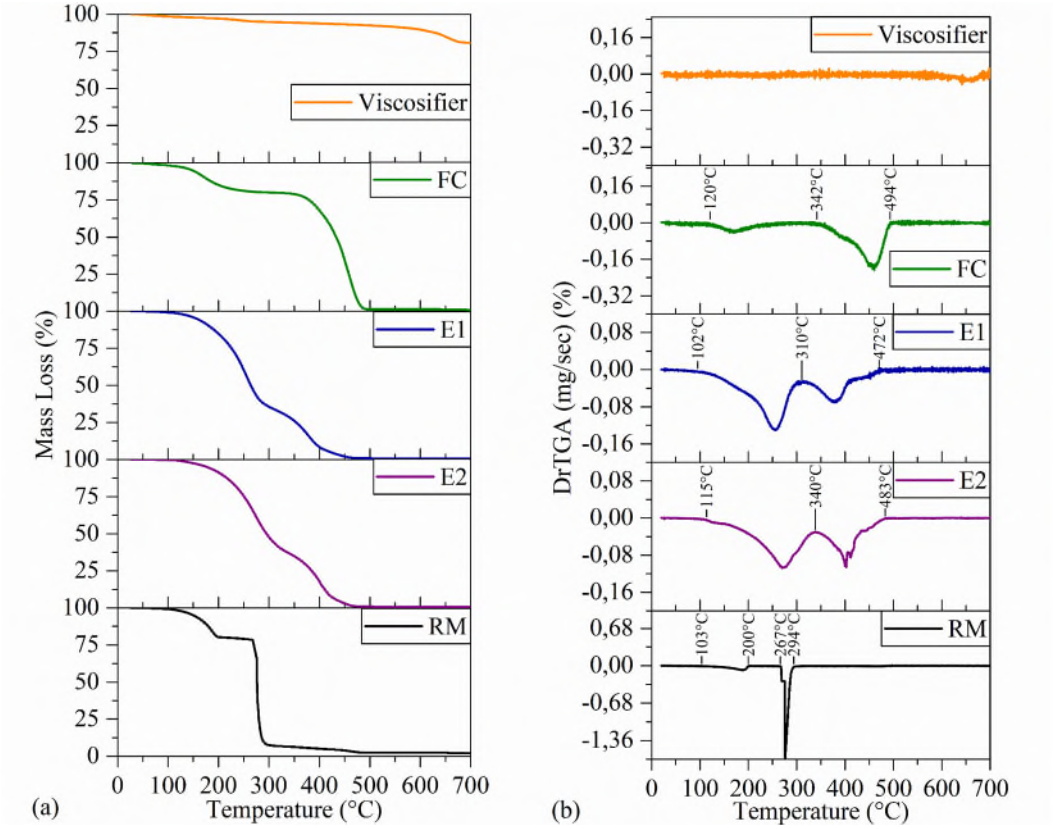
significance of regression coefficients was tested using Student's t-test, retaining only statistically significant terms while respecting model hierarchy. Model assumptions were verified through residual analysis, including tests for normality (Shapiro–Wilk), homoscedasticity, and independence, and goodness of fit was evaluated using the coefficient of determination (R^2). Response surface plots were generated exclusively for rheological parameters to illustrate the influence of temperature and aging time.

3. Results and discussion

3.1 Thermal Stability of Fluid Components

Thermogravimetric analysis was performed on the main pure reagents used in the drilling fluid formulation, including the rheological modifier (RM), primary and secondary emulsifiers (E1 and E2), filtration control additive (FC), and viscosifier (Fig. 2). Previous studies have shown that organic compounds typically undergo thermal degradation between 100 °C and 500 °C (Ghaderi and Dargazany 2022). As shown in Fig. 2, all components remained thermally stable up to 100 °C

Fig. 2 Thermogravimetric (TGA) and derivative thermogravimetric (DrTGA) analysis of the main pure reagents used in the drilling fluid formulation: (a) TGA curves and (b) DrTGA curves



The primary emulsifier and the filtration control additive exhibited the onset of degradation at approximately 115 °C and 120 °C, respectively, reaching mass losses of about 4% at 150 °C. In contrast, the viscosifier showed high thermal resistance, remaining stable above 200 °C. These results support the interpretation of subsequent changes in emulsion stability, filtration performance, and rheological behavior, since thermal degradation of these additives directly affects interfacial integrity and fluid structure.

To complement these findings, TGA and DrTGA analyses were also conducted on the formulated fluid before and after aging at 100, 125, and 150 °C for 48 h (Online Resource 1). The results show that, unlike the isolated pure additives, the formulated fluid exhibited no mass loss above 200 °C under any condition, with all remaining components thermally stable up to 700 °C. The dense fraction increased from approximately 30% in the UDF to 45% in the fluid aged at 150 °C, indicating that lighter interfacial components were preferentially lost during aging. Furthermore, the DrTGA peak associated with volatile components shifted from ~130 °C (UDF, 100 °C, and 125 °C) to ~115 °C in the fluid aged at 150 °C, reflecting a change in the composition of the volatile fraction consistent with selective degradation of the more thermally labile emulsifier constituents.

These observations indicate that emulsifier degradation in the formulated fluid under pressurized conditions (5 bar N_2) is progressive and selective rather than abrupt, which is mechanistically distinct from the bulk degradation onset identified by TGA of pure additives under atmospheric inert conditions. Therefore, TGA results of pure emulsifiers should be interpreted only as an indication of their thermal sensitivity and not as a direct representation of their behavior at the brine/oil interface within the emulsion.

