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Research Article

Methodology for Evaluating H_2S Scavenger Performance in Crude Oil

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Abstract

The exploration and production of oil in Brazil are increasingly focused on deeper reservoirs and water columns, significant technological challenges related to material selection and corrosion control. The presence of H_2S in crude oil undermines the integrity of industrial equipment and the quality of derived products, contributing to environmental and occupational issues that lead to heightened costs and risks associated with the operation of these industrial units. One of the solutions is the continuous injection of liquid H_2S scavengers to mitigate this contaminant in industrial fluids. Testing yields important information regarding the performance of these products; however, the multitude of variables present in these tests complicates the ability to draw conclusive and reproducible observations. Furthermore, the impact of new products on subsequent processes following the injection point complicates the execution of field tests, and the careful implementation of these tests directly disrupts the normal operational and production routine. This article aims to present a detailed methodology for comparing the performance of H_2S scavengers composed of different active materials in a predominantly organic medium at temperatures reaching up to 130°C, conditions resembling those encountered at the onset of production from new oil-producing wells with water content of less than 1 %(v/v). Consequently, the methodologies described allow for the assessment, comparison, and differentiation of the H2S scavenging capacity of various commercial H_2S scavengers used in the oil industry, enabling their classification according to efficiency. Additionally, it consolidates in single test conditions that are closer to field application and capable of evaluating mixtures of water and oil in proportions ranging from 0 to 100 %(v/v), aqueous solutions with salinity up to 200 g/L in NaCl, temperatures between 30°C and 250°C, and pressures from atmospheric pressure up to 1034 kPa. The methodology allowed for obtaining, in addition to information on H_2S scavenging capacity, an indication of the reaction time and rate required to achieve the minimum H_2S content in both gas and liquid phases, facilitating the optimization of treatment protocols in oil platforms, onshore and offshore, subsea and topside, terminals, tanks, and pipelines. Among the commercial H_2S scavengers evaluated in this study, the one based on ethoxylated compounds (ETO-C) demonstrated superior performance compared to the MEA-triazine-based product (TRI-C) under the same experimental conditions.

Keywords

H_2S Scavenger, Hydrogen Sulfide, Crude Oil, H_2S Scavenging Capacity, MEA-Triazine, Ethoxylated Compounds

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1. Introduction

The exploration and production of oil in Brazil are increasingly focused on deeper reservoirs and water columns, creating significant technological challenges related to material selection and corrosion control. The presence of CO_2 and H_2S as contaminants in produced fluids complicates this situation [1, 2]. Moreover, the nature of produced water from reservoirs prone to high scaling and $CaCO_3$ deposition potential poses an additional challenge.

The presence of H_2S in produced fluids not only compromises the integrity of industrial equipment [3, 4] and the quality of derived products but also generates environmental and occupational issues [5, 6] that affect the entire production chain. One common strategy to reduce H_2S content in these fluids is the injection of liquid H_2S scavenging additives into the wells, which can react with species present in the H_2S equilibrium equation, converting them to less reactive forms. In the oil and gas production, effective H_2S scavengers, must have a high scavenging capacity and rapid conversion rate, ensuring that the reaction for capturing H_2S is irreversible. Additionally, they should not stabilize emulsions, generate foam, form gels, or precipitates, and must exhibit low corrosivity and minimal environmental impact. Additionally, low cost and ease of handling of the raw products are desirable, considering toxicity and viscosity. Various chemical substances are utilized for H_2S scavenging, such as iron or zinc oxides and carboxylates, amines, triazines, aldehydes, ethoxylated compounds, and oxidizing agents [7-10].

Naturally, there is a demand for the development of increasingly efficient H_2S scavenging products with minimal impact on the process, as well as for determining the H_2S scavenging capacity under conditions that closely resemble those of the application site, even simulating potential interferences. Souza [11] conducted a comprehensive survey of laboratory procedures referenced in the literature developed for this purpose, presenting varying degrees of sophistication, with advantages and disadvantages related to cost, ease of execution, H_2S detection limits, the possibility of using organic fluid or not, and safety limitations in the use of H_2S.

Field tests are also documented in the literature as a method of evaluating H_2S scavengers, providing important information about the performance of these products under real application conditions; however, the numerous variables involved often make it difficult to obtain conclusive and reproducible results. Additionally, the impact of new products on subsequent processes following the injection point complicates the execution of field tests, and the meticulous conduct of these tests directly interferes with the normal operational and production routine.

It is also noted that most technical publications are directed toward studies of H_2S scavengers intended for the treatment of gaseous hydrocarbons and aqueous fluids at temperatures that do not significantly exceed ambient conditions. In contrast, there are few references for studying the performance of H_2S scavengers in liquid organic mediums, typically focused on condensates of light petroleum compounds or organic fluids in well drilling operations, and generally at temperatures below 70°C. We understand that the lack of information on H_2S scavenging capacity at higher temperatures and/or in more complex organic fluids is often related to limitations in testing apparatus, available analytical instrumentation, and the risk of H_2S exposure, despite the importance of such information for the oil and gas industry [12].

This article aims to present a detailed methodology employed by Petrobras since 2007 to study and compare the performance of H_2S scavengers composed of different active ingredients in a predominantly organic medium, as well as to evaluate the behavior of these products when used at temperatures up to 130°C - conditions that resemble those encountered at the onset of production from new oil-producing wells on the Brazilian coast, where the water content is less than 1 %(v/v) [12]. This consolidates a laboratory testing methodology, still little disseminated, capable of classifying different H_2S scavenging products under temperatures exceeding 100°C and organic media.

The information obtained through this methodology enables informed decision-making on the most effective product for oil production scenario, optimizing efficiency and minimizing the volume of injected H_2S scavenger. The success of this treatment primarily implies a reduction in the risk of material failure due to H_2S exposure, compliance with legal and operational requirements, and minimal impact on the refining stages of the produced oil, both due to residual scavengers and reaction products that remain present in the oil.

2. Materials and Methods

2.1. H_2S Scavengers

Two commercial H_2S scavengers samples designed for oil and gas production were used, containing MEA-triazine (TRI-C) and ethoxylated compounds (ETO-C) as actives substances.

2.2. Crude Oils

The commercial H_2S scavengers were evaluated in four types of crude oils with distinct physicochemical characteristics, collected from Brazilian producing fields. The characteristics of these crude oils are presented in Table 1.