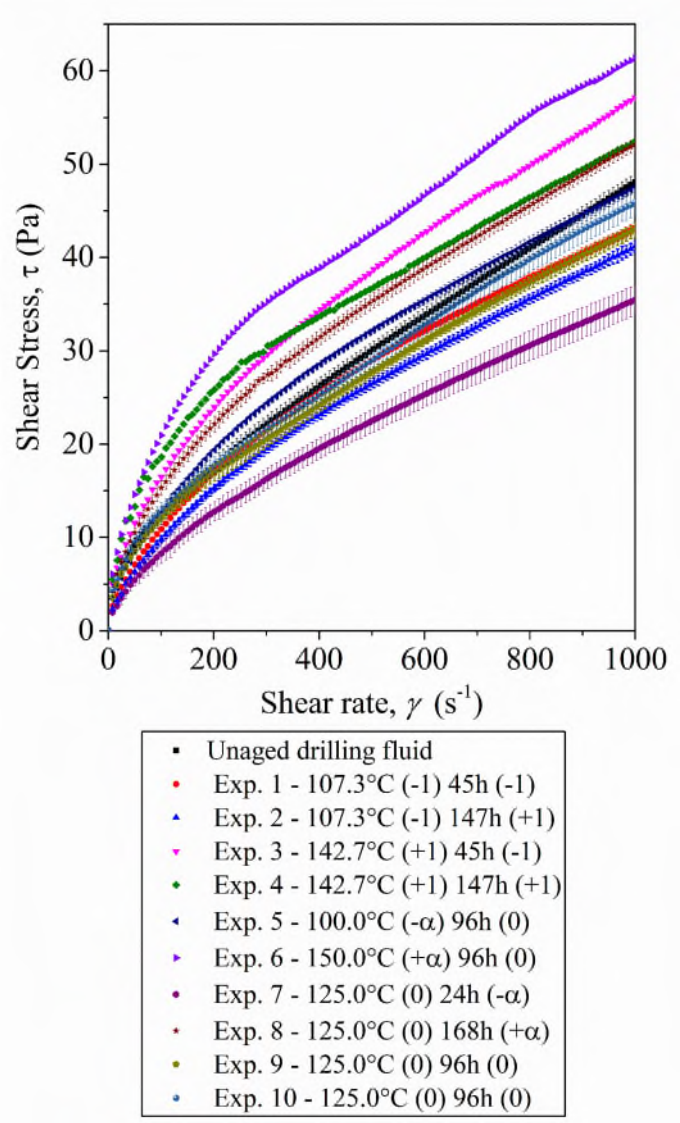
3.2 Rheological behavior

Flow curves of aged fluids are presented in Fig. 3. A nonlinear behavior is observed at low shear rates (0.1–500 s^{-1}), while near-linear trends appear at higher shear rates (500–1000 s^{-1}), with slopes dependent on aging temperature. This highlights the relevance of low shear rates for capturing pseudoplastic behavior in drilling (Malkin and Isayev 2006; Irgens 2014).

A pronounced increase in shear stress was observed for fluids aged at temperatures ≥142.7 °C, particularly at low shear rates (~300 s^{-1}), consistent with previous reports attributing this behavior to surfactant degradation and clay dispersion (Zhuang et al. 2017). Annis (1967) proposed that high temperatures enhance clay platelet dispersion, modifying the fluid's structure. This is supported by TGA (Fig. 2), which showed that rheological additives begin degrading near the aging temperatures. Prolonged

exposure further intensified this effect; for example, at 125 °C, aging for 168 h resulted in significantly higher shear stress than 24 h, potentially increasing pumping energy requirements and impairing solids transport.

Fig. 3 Flow curve before and after aging under different temperature and aging time conditions



The Herschel–Bulkley model (Eq. 1) adequately described all flow curves, and the corresponding parameters yield stress (τ_0), consistency index (K), and flow behavior index (n) are summarized in Table 2. Based on the experimental design, empirical models were developed as functions of the coded variables temperature (X_T) and aging time (X_t) (Eqs. 4-6), all statistically significant at $p \leq 0.05$.

$$\tau_0 = 0.25X_T - 1.48X_T^2 - 1.28X_t^2 - 3.14 \quad (4)$$

$$K = 0.63X_T^2 + 0.51X_T + 0.23X_t^2 + 0.27X_t + 0.34X_TX_t + 0.38 \quad (5)$$

$$n = -0.09X_T^2 - 0.04X_T - 0.05X_t^2 - 0.03X_t - 0.03X_TX_t + 0.68 \quad (6)$$

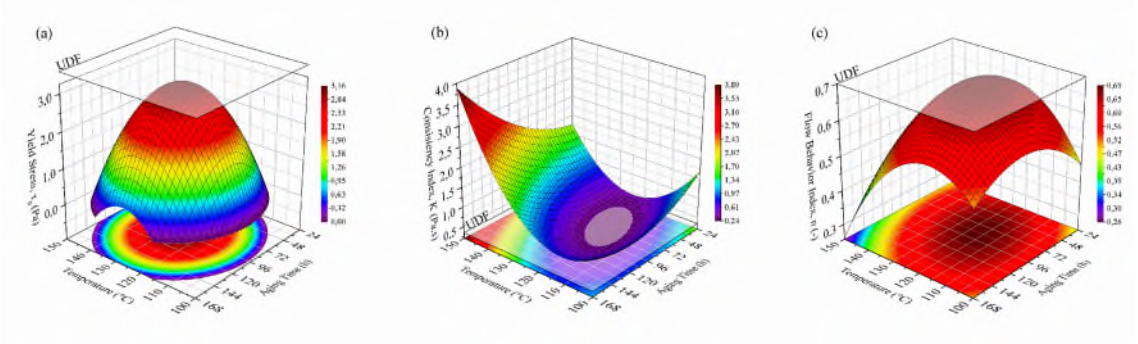
Table 2 Results of central composite design for drilling fluid before and after aging process.

Exp.	Operational conditions				Experimental results			
	Temperature (X_T) (°C)		Aging Time (X_t) (hr)		Herschel-Bulkley Model			
					τ_0 (Pa)	K (Pa.s)	n (-)	R^2
	UDF*				3.57 ± 0.1	0.34 ± 0.08	0.70 ± 0.03	0.9987
1	(-1)	107.3	(-1)	45	0.00	0.77	0.58	0.9997
2	(-1)	107.3	(+1)	147	0.00	0.73	0.59	0.9999
3	(+1)	142.7	(-1)	45	1.15	0.79	0.61	0.9994
4	(+1)	142.7	(+1)	147	0.37	2.47	0.44	0.9969
5	(-α)	100.0	(0)	96	0.00	0.97	0.56	0.9998
6	(+α)	150.0	(0)	96	0.55	2.24	0.48	0.9970
7	0	125.0	(-α)	24	0.50	0.40	0.65	0.9999
8	0	125.0	(+α)	168	0.68	1.27	0.54	0.9996
9	0	125.0	0	96	2.93	0.38	0.67	0.9987
10	0	125.0	0	96	3.36	0.37	0.69	0.9980

*Unaged Drilling Fluid

The models exhibited high coefficients of determination ($R^2 \geq 0.98$), with residuals showing normality and independence. Temperature and aging time exerted negative quadratic effects on τ_0 and n, while K increased with both variables. For comparison, a reference plane corresponding to the rheological parameters of the unaged drilling fluid (UDF) is also included, providing a baseline to visualize the changes induced by thermal aging.

Fig. 4 Response surface plots for (a) yield stress, (b) consistency index, and (c) flow behavior index



In Fig. 4(a), aging results in an approximately 15% reduction in τ_0 relative to the unaged drilling fluid, particularly at intermediate temperature and time conditions, indicating weakening of the internal network responsible for yield stress. Yield stress reflects the force required to disrupt the microstructure formed by interparticle interactions, which are strongly influenced by temperature and particle–fluid interfacial phenomena (Alderman et al. 1988; Briscoe B. J. et al. 1994).

Fig. 4(b) shows that the consistency index K initially decreases with temperature and subsequently increases sharply, reaching values up to seven times higher than the unaged fluid at 142.7 °C and 147 h. Despite constant solid content, this increase is attributed to clay platelet reorganization into house-of-cards structures, which intensify internal friction (Annis 1967). İbanoğlu (2002) also highlighted the role of particle aggregation under thermal and ionic effects in increasing viscosity.

The increase in K under high-temperature aging conditions is therefore associated with enhanced molecular mobility, structural reorganization, and intensified particle interactions, which collectively increase flow resistance. While sufficient viscosity is required for cuttings suspension, excessive viscosity may impair pumping efficiency, reduce rate of penetration, and complicate pressure control, negatively affecting operational performance.

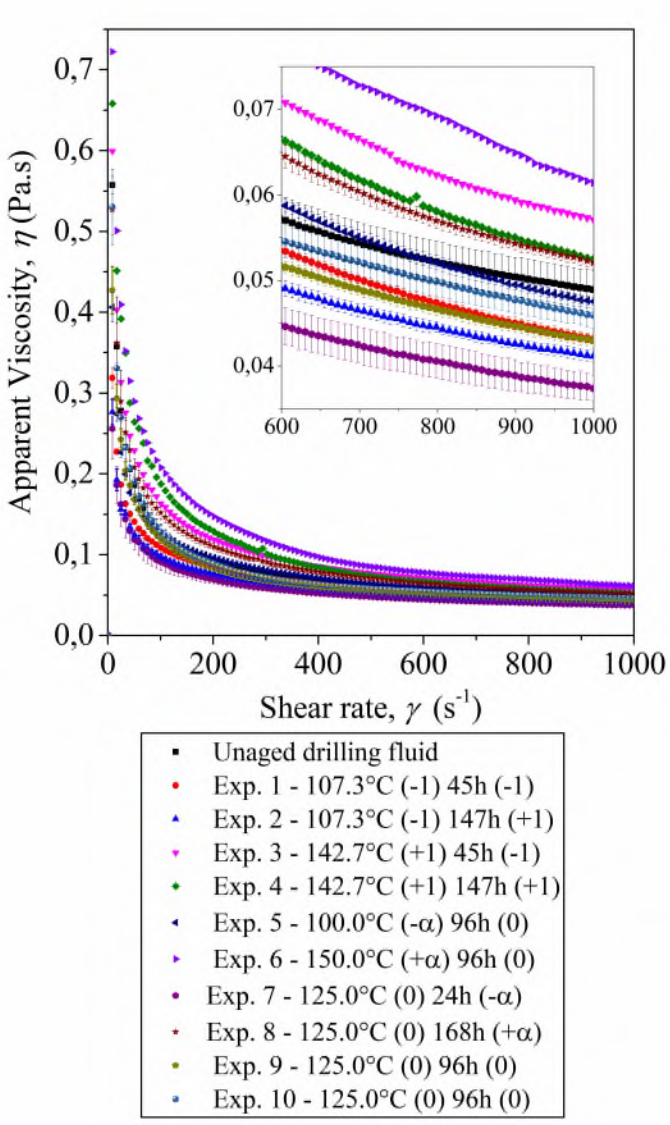
Fig. 4(c) shows that the flow behavior index n decreases with increasing temperature and aging time, indicating enhanced pseudoplasticity, consistent with thermally induced disruptions of internal structures and interfacial films reported by Husin and Hussain (2018). In this study, the simultaneous increase in K and decrease in n indicate structural reorganization and intensified interactions among dispersed particles during thermal aging, leading to a denser and more frictional internal network. As a result, the fluid becomes more resistant to flow initiation at low shear while exhibiting greater shear sensitivity at high shear, a characteristic feature of pseudoplastic fluids.

Apparent viscosity curves are shown in Fig. 5. At lower aging temperatures, viscosity decreased relative to the unaged fluid, whereas aging at 142.7 °C and 150 °C caused a marked increase. At the lowest shear rate (8 s^{-1}), viscosity increased by 8% at 142.7 °C (45 h), 18% at the same temperature after 147 h, and 30% at 150 °C for 96 h, with similar trends observed at higher shear rates.

These increases are associated with emulsifier degradation, emulsion destabilization, and clay particle reorganization into “house-of-cards” structures, which intensify interparticle friction (Annis 1967). Such changes result in a fluid that is more shear-sensitive but structurally stronger at rest, affecting pumping efficiency and solids suspension during static intervals.

These nonlinear trends indicate the presence of a transition region in the temperature range of approximately 142–145 °C. This region corresponds to the intermediate axial point (142.7 °C) defined by the central composite design, which is critical for capturing the system response near the boundary between stable and unstable regimes. Within this range, reversible physicochemical changes progressively give way to irreversible degradation processes, affecting both rheological behavior and emulsion stability.

Fig. 5 Apparent Viscosity Curves at Different Temperatures and Aging Times



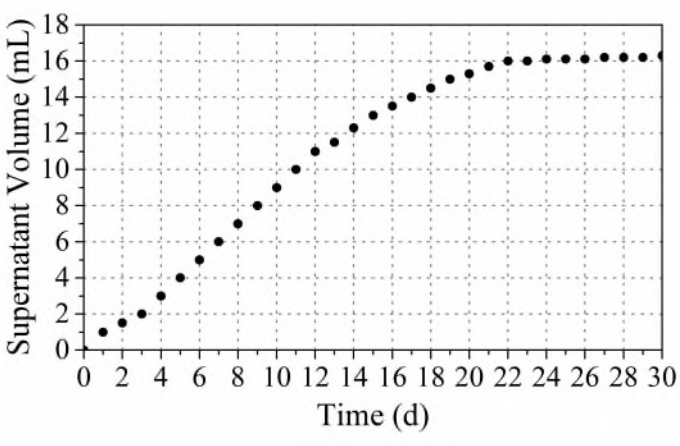
3.3 Emulsion Stability

The unaged drilling fluid exhibited nonlinear olefin separation, stabilizing at approximately 16.3 mL (47% of the initial olefin content) over time (Fig. 6). This behavior is associated with the combined effects of

droplet size distribution, density contrasts, and surfactant-mediated interfacial interactions (Abismaïl et al. 1999), and does not necessarily indicate complete emulsion breakdown.