Table 1. *Physicochemical Characteristics of the Crude Oil Samples Used in the Performance Evaluation of H_2S Scavengers.*

Oils		O12 [1]	O19	O24	O28
Density °API		12,1	18,9	24,3	28
Density at 20°C / 4°C		0,9815	0,9372	0,9047	0,8835
Water content (%m/m)		0,32	0,97	0,0621	0,40
Total Sulfur (%m/m)		0,944	0,744	0,481	0,338
Kinematic Viscosity (mm^2/s)	20°C	1861 (at 50°C)	608,2	96,28	36,56
	30°C	810,1 (at 60°C)	293,0	57,97	24,09
	50°C	188,7 (at 82°C)	90,76	23,79	11,97
Dynamic Viscosity (mPa.s)	20°C	1793 (at 50°C)	570,3	87,05	32,3
	30°C	775,4 (at 60°C)	272,8	52,02	21,12
	50°C	178,0 (at 82°C)	83,37	21,03	10,33
Composition (%m/m)	Saturates	31,4	39,5	43,1	45,2
	Aromatics	27,2	32,5	22,8	21,8
	Resins	35,7	24,9	29,8	28,9
	Asphaltenes	5,7	3,1	4,3	4,1

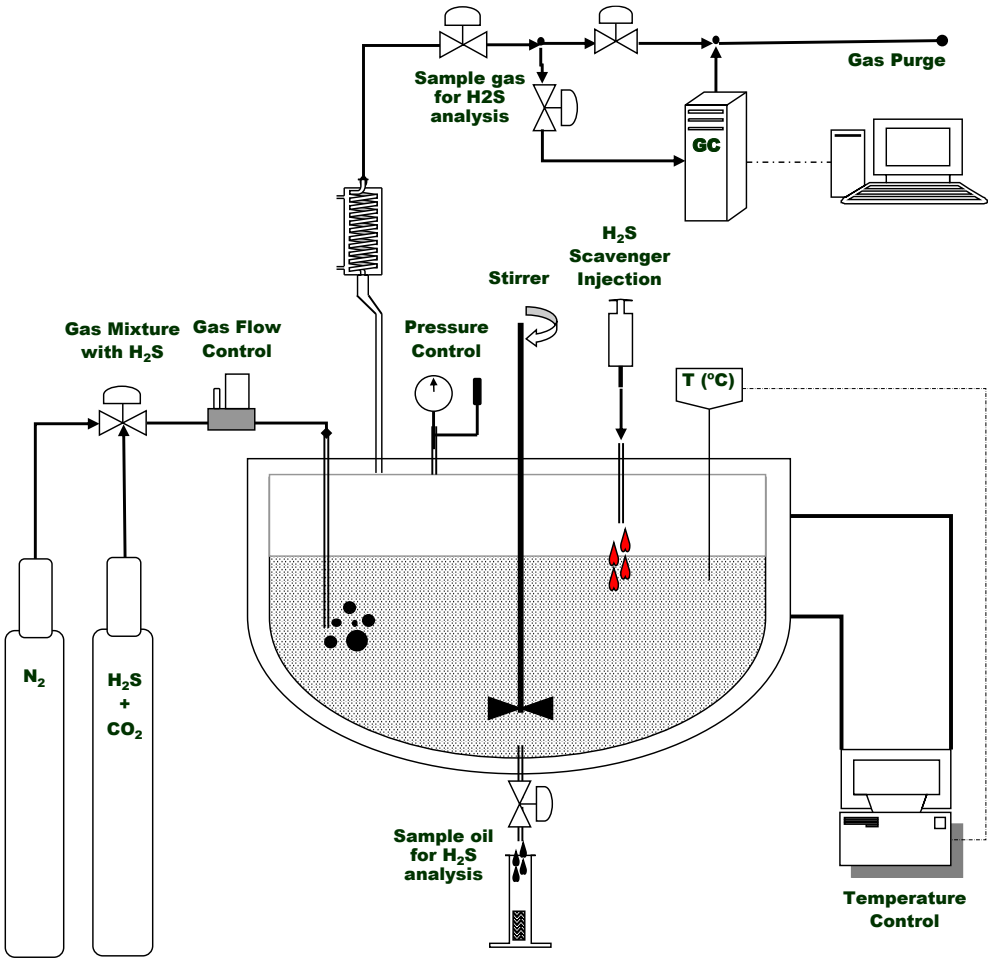


Figure 1. *Schematic Diagram of the Performance Evaluation Setup for H_2S Scavengers.*

2.3. Experimental Setup

The experimental setup used in the evaluations (Figure 1) consists of a 1-liter Hastelloy® C22 autoclave, equipped with mechanical stirring and instrumentation for monitoring and controlling the temperature, pressure, and gas flow within the reaction system.

In this experimental setup, a Micro-GC Varian® model CP-4900 gas chromatograph was used, equipped with a thermal conductivity detector (TCD) and a 10-meter Poraplot Q (PPQ) chromatographic column. Helium (99.999 %(v/v) purity) served as the carrier gas to monitor H_2S and CO_2 levels in the gas phase throughout the test, with analysis conducted every 2 minutes. Calibration was performed with a certified gas standard mixture containing 3.2 %(v/v) of H_2S and 96.8 %(v/v) of CO_2. To determine the dissolved H_2S content in the oil, an automatic potentiometric titrator Metrohm 785 DMP Titrino® was used, equipped with a silver-silver sulfide indicator electrode and an Ag/AgCl reference electrode. The analysis was conducted on 5 mL aliquots of oil collected from the reaction system throughout the test, placed in a container containing isopropanol, toluene, and ammonium hydroxide. A 0.01 N silver nitrate titrant solution was used to obtain the titration curve, and calibration was periodically performed with a standard sodium chloride solution as described in UOP 163 [13, 14].

2.4. Methodology for Performance Evaluation of H_2S Scavengers

Two methodologies were employed: the first monitored the concentration of H_2S present in the gas phase maintained at a constant flow (*Methodology A*), and the second monitored the concentration of H_2S in the oil phase with the closed testing apparatus, thus without gas flow, after saturation with the gas mixture (*Methodology B*). The objective of these tests is to differentiate commercial H_2S scavengers based on performance, identify the most effective commercial product, and evaluate the evolution of H_2S levels in both gas and oil phases throughout the tests following the injection of the scavenger.

Methodology A was initially developed as a prototype through a partnership between Petrobras and CCTechnologies-DNV (USA) and later refined and standardized at the Petrobras Research Center/CENPES [12, 15]. This methodology involves subjecting the fluid to be evaluated to a constant flow of 0.6 L/min of gas containing a known concentration of H_2S at the partial pressure and temperature of the product application point in the field. The concentration of H_2S in the gas phase is measured, along with ambient temperature and atmospheric pressure, throughout the test period after passing through the reaction system, using gas chromatography. Once the reaction medium is saturated with the gas mixture, a measured aliquot of the H_2S scavenger under evaluation is introduced.