This behavior is also consistent with the characteristics of low-HLB emulsifiers, such as amide/imidazoline-type surfactants derived from tall-oil fatty acids, which are highly lipophilic and preferentially stabilize water-in-oil emulsions by forming interfacial films around brine droplets. The stability of such systems strongly depends on the integrity and packing of these interfacial films, which are sensitive to temperature and chemical degradation (Binks and Horozov 2006).

Fig. 6 Volume of supernatant from the unaged drilling fluid over time during the stability test

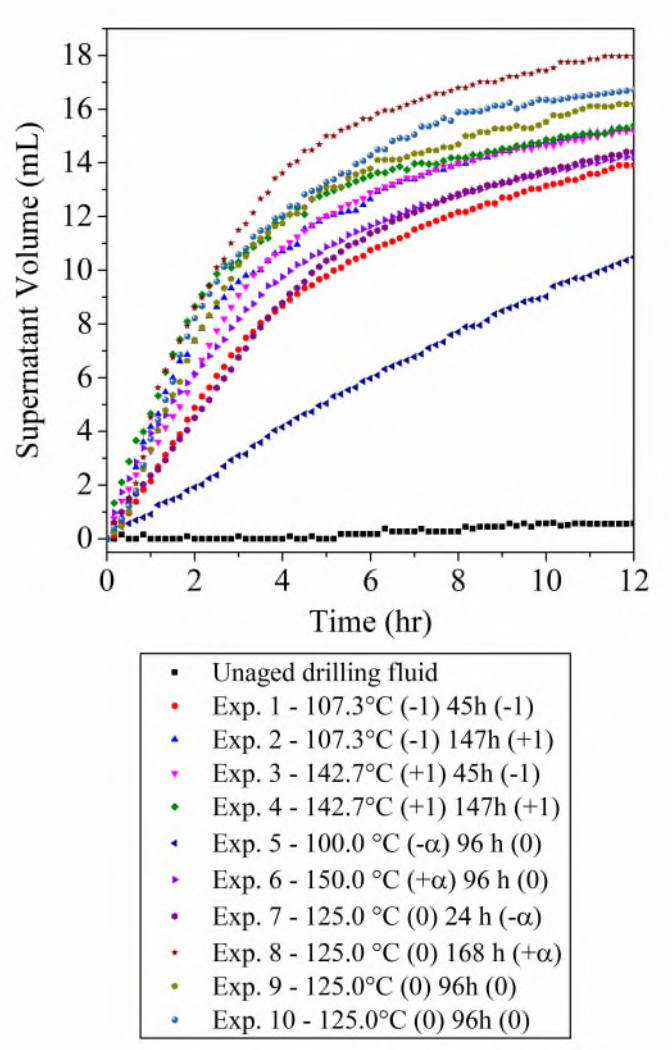


For fluids aged at 125 °C, prolonged exposure intensified olefin separation (Fig. 7). At 24 h, a rapid increase was observed, stabilizing near 14.4 mL, whereas the unaged fluid reached only 0.56 mL after 12 h. At higher temperatures and intermediate aging times, separation initially increased but decreased near 150 °C, suggesting structural rearrangements that limit droplet migration. These trends are consistent with rheological changes, where increased K and reduced n indicate a denser internal network restricting phase separation under static conditions.

However, this behavior is strongly associated with the significant increase in viscosity observed at elevated temperatures, which can hinder droplet mobility and limit phase migration. This interpretation is supported by the substantial increase in the consistency index (up to sevenfold), indicating the formation of a highly structured system. In this context, reduced supernatant separation does not necessarily indicate improved emulsion stability, but may instead reflect restricted droplet movement in a highly structured or

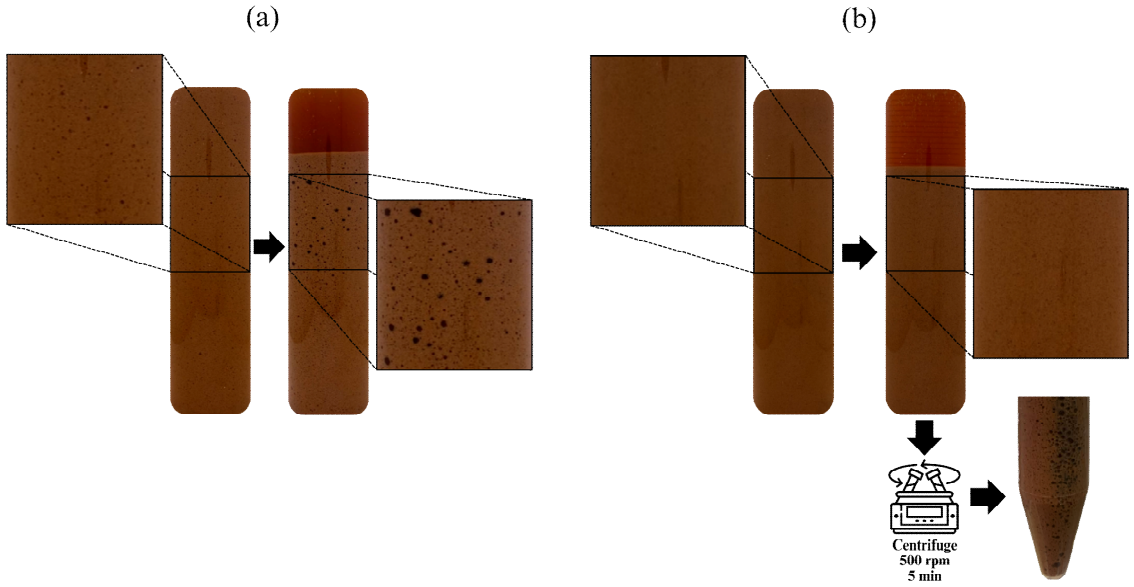
partially gelled system. This is further supported by the centrifugation results (Fig. 9), which reveal ongoing destabilization despite the reduced visible supernatant separation.

Fig. 7 Supernatant volume during static stability testing



Visual inspection revealed droplet coalescence after 12 h of static aging (Fig. 8a), indicating weakening of interfacial films with increasing temperature and time. Even samples appearing homogeneous exhibited brine droplets after gentle centrifugation (500 rpm, 5 min), a condition selected to enhance visualization without inducing artificial emulsion breaking (Furtado et al. 2015; He et al. 2016), as shown in Fig. 8b.

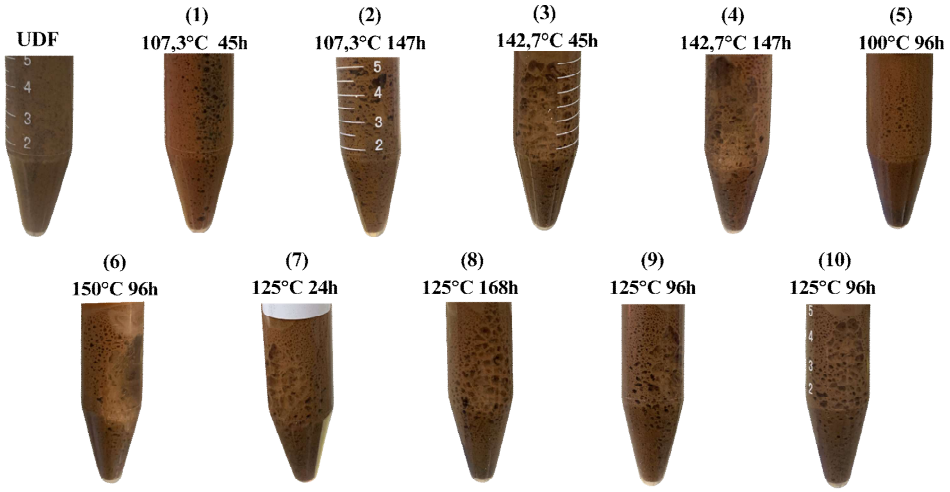
Fig. 8 Visual appearance of aged drilling fluids after (a) 12 h of static stability testing and (b) subsequent gentle centrifugation (500 rpm, 5 min)



Extending this approach, all aged samples were analyzed under the same centrifugation conditions. Fig. 9 summarizes the influence of temperature and aging time on brine manifestation after stability testing and centrifugation. More severe conditions accelerated droplet growth and visible coalescence, whereas milder conditions masked early destabilization, detectable only after centrifugation.

At lower aging temperatures, the brine phase appeared clearer and more distinct, while higher temperatures and longer aging times led to a more pronounced separation, as observed in Exps. 3, 4, and 6. These findings indicate that the service life of inverse emulsions is governed by nonlinear destabilization mechanisms. This behavior can be partially attributed to the thermal degradation of surfactants, as indicated by the TGA and DrTGA results (Fig. 2), which show that secondary and primary emulsifiers begin to degrade at approximately 102 °C and 115 °C, respectively. Such early degradation compromises interfacial stability and promotes the appearance of the brine phase. This behavior is consistent with the known thermal sensitivity of amide/imidazoline-based emulsifiers, whose interfacial activity depends on their molecular structure and adsorption at the oil–water interface. Thermal degradation or partial desorption of these surfactants reduces interfacial film strength, promoting droplet coalescence and phase separation (Sjöblom et al. 2003; Binks and Horozov 2006).

Fig. 9 Effect of temperature and aging time on brine appearance after centrifugation



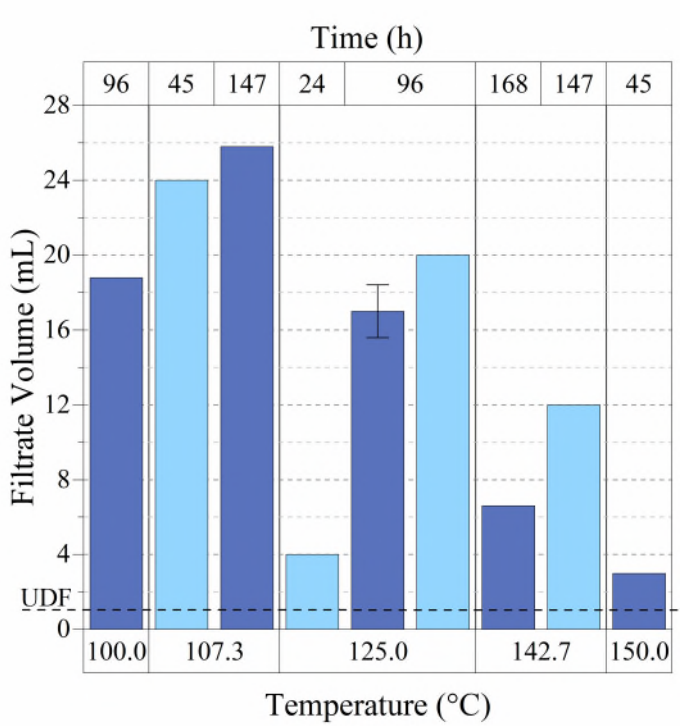
This interpretation is further supported by the TGA analysis of the formulated fluid (Online Resource 1), which indicates selective degradation of interfacial emulsifier components during thermal aging. As discussed in Section 3.1, this degradation occurs progressively rather than abruptly, affecting interfacial film integrity without complete bulk structural collapse. Consequently, even though the emulsion remains macroscopically intact, interfacial weakening promotes droplet coalescence and phase separation.

These findings have direct operational implications, as phase separation and brine coalescence reduce solids suspension capacity and may promote formation invasion, increasing the need for emulsifier replenishment. From a physicochemical perspective, these results indicate that emulsion stability in low-HLB systems is governed not only by droplet size distribution but also by the integrity of the interfacial film, which can be progressively weakened under thermal exposure, leading to delayed but irreversible destabilization.

3.4 Filtration Volume

Fig. 10 shows that both temperature and aging time significantly influence filtrate volume. At constant temperatures, filtrate volume increased with aging time, reflecting fluid destabilization due to emulsifier degradation and droplet coalescence (Fayad et al. 2021).