Figure 2 illustrate the typical behavior of the H_2S concentration in the gas phase over time during each stage of the procedure: (1) Deaeration with N_2, (2) Saturation with H_2S, (3) H_2S Scavenging, and (4) Area equivalent to the mass of H_2S scavenged per volume of scavenger used (kg H_2S/L Scav). For the tests evaluating the H_2S scavenging capacity, N_2 with 99.999 %(v/v) purity was used during the deaeration step to remove the oxygen present in the reaction system at the beginning of the assay and at the end of the test to eliminate excess H_2S. Saturation of the reaction system was performed using a certified gas mixture containing 3.2 %(v/v) of H_2S and 96.8 %(v/v) of CO_2.

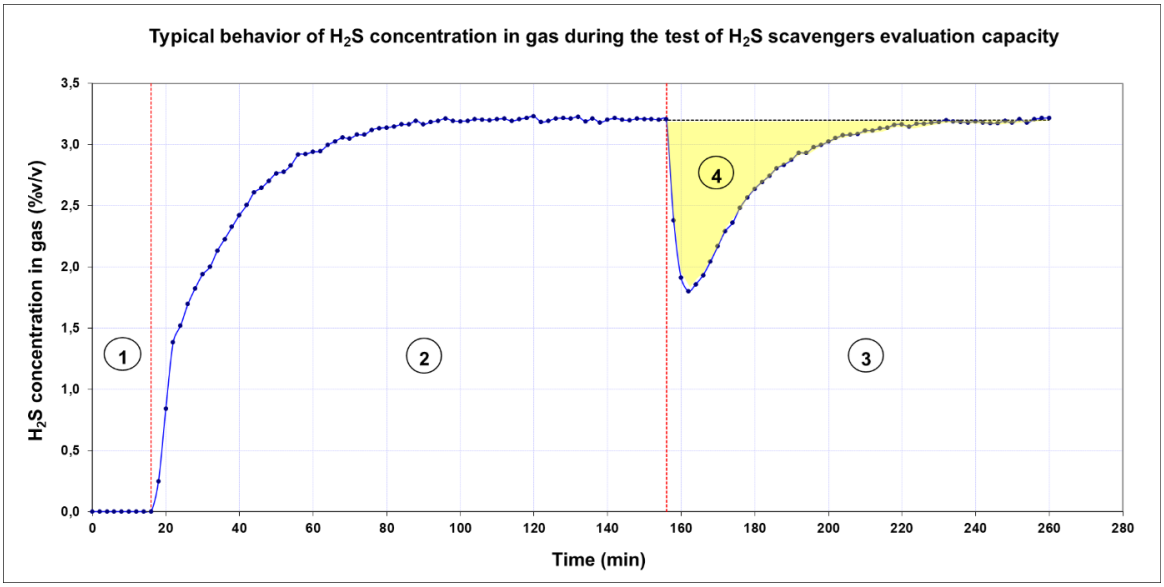


Figure 2. *Typical Profile of H_2S Concentration in the Gas Phase Over Time During the Testing Period, Determined by Gas Chromatography: ① Deaeration with N_2, ② Saturation with H_2S, ③ H_2S Scavenging, and ④ Mass of H_2S Scavenged per Volume of Scavenger Used (kg H_2S/L Scav).*

The mass of H_2S scavenged by the product added to the fluid is calculated from the area under the curve indicated by region④. Using conventional spreadsheet software, the area as a function of time for each tested product can be calculated through integration (Equation (1)).

$$Area = \int_0^{60} C_g^{H2S}.dt \Rightarrow Area = C_g^{H2S}.\Delta t \quad (1)$$

$$C_g^{H2S} = \frac{V_g^{H2S}}{V_g^{Total}} \times 100 \quad (2)$$

$$V_g^{Total} = Q_g^{Total}.\ \Delta t \quad (3)$$

From Equations (1), (2), and (3), the volume in liters of H_2S scavenged, Vg^{H2S} (Equation (4)), can be determined during the testing period, considering a controlled and constant gas mixture flow rate:

$$V_g^{H2S} = \frac{Area.Q_g^{Total}}{100} \quad (4)$$

Where,

C_g^{H2S}, is the concentration of H_2S in the gas mixture in contact with the liquid under test, in %(v/v);

Δt, is the contact period between the gas mixture and the liquid, in minute;

$Área$, is the integrated area under the curve obtained in the test after the injection of the H_2S scavenger, in% v.min;

V_g^{Total}, the volume of gas mixture in contact with the liquid during the testing period, in liter;

V_g^{H2S}, is the volume of H_2S in contact with the liquid during the testing period, in liter.

Q_g^{Total}, is the flow rate of the gas mixture used in the test, in L/min.

Considering the Ideal Gas Law, P.V = n.R.T, where n = m / MM, and with the information on the volume of H_2S, pressure, and temperature at the gas sampling point, the mass of H_2S scavenged can be determined, in grams:

$$m^{H2S} = \frac{P.V_G^{H2S}.MM^{H2S}}{R.T} \quad (5)$$

Where,

m^{H2S}, is the mass of H_2S scavenged, in gram;

P, is the pressure at the gas sampling point, in kPa;

V_g^{H2S}, is the volume of H_2S in contact with the liquid during the testing period, in liter;

MM^{H2S}, is the molar mass of H_2S, 34.081 g/mol;

R, is the universal gas Constant, 8.314462 (L.kPa)/(K.mol);

T, is the temperature, in K.

Substituting (4) into (5), we have:

$$m^{H2S}\ (g) = \frac{P.Q_g^{Total}.MM^{H2S}}{R.T.100}.Area \quad (6)$$

Thus, for P = 100 kPa, Q_G^{Total} = 0,6 L/min, T = 298,15 K e C_g^{H2S} = 3,2 %v/v, the total mass of H_2S that passes through the experimental system saturated without H_2S scavengers over 1 hour corresponds to 1.584 g, given that the Area = 192 %v.min.