Fig. 10 Filtrate volume as a function of temperature and aging time



When temperature is analyzed independently, a different trend emerges. From 100.0 °C to 107.3 °C, filtrate volume increases. However, at 125.0 °C and higher, shorter aging durations show a significant reduction, especially at 150.0 °C and 96 h, where the lowest filtrate volume was observed. This suggests that higher temperatures may initially enhance the effectiveness of the fluid loss additive.

To verify this, an additional test was conducted by aging 50 mL of the filtration control additive at 150 °C for 96 h. After thermal exposure, the additive exhibited a noticeable change in physical consistency, becoming a rubber-like solid. The aged material was subsequently incorporated into a new drilling fluid formulation and tested under the same filtration conditions. The resulting fluid produced only 1 mL of filtrate, which is even lower than the value obtained for the unaged drilling fluid.

This observation suggests that thermal aging may alter the physical state of the additive, possibly generating solid or partially insoluble residues capable of contributing to pore sealing within the filter cake, thereby reducing its permeability and filtrate volume. Thermogravimetric analysis (Fig. 2) indicates that the filtration control additive begins to thermally degrade at approximately 120 °C, suggesting that the additive is thermally sensitive within the temperature range investigated in this study. However, TGA evaluates the thermal behavior of the isolated additive under controlled conditions and does not fully reproduce the complex physicochemical environment of the additive within the water-in-oil drilling fluid

system. Therefore, the TGA results should be interpreted only as an indication of the additive's thermal susceptibility rather than as a direct representation of its behavior within the emulsion.

The rubber-like consistency developed by the filtration control additive after thermal aging at 150 °C for 96 h is consistent with the known thermal degradation behavior of acrylic-based polymers. McGaugh and Kottle (1967) reported that poly(acrylic acid) begins to form cyclic anhydride structures at 150 °C, with anhydride formation identified as the dominant reaction in the temperature range of 25 to 150 °C. The authors further demonstrated that both intra- and intermolecular crosslinking occur through anhydride formation, a process that would be substantially more extensive under prolonged thermal exposure such as the 96 h aging applied in the present study. Such structural reorganization, involving crosslink formation and chain rigidification, provides a plausible mechanistic interpretation basis for the physical transformation observed in the aged additive and for the formation of a denser, less permeable filter cake.

A similar effect was reported by Meng et al. (2025), who attributed the reduction of API filtration loss after high-temperature aging (220 °C, 16 h) to the excellent thermal resistance of the buffering polymer PSA (polystyrene–acrylic resin) and its ability to form a low-permeability mud cake. In their study, the PSA maintained its particle size and structural integrity, resulting in a 58% decrease in filtrate volume. Although the present work employs a coded additive of unknown composition, the observed solidification after thermal exposure suggests an analogous mechanism, in which the degradation of the additive generates fine, insoluble residues that improve the sealing of pores and the compactness of the filter cake, consequently reducing permeability.

It is important to note that emulsion stability and filtration performance are not independent responses in oil-based drilling fluids. The integrity of the interfacial film surrounding water droplets directly influences the cohesiveness and sealing capacity of the filter cake, while droplet coalescence resulting from emulsifier degradation can generate free water that disrupts cake structure and increases filtrate volume.

In the present study, fluids aged at 150 °C exhibited clear phase separation and droplet coalescence, yet produced the lowest filtrate volumes observed. This apparent contradiction can be interpreted as suggesting that the physical transformation of the filtration control additive at this temperature, involving structural crosslinking and rigidification as discussed above, exerted a dominant effect on filtration performance that outweighed the destabilizing influence of emulsifier degradation. This behavior highlights the importance of considering the coupled thermal responses of multiple fluid components when interpreting filtration data under high-temperature aging conditions.

Direct characterization of the filter cake structure (e.g., SEM or micro-CT) was not performed in the present study and should be considered in future work to further validate the proposed mechanisms.

Similar findings were also reported by Ogiriki et al. (2017), who observed that increasing the aging temperature in a water-based fluid led to a reduction in filtrate volume due to the formation of a thinner and more effective filter cake. In drilling operations, the formation of a compact and low-permeability filter cake is essential for minimizing fluid invasion into the reservoir. This low-permeability layer is formed by the deposition of suspended solids and filtration control additives on the porous medium, contributing to filtration control and reduced fluid invasion (Bageri et al. 2020).

4. Conclusion

This study investigated the coupled effects of temperature and prolonged static aging time on the rheological behavior, emulsion stability, and filtration performance of an olefin-based synthetic drilling fluid formulated as an inverse emulsion, addressing the limited understanding of long-term static aging beyond conventional short-duration protocols.

Aging temperature and time significantly affected the rheological properties, apparent viscosity, emulsion stability, and filtration volume of the drilling fluid. Aging at elevated temperatures, particularly at 142.7 °C and 150 °C, resulted in increased shear stress, consistency index, and apparent viscosity, accompanied by a reduction in the flow behavior index, indicating enhanced pseudoplasticity. These variations are attributed to the thermal degradation of emulsifiers and filtration control agents, as suggested by thermogravimetric analysis showing initial mass losses between 102 °C and 120 °C. Such degradation likely modifies the internal structure, solid-phase organization, and interfacial arrangement of the fluid, promoting greater internal friction and resistance to flow under high-temperature conditions.

Response surface analysis confirmed that both temperature and aging duration exert nonlinear and interactive effects on the Herschel–Bulkley parameters, with temperature emerging as the dominant factor. These nonlinearities reveal a transition region near 142–145 °C, where reversible physicochemical changes give way to irreversible additive degradation, phase reorganization, and structural changes in the multicomponent fluid. This behavior directly impacts the fluid's capacity to transport cuttings and maintain wellbore stability, particularly under extended static conditions.

Regarding emulsion stability, prolonged aging at higher temperatures led to different degrees of phase separation, with some samples showing greater destabilization, as indicated by changes in brine

appearance, droplet coalescence, and larger droplet formation. Filtration behavior also exhibited a nonlinear response: filtrate volume initially decreased at higher temperatures, likely due to physical changes in the filtration control additive and formation of a denser filter cake, but increased with prolonged aging as additive degradation and emulsion destabilization became more pronounced.

This study shows that several degradation phenomena in inverse-emulsion drilling fluids only become evident after long-term static aging, which is not captured by the short aging times commonly used in previous studies and conventional protocols, typically limited to ≤16 h. The results confirm that aging time is a key factor governing the long-term integrity of olefin-based synthetic drilling fluids and fill an important gap in the literature, which has focused mainly on temperature effects. By identifying temperature–time conditions associated with irreversible degradation, interfacial destabilization, structural reorganization, and changes in filtration behavior, this work provides a more realistic basis for predicting performance loss during extended static intervals typical of deepwater operations.

These findings establish temperature–time conditions associated with the onset of interfacial destabilization and structural degradation, providing a framework for anticipating fluid performance loss under prolonged static thermal exposure. Such conditions are representative of operational scenarios including BOP tests, maintenance operations, wiper trips, well control interventions, and equipment-related operational failures, in which drilling fluids may remain static for extended periods.

Future research should extend these observations to dynamic aging and alternative base fluids, incorporating in-situ high-temperature rheometry and particle-scale imaging to validate the proposed degradation pathways. Studies under pressure conditions representative of deepwater wells are also needed, since the custom-built equipment used here cannot operate at elevated pressures. Additionally, electrical stability (ES) measurements should be included in future work to complement the evaluation of emulsion stability, as this industry-standard parameter was not available during the present study.

Acknowledgments

The authors acknowledge Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil (CAPES), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), and Petróleo Brasileiro S.A. (Petrobras) for their support.

Statements and Declarations

Funding

This study was supported by Petróleo Brasileiro S.A. (Petrobras) under agreement SAP 2023/00105-9, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil (CAPES), and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

Competing interests

Elessandre Alves de Souza is affiliated with Petróleo Brasileiro S.A. (Petrobras), which provided support for this study under agreement SAP 2023/00105-9. The authors declare that there are no other relevant financial or non-financial interests to disclose.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Ethics approval

Not applicable. This study did not involve human participants, human data, or animals.

Supplementary Information

Online Resource 1 Thermogravimetric (TGA) and derivative thermogravimetric (DrTGA) analyses of the formulated drilling fluid before aging and after aging at 100, 125, and 150 °C for 48 h

References

Abismaïl B, Canselier JP, Wilhelm AM, et al (1999) Emulsification by ultrasound: drop size distribution and stability. Ultrason Sonochem 6:75–83. https://doi.org/10.1016/S1350-4177(98)00027-3

Alderman NJ, Gavignet A, Guillot D, Maitland GC (1988) High-Temperature, High-Pressure Rheology of Water-Based Muds. SPE

Annis MR (1967) High-Temperature Flow Properties of Water-Base Drilling Fluids. Journal of Petroleum Technology 19:1074–1080. https://doi.org/10.2118/1698-PA

API (2016) Recommended Practice for Laboratory Testing of Drilling Fluids (API RECOMMENDED PRACTICE 13I. API, Washington

API (2023) Standard Procedure for Field Testing Oil-Based Drilling Fluids (API RECOMMENDED PRACTICE 13B-2). API, Washington

Apostolidou C, Sarris E, Georgakopoulos A (2022) Dynamic thermal aging of water-based drilling fluids with different types of low-rank coals as environmental friendly shear thinning additives. J Pet Sci Eng 208:109758. https://doi.org/10.1016/j.petrol.2021.109758

Arain AH, Ridha S (2025) Effect of multifunctional boron nitride nanoparticles on the performance of oil-based drilling fluids in high-temperature unconventional formation drilling. Geoenergy Science and Engineering 247:213722. https://doi.org/10.1016/j.geoen.2025.213722

ASME (2005) Drilling fluids processing handbook by Shale Shaker Committee. Elsevier

Assi AH, Almahdawi FHM, Khalti QA (2021) The Influence of Glass Fiber and Milled Glass Fiber on the Performance of Iraqi Oil Well Cement. Journal of Petroleum Research and Studies 11:30–48. https://doi.org/10.52716/jprs.v11i2.496

ASTM International (2020) ASTM E1131-20 Standard Test Method for Compositional Analysis by Thermogravimetry. ASTM International, West Conshohocken

Bageri BS, Adebayo AR, Al Jaberi J, Patil S (2020) Effect of perlite particles on the filtration properties of high-density barite weighted water-based drilling fluid. Powder Technol 360:1157–1166. https://doi.org/10.1016/j.powtec.2019.11.030

Binks BP, Horozov TS (2006) Colloidal particles at liquid interfaces. Cambridge University Press

Binks BP, Rocher A (2009) Effects of temperature on water-in-oil emulsions stabilised solely by wax microparticles. J Colloid Interface Sci 335:94–104. https://doi.org/10.1016/j.jcis.2009.03.089

Bradski G (2000) The opencv library. Dr Dobb's Journal: Software Tools for the Professional Programmer 25:120–123

Briscoe BJ, Luckham PF, Ren SR (1994) The properties of drilling muds at high pressures and high temperatures. Philosophical Transactions of the Royal Society of London Series A: Physical and Engineering Sciences 348:179–207. https://doi.org/10.1098/rsta.1994.0088

Caenn R, Darley HCH, Gray GR (2016) Composition and Properties of Drilling and Completion Fluids: Seventh Edition. Elsevier Inc.

Celino KN, Fernandes R da S, de Morais SC, et al (2022) Emulsion-based drilling fluids: Rheological properties preservation facing changes on the temperature, pressure and dispersed phase. J Mol Liq 352:118753. https://doi.org/10.1016/j.molliq.2022.118753

Fayad MM, Mohamed DE, Soliman EA, et al (2021) Optimization of invert emulsion oil-based drilling fluids performance through heterocyclic imidazoline-based emulsifiers. Colloids Surf A Physicochem Eng Asp 613:126092. https://doi.org/10.1016/j.colsurfa.2020.126092

Fookes F, Villada Y, Taverna ME, et al (2024) Application of mesoporous silica particles as an additive for controlling rheological, thermal, and filtration properties of water-based fluids. Colloids Surf A Physicochem Eng Asp 700:134703. https://doi.org/10.1016/j.colsurfa.2024.134703

Friaça FG, Pereira MS, Ataíde CH (2023) Rheology and stability of drilling fluids formulated with saturated NaCl and CaCl2 solutions. Chem Eng Sci 275:118752. https://doi.org/10.1016/j.ces.2023.118752

Furtado GF, Picone CSF, Cuellar MC, Cunha RL (2015) Breaking oil-in-water emulsions stabilized by yeast. Colloids Surf B Biointerfaces 128:568–576. https://doi.org/10.1016/j.colsurfb.2015.03.010