The ratio of the mass of H_2S scavenged per volume of scavenger used in the test, that is, kg of H_2S per L of Scavenger, represents the H_2S *Scavenging Capacity (SC)* and allows for a relative ranking among the evaluated products under the same experimental conditions. Optionally, the performance results can also be presented as the inverse of this relationship, that is, the volume of scavenger needed to reduce 1 kg of H_2S (L of Scavenger / kg of H_2S). Thus, SC_v can be calculated by:

$$SC\ \left(\frac{L}{kg}\right) = \frac{V^{Seq}}{m^{H2S}} = \frac{\text{Volume of H2S scavenger } (Liter)}{\text{Mass of H2S scavenged } (kg)} \quad (7)$$

This methodology can be applied to evaluate single-phase or multiphase systems (gas, oil, and water) under constant mechanical agitation and varying experimental conditions of BSW, RGO, and/or RGL. It also allows for the monitoring and control of temperature, pressure, H_2S concentration, and scavenger concentration. Additionally, in purely aqueous media, the behavior of pH can be monitored throughout the test using a pH electrode resistant to the temperature, pressure, and presence of H_2S conditions employed.

Methodology B involves monitoring the H_2S content in the liquid phase using potentiometric titration. The reaction system is first saturated with a gas mixture containing H_2S until the H_2S content in the oil remains constant. Once saturation is achieved, the gas flow is stopped, and the system is maintained closed for 30 minutes under constant agitation. At this point, a known dosage of H_2S scavenger is injected, and oil aliquots are collected after 1, 10, 20, 30, and 40 minutes. The samples are collected from the bottom of the reaction vessel, passing through a small coiled tube jacketed at a temperature of 15°C directly into containers containing isopropanol, toluene, and ammonium hydroxide as titration solvent, and are immediately taken to the automatic potentiometric titrator for determination of H_2S concentration in the oil. The sample volume taken at each collection was minimized to approximately 5 mL, so as not to significantly impact the total pressure of the system with each collection, which could interfere with the equilibrium of H_2S between the gas phase and the liquid phase (oil). The pressure variation observed in each collection was only 3.4 kPa. The titration curves obtained were evaluated as described in UOP Method 163 [13]. Figure 3 presents a typical result obtained by this methodology using a gas mixture containing 3.2 %(v/v) of H_2S in CO_2, at atmospheric pressure and ambient temperature, showing the measured H_2S content in oil for aliquots collected during the saturation stage and after the injection of an H_2S scavenger.

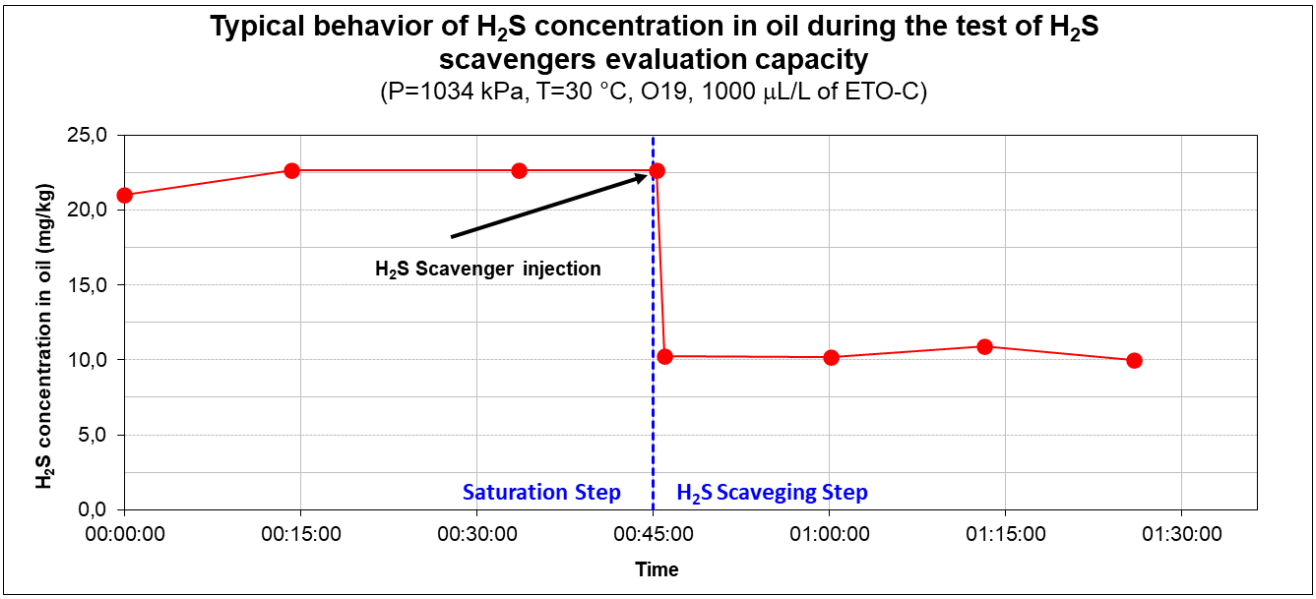


Figure 3. *A typical profile of H_2S concentration in oil determined by potentiometric titration throughout a test, saturated with a gas mixture containing 3.2 %(v/v) H_2S and added 500 µL/L [(2)] of product.*

By analyzing the variation in H_2S concentration before and after the injection of the product, this methodology can also be used to compare different H_2S scavengers under the identical experimental conditions and determine which one achieves the highest rate of reduction of H_2S content in the liquid phase.

2.5. Experimental Conditions

The experimental conditions for the H_2S scavenging capacity evaluation test are described below and aim to approximate the scenario of wells producing oil with low water content and temperatures close to 130°C, as follows:

Total Pressure: 1034 kPa
Partial Pressure of H_2S: 33.1 kPa
Temperature: 130°C
Type of Oil: Described in Table 1
Water Cut: < 1 %(v/v) (original sample content)
Gas Flow Rate: 0.6 L/min
H_2S Content in Injected Gas: 3.2 %(v/v) (balance in CO_2)
Scavenger Dosage: 500 µL/L and 1000 µL/L
Commercial Scavengers: TRI-C and ETO-C

3. Results and Discussion

The results presented below are part of a broader set of experiments conducted and reported by the author of this work during the attainment of the Master of Science degree [12].

3.1. Chemical Characteristics of the H_2S Scavengers Evaluated

The H_2S scavengers evaluated, TRI-C and ETO-C, were characterized based on the type and content of active components using Nuclear Magnetic Resonance (NMR ^{13}C), gas chromatography coupled with mass spectrometry (GC/MS), and atomic absorption spectrometry (AAS). The water content was determined using the Karl Fischer coulometric method. The results are presented in Table 3 and indicate that the commercial sample TRI-C contains approximately 57 %(m/m) of 1,3,5-tri-(2-hydroxyethyl)-hexahydro-triazine (CAS 4719-04-4) and 43 %(m/m) of water. For the ETO-C sample, the analyses indicate that the active material consists of glycols, such as 2-(hydroxymethoxy)ethoxymethanol or (ethylene glycol)dimethanol (CAS 3586-55-8) and a homologous series of polyglycols with the addition of monoethylene glycol (MEG) units. The total glycol content in ETO-C was estimated at 92 %(m/m) with a water content of 7.2 %(m/m) (Table 3).

The samples were characterized to confirm the expected structure and concentration of the active material and the solvent present. Deuterated dimethyl sulfoxide (DMSO-d6) was used for NMR to lock the magnetic field and as a chemical shift reference.

Table 2. *Molecular structure of the major active materials in the evaluated samples.*

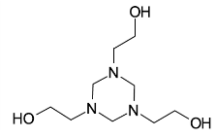
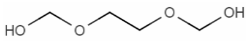
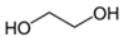
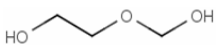
H_2S Scavengers	Structural formula of the active material	Name	N° CAS
TRI-C		1,3,5-tri-(2-hydroxyethyl)-hexahydro-triazine	4719-04-4
ETO-C		2-(hydroxymethoxy)ethoxymethanol	3586-55-8
		1,2-ethanediol (MEG)	107-21-1
		2-(Hydroxymethoxy)ethanol and others homologous compounds	13149-79-6

Table 3. *Characteristics of the evaluated commercial H_2S scavengers.*

H_2S Scavengers	Active material content	Water content
TRI-C	57 %(m/m)	43 %(m/m)
ETO-C	92 %(m/m)	7,2 %(m/m)

3.2. Variability of the Performance Evaluation Method

The repeatability of the H_2S scavenging capacity evaluation methodology for commercial products was assessed to determine the degree of agreement between the results of tests conducted under the same experimental conditions (item 2.5). The products TRI-C and ETO-C were evaluated at 1034 kPa, 130°C, using oil with °API 19 and a scavenger dosage of 1000 µL/L. The obtained curves are presented in Figure 4 and indicate good agreement among themselves for each tested product. The scavenging capacity, in L/kg, for each of the tests and the statistical parameters, including mean (µ), standard deviation (σ), and relative standard deviation (RSD), are presented in Table 4. The RSD was less than 10% for both tested products, confirming good agreement between the results. Additionally, it is observed that there is no overlap of the Confidence Intervals obtained for the tested products, indicating that the means are statistically different, and that the methodology can differentiate these chemical products with 95% confidence. The same results can be presented as the mass of H_2S consumed per unit volume of scavenger added, kg of H_2S / L of Scavenger, by calculating the inverse of the values presented in Table 4.

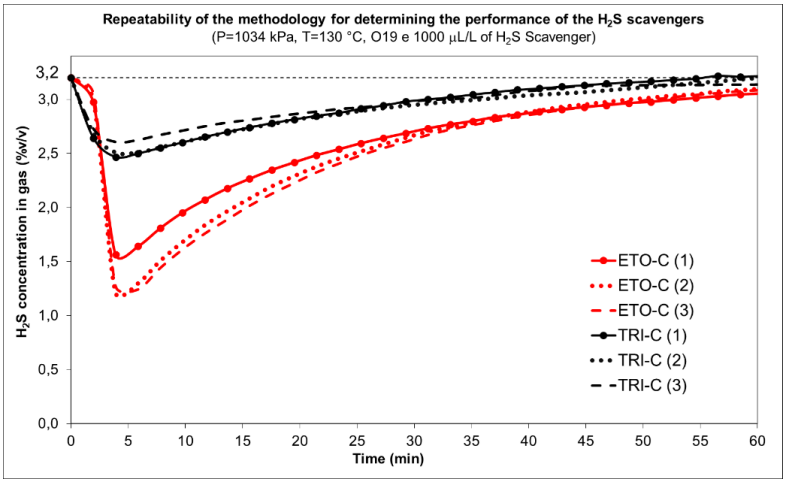


Figure 4. *Repeatability of the performance evaluation methodology for H_2S scavengers with monitoring of the gas phase.*

Table 4. *Results of the variability in the performance evaluation methodology for H_2S scavengers.*

H2S Scavenger	SC_v (L Scav/kg H_2S)	SC_v Average [3] (L Scav/kg H_2S)	Standard Deviation (s) (L Scav/kg H_2S)	RSD (%)	Confidence Interval (95 % confidence)
	5,62				
TRI-C	5,09	5,56	0,433	7,78	= 5,56 ± 1,07 (L Scav / kg H_2S)
	5,95				
	2,13				
ETO-C	2,50	2,29	0,194	8,49	= 2,29 ± 0,48 (L Scav / kg H_2S)
	2,23				

3.3. Performance of Commercial H_2S Scavengers with Different Active Materials

Monitoring of H_2S Concentration in the Gas Phase

The commercial H_2S scavenger samples, TRI-C and ETO-C, were evaluated in terms of their H_2S scavenging capacity using Methodology A. Figure 5 presents the monitoring of H_2S levels in the gas phase following the injection of each tested product at two different concentrations, 1000 µL/L and 500 µL/L, with the dosage calculated relative to the volume of liquid to be treated. It is observed that the methodology for monitoring H_2S levels in the gas phase allowed for the differentiation of performance between the H_2S scavenging products at both concentrations.

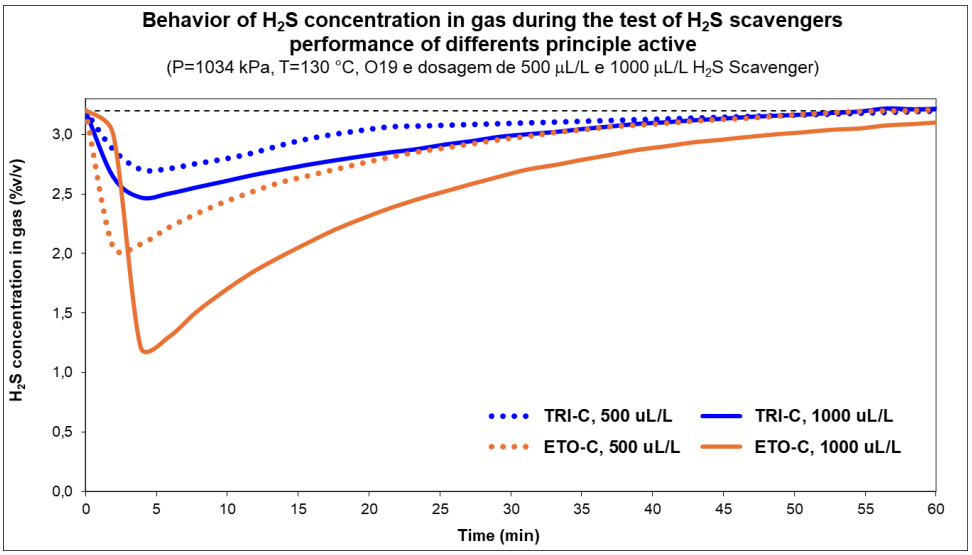


Figure 5. *Monitoring of H_2S Levels in the Gas Phase After Injection of 500 µL/L and 1000 µL/L of H_2S Scavengers with Different Active Materials.*

Table 5 shows the mass of H_2S consumed by each tested product, calculated from the previous curves at the two mentioned concentrations. This figure also displays the percentage reduction of H_2S relative to the original mass of H_2S (1.584 g) that passed through the reaction system during the testing period for each product at the two dosages used.