Ghaderi A, Dargazany R (2022) Modeling the Burning of Polymer Matrix: Training Collocation Physics-Informed Neural Network. In: Volume 9: Mechanics of Solids, Structures, and Fluids; Micro- and Nano-Systems Engineering and Packaging; Safety Engineering, Risk, and Reliability Analysis; Research Posters. American Society of Mechanical Engineers

Goodwin JW (2004) Colloids and interfaces with surfactants and polymers : an introduction. J. Wiley

Hassan A, Murtaza M, Alade O, et al (2023) Interactions of drilling and completion fluids during drilling and completion operations. pp 41–74

He X, Zhong C, Zeng G, et al (2024) Anti-aging and rheological behaviors, and supra-molecular structures in water for the composite of a biopolymer with nano-SiO2 applied in workover fluids of ultra-deep wells. Colloids Surf A Physicochem Eng Asp 684:133100. https://doi.org/10.1016/j.colsurfa.2023.133100

He Y-M, Ling Z-X, Zhou Y, et al (2016) Application of extraction induced by emulsion breaking for trace multi-element determination in jet fuel by inductively coupled plasma-mass spectrometry. Spectroscopy Letters 49:37–43. https://doi.org/10.1080/00387010.2015.1061556

Hossain ME, Al-Majed AA (2015) Fundamentals of Sustainable Drilling Engineering. Wiley

Husin H, Hussain HH (2018) Temperature Effect on Shear Thinning Behavior of Low-Viscous Oilfield Emulsion. In: Science and Technology Behind Nanoemulsions. InTech

İbanoğlu E (2002) Rheological behaviour of whey protein stabilized emulsions in the presence of gum arabic. J Food Eng 52:273–277. https://doi.org/10.1016/S0260-8774(01)00115-7

IEA (2023) Growth in global oil demand is set to slow significantly by 2028 - News - IEA. https://www.iea.org/news/growth-in-global-oil-demand-is-set-to-slow-significantly-by-2028. Accessed 18 Jul 2023

IOGP (2016) Drilling waste management technology review

Irgens F (2014) Rheology and Non-Newtonian Fluids. Springer International Publishing, Cham

Jiang H, Liu X, Xu Y, Jia Y (2024) Study on the effect and mechanism of temperature and shear on the stability of water–in–oil emulsion stabilized by asphaltenes. Colloids Surf A Physicochem Eng Asp 697:134470. https://doi.org/10.1016/j.colsurfa.2024.134470

Kania D, Yunus R, Omar R, et al (2021) Rheological investigation of synthetic-based drilling fluid containing non-ionic surfactant pentaerythritol ester using full factorial design. Colloids Surf A Physicochem Eng Asp 625:126700. https://doi.org/10.1016/j.colsurfa.2021.126700

Lee J, Shadravan A, Young S (2012) Rheological Properties of Invert Emulsion Drilling Fluid under Extreme HPHT Conditions. In: IADC/SPE Drilling Conference and Exhibition. SPE

Malkin AY, Isayev AI (2006) Rheology: Concepts, Methods, & Applications, 1st edn. ChemTec Publishing, Toronto

McGaugh MC, Kottle S (1967) The thermal degradation of poly(acrylic acid). J Polym Sci B 5:817–820. https://doi.org/10.1002/pol.1967.110050916

Meng X, Huang X, Sun J, et al (2025) Ultra-high temperature resistant polystyrene/acrylic resin microspheres for enhanced wellbore stability of oil-based drilling fluids. Colloids Surf A Physicochem Eng Asp 725:137637. https://doi.org/10.1016/j.colsurfa.2025.137637

Montgomery DC (2017) Design and Analysis of Experiments, 9th Edition. Wiley

OFITE (2019) HTHP Filter Press for Drilling Fluid Testing - Instruction Manual. Texas

Ogiriki S, Ekaette N, Okologume W (2017) EFFECT OF AGING ON WATER BASED MUD. International Journal of Engineering and Modern technology (2504-8848) 3:

Peixoto RDL, Bicudo TC, Moura HOM de A, et al (2021) Synthesis of decyl methyl carbonate and a comparative assessment of its performance as the continuous phase of synthetic-based drilling fluids. J Pet Sci Eng 199:108301. https://doi.org/10.1016/j.petrol.2020.108301

Petrobras (2025) Exploration and Production of Oil and Gas. https://petrobras.com.br/pt/nossas-atividades/areas-de-atuacao/exploracao-e-producao-de-petroleo-e-gas/. Accessed 19 Mar 2025

Razali SZ, Yunus R, Abdul Rashid S, et al (2018) Review of biodegradable synthetic-based drilling fluid: Progression, performance and future prospect. Renewable and Sustainable Energy Reviews 90:171–186. https://doi.org/10.1016/j.rser.2018.03.014

Shi J, Chen L, Xie R, et al (2025) Rheological and thermal property of KH570-modified nano-SiO2 grafted xanthan gum and its application in drilling fluid system. Carbohydr Polym 351:123013. https://doi.org/10.1016/j.carbpol.2024.123013

Sjöblom J, Aske N, Harald Auflem I, et al (2003) Our current understanding of water-in-crude oil emulsions. Adv Colloid Interface Sci 100–102:399–473. https://doi.org/10.1016/S0001-8686(02)00066-0

Stout SA, Payne JR (2017) Footprint, weathering, and persistence of synthetic-base drilling mud olefins in deep-sea sediments following the Deepwater Horizon disaster. Mar Pollut Bull 118:328–340. https://doi.org/10.1016/J.MARPOLBUL.2017.03.013

Tian Y, Zhou J, He C, et al (2022) The Formation, Stabilization and Separation of Oil–Water Emulsions: A Review. Processes 10:738. https://doi.org/10.3390/pr10040738

Vasconcelos AN, Paixão MVG, Marques N do N, et al (2022) Dimer fatty acid and fatty amide effects on the properties of synthetic-based drilling fluids. J Mol Liq 359:119270. https://doi.org/10.1016/j.molliq.2022.119270

Zhao Z, Sun J, Wang R, et al (2024) Shape memory resin with high temperature resistance for plugging fracture formations drilled with oil-based drilling fluid. Geoenergy Science and Engineering 243:213355. https://doi.org/10.1016/j.geoen.2024.213355

Zhuang G, Wu H, Zhang H, et al (2017) Rheological properties of organo-palygorskite in oil-based drilling fluids aged at different temperatures. Appl Clay Sci 137:50–58. https://doi.org/10.1016/j.clay.2016.12.015

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- ESM1.tif