Table 5. *Performance of Scavengers with Different Active Materials at Two Different Concentrations (1000 µL/L and 500 µL/L) at P = 1034 kPa, T = 130°C, and Oil °API 19.*

H_2S Scavenger	Dosage (µL/L)	Mass of H_2S scavenged (mg)	Percentage of H_2S scavenged (%m/m)	SC_v (V Scav / m H_2S gas) (L/kg)	SC (m H_2S gas / V Scav) (kg/L)
ETO-C	500	0,1840	10,6	2,17	0,460

H_2S Scavenger	Dosage (µL/L)	Mass of H_2S scavenged (mg)	Percentage of H_2S scavenged (%m/m)	SC_v (V Scav / m H_2S gas) (L/kg)	SC (m H_2S gas / V Scav) (kg/L)
TRI-C	500	0,0842	4,8	4,75	0,211
ETO-C	1000	0,3594	20,6	2,23	0,449
TRI-C	1000	0,1423	8,2	5,62	0,178

The ETO-C-based product proved to be more efficient than TRI-C at both dosages, as it exhibited a greater reduction in H_2S levels in the gas phase relative to the initial concentration and, therefore, a higher mass of H_2S scavenged over time. It is worth noting that TRI-C contains 57 %(m/m) of MEA-triazine and 43 %(m/m) of water, while ETO-C comprises 92 %(m/m) of ethoxylated compounds and 7.21 %(m/m) of water (Table 3).

These results further demonstrate that the mass of H_2S scavenged is directly proportional to the amount of product dosed, as the amount of H_2S consumed at the 500 µL/L dosage was nearly half of that found when dosing 1000 µL/L of each product. Thus, based on the curves obtained for each product, a scale of H_2S scavenging capacity can be established under the tested conditions, measured in mass of H_2S consumed per volume of H_2S scavenger used, that is, kg of H_2S scavenged / L of scavenger.

It can be observed that the performance of the scavengers (kg H_2S / L Scav) was the same, regardless of the product concentration used, whether 500 or 1000 µL/L, as the scavenging capacities showed virtually no variation with changes in dosage.

Monitoring of H_2S concentration in the oil phase

A second set of tests was conducted following Methodology B, as described in section 2.4, wherein, after saturating the oil with the gas mixture containing 3.2 %(m/m) of H_2S, the system was closed, and the gas flow was interrupted. After an equilibrium period of 30 minutes, small volumes of oil samples were withdrawn from the system and analyzed. The average dissolved H_2S content in the oil with °API 19, before the addition of the H_2S scavengers, was 225.5 ± 6.8 mg/kg of H_2S, which corresponds to a mass of 0.1674 g of H_2S in the volume of oil used.

After saturation, to assess the effect of the scavenger on the reduction of dissolved H_2S content in the oil, 1000 µL/L of each of the previously tested products was injected. The H_2S content in the oil was monitored for approximately 40 minutes, and the reduction in its content following the injection of each product is shown in Figure 6.

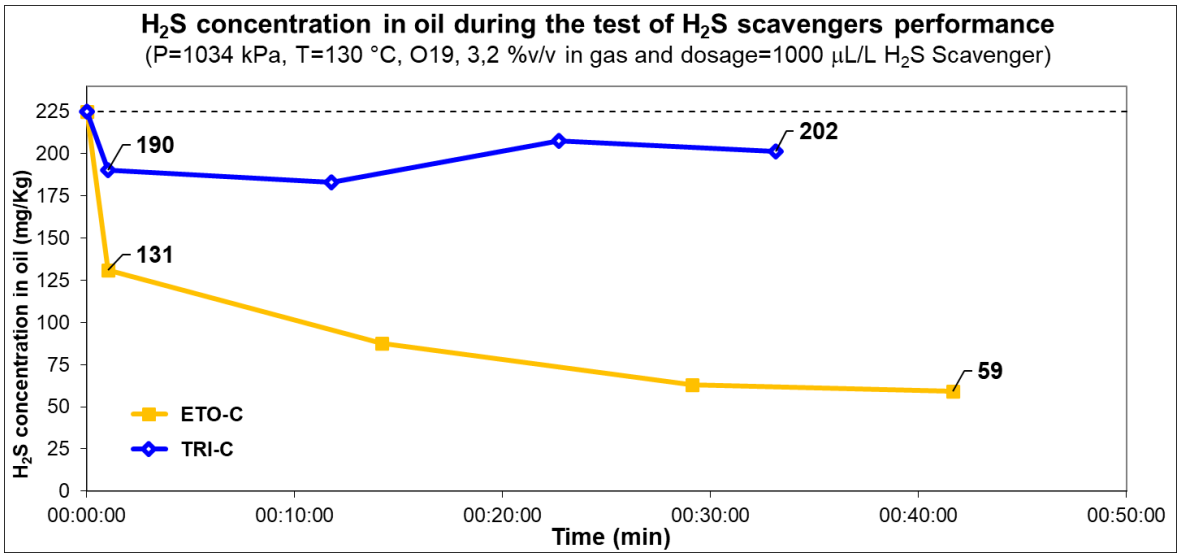


Figure 6. *Behavior of H_2S Levels in Oil After Addition of the Evaluated H_2S Scavengers.*

It was observed that the ethoxylated product reduced the dissolved H_2S content in the oil to lower levels than TRI-C and did so at significantly faster rate. Figure 6 highlights the residual H_2S levels in the oil at 1 minute and 40 minutes after the injection of each commercial H_2S scavenger, providing insight into the reaction rate and scavenging capacity of each product., After40 minutes, all of the injected product had reacted with the H_2S. Table 6 presents the mass of H_2S con-

sumed and the equivalent percentage fraction relative to the original H_2S content, consolidating the performance results obtained from monitoring H_2S in the oil for each scavenger tested. The distribution was the same as observed in the gas phase monitoring. Therefore, both methodologies are suitable in evaluating and distinguishing the performance of H_2S scavengers.

Performance: Ethoxylated > Triazine

Table 6. *Measured Parameters After Addition of the Tested H_2S Scavengers in Oil °API 19 at a Dosage of 1000 µL/L.*

Commercial Scavenger	Time (min)	Concentration of H_2S in Oil (mg/kg)	Mass of H_2S in Oil (mg)	Percentage of H_2S Consumed (%m/m)	Vol Scav / m H_2S oil (L/kg)	m H_2S oil / Vol Scav (kg/L)
ETO-C	1	131	70	42	-	-
ETO-C	40	59	123	74	6,49	0,154
TRI-C	1	190	26	15	-	-
TRI-C	40	202	17	10	45,77	0,022

3.4. Performance of H_2S Scavengers in Distinct Types of Crude Oils

Given that the ethoxylated product demonstrated the best performance among the tested products, an investigation was conducted to assess whether the type of oil treated with this product affects its performance. Four types of oil, described in Table 7, with different viscosity and density characteristics, were saturated with a gas mixture containing 3.2 %(m/m) of H_2S and treated with 1000 µL/L of the ethoxylated scavenger. The evaluation followed the same methodology as the previous section, monitoring the levels of H_2S in the gas phase and dissolved in the oil.

Monitoring of H_2S Concentration in the Gas Phase

The results indicate that the type of oil used as the test fluid has little influence on the behavior of H_2S levels in the gas phase after the addition of the ethoxylated product ETO-C (Figure 7). The results for H_2S scavenging capacity and the mass of H_2S consumed obtained in this set of tests are presented in Table 7 and indicate that the performance of the ethoxylated product was practically the same across crude oils with different densities: °API 28, °API 24, °API 19, and °API 12. It is worth noting that the higher the °API, the less dense the oil. The percentage fraction of H_2S consumed, relative to the original amount of H_2S present in the gas, remained around 20 %(m/m) in the tested oils. In the oil with °API 24, a slight increase in the mass of H_2S consumed was observed, which may be attributed to the inherent variability of the methodology.

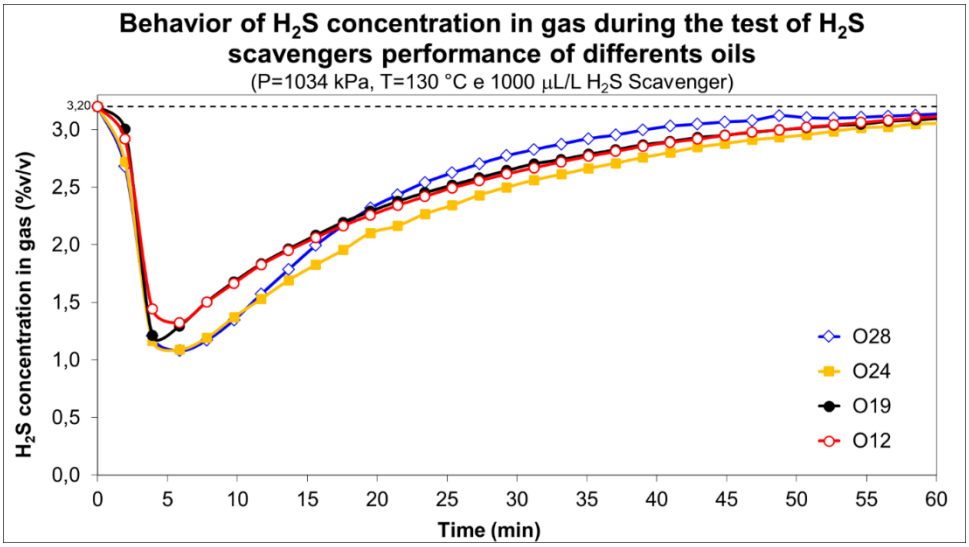


Figure 7. *Monitoring of H_2S Levels in the Gas Phase After Injection of 1000 µL/L of ETO-C in different crude oils.*

Table 7. Performance of 1000 µL/L of ETO-C in different types of oil.

Oil		Mass of H_2S Consumed (mg)	Percentage H_2S consumed (%m/m)	SC_v (Vol Scav / m H_2S gas) (L/kg)	SC (m H_2S gas/V Scav) (kg/L)
(+) Density	O12	0,3623	20,78	2,21	0,4528
	O19	0,3594	20,62	2,23	0,4492
	O24	0,4390	25,18	1,82	0,5487
(-) Density	O28	0,3535	20,28	2,26	0,4418

Monitoring of H_2S concentration in the oil phase

Using Methodology B, the dissolved H_2S content in each oil was measured immediately after saturation with the gas mixture containing 3.2 %(v/v) H_2S, prior to the injection of ETO-C (Table 8). The water content present in these samples is less than 1.0 %(m/m), and the other physicochemical characteristics are presented in the Table 3.

Table 8. Dissolved H_2S Content in Each Tested Oil After Saturation, Before Injection of ETO-C.

Oil	°API	Dynamic Viscosity at 50°C (mPa.s)	Mass of H_2S in oil after saturation (mg)	Concentration of H_2S in oil after saturation (mg/kg)
O12	12	1793,0	161,45	217
O19	19	83,37	167,40	225
O24	24	21,03	183,77	247
O28	28	10,33	198,65	267

Although a slight reduction in the amount of dissolved H_2S in the oil is observed as the oil density increases, it is clear that the dissolved H_2S content is not significantly influenced by the physical characteristics of each oil. This behavior might be influenced by other factors, such as, the distribution of polar and non-polar compounds within each one; however, the study of this correlation is beyond the scope of this work.

After determining the initial saturated H_2S content in the oil, 1000 µL/L of the ethoxylated scavenger, ETO-C, was injected. The evolution of H_2S levels in each oil was then monitored over a period of approximately 40 minutes, as illustrated in Figure 8.

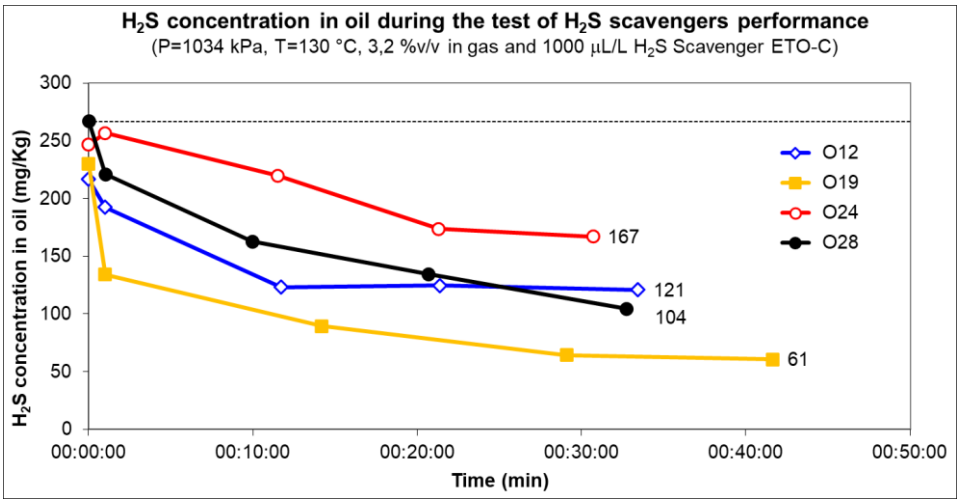


Figure 8. Behavior of H_2S Levels After the Addition of ETO-C in Different Crude Oils.

As the initial H_2S levels in each oil were found to be similar but different from one another, the mass of H_2S consumed was determined to compare the performance of ETO-C in the different tested oils, along with the respective percentage fraction relative to the original content of each oil, after 1 minute and 40 minutes following the injection of the ethoxylated scavenger (Table 9).

Table 9. *H_2S consumed and H_2S Scavenging Capacity (SC) after addition of 1000 µL/L of ETO-C Product at P = 1034 kPa and T = 130°C.*

Oil	Mass of H_2S Consumed ($m° - m_t$) (mg)		H_2S Consumed in Oil (%m/m)	Scavenging Capacity	
	t = 1 min	t = 40 min	t = 40 min	SC_v (L Scav / kg H_2S)	SC (kg H_2S / L Scav)
O12	18,1	71,41	44,2	11,20	0,089
O19	69,9	123,3	73,7	6,35	0,158
O24	0,0	59,32	32,3	13,49	0,074
O28	34,2	121,03	60,9	6,61	0,151

In oils O19 and O28, a greater consumption of H_2S by the ethoxylated product was observed, while in oils O12 and O24, the reduction of H_2S was less pronounced, reflecting a similar trend in performance. These results suggest that there is no direct relationship between the performance of ETO-C and the viscosity and/or density of the oil being treated. Among the other parameters analyzed in these oils, previously presented in Table 1, only the water content follows the trend observed with the performance of the ethoxylated product in the tested oils. However, given the low water levels in these oils (<1 %(m/m)), a more detailed evaluation is needed to confirm this correlation. This evaluation is recommended for future work.

Unlike the results observed in the gas phase monitoring tests (Methodology A), discussed in the previous section, where the performance of the ethoxylated product was unaffected by the type of oil, the monitoring of H_2S content in the liquid phase (Methodology B) revealed performance variations across the different oils. This indicates that the performance of the scavenger is sensitive to the type of oil to which it is applied. From this perspective, the type of oil appears to influence the scavenger's performance.

However, it is important to consider the procedural differences between the two methodologies. In Methodology A, the flow of H_2S is continuous throughout the entire test, maintaining a constant partitioning and amount of H_2S available for dissolution in the oil and, consequently, for reaction with the ethoxylated product. This makes performance independent of the type of oil and primarily dependent on the mass transfer rate between the gas and the oil. Conversely, in Methodology B (item 2.4), the gas flow is stopped after saturation, and the dissolved H_2S in the oil depends on the partitioning between the gas and liquid phases. As previously mentioned, this partitioning is influenced by the type of oil, which likely explains the observed performance variations in the liquid phase.

3.5. Relationship Between Performance and Dosage of H_2S Scavenger

Given that the ethoxylated scavenger, ETO-C, exhibited the best performance, an additional study was conducted using a broader dosage range of 250 µL/L, 500 µL/L, 1000 µL/L, and 2000 µL/L in oil O19. This series of tests was conducted by monitoring H_2S exclusively in the gas phase, with the result behavior of H_2S levels presented in Figure 9.

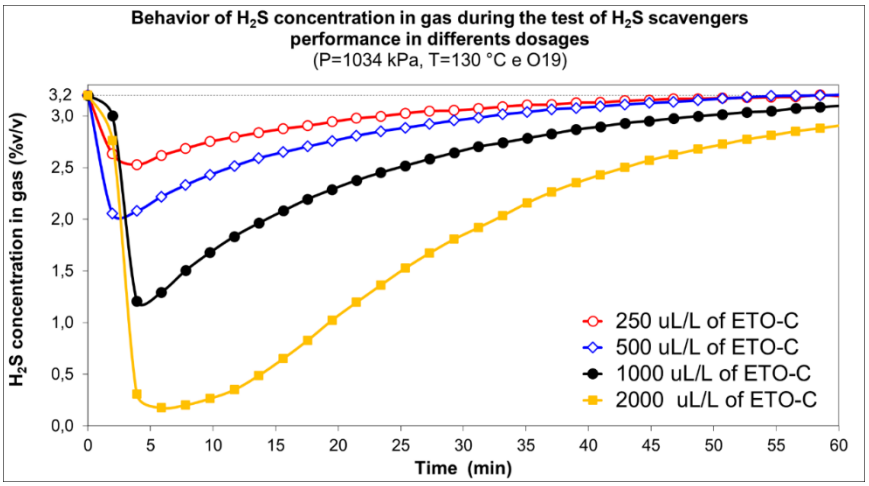


Figure 9. *Monitoring of H_2S Levels in the Gas Phase After Addition of ETO-C at Different Dosages.*

Calculating the H_2S scavenging capacity of ETO-C for each dosage, it is observed that it remains practically constant between the dosages of 250 µL/L and 2000 µL/L, as presented in Table 10. The results for the mass of H_2S consumed and the corresponding percentage for each dosage are also shown.

Table 10. *Relationship Between ETO-C Dosage and H_2S Consumed.*

Dosage of ETO-C (µL/L)	Mass of H_2S Consumed (g)	H_2S Consumed (%m/m)	SC_v (L/kg)	SC (kg/L)
250	0,1070	6,14	1,87	0,5351
500	0,1839	10,55	2,17	0,4598
1000	0,3594	20,62	2,23	0,4492
2000	0,7713	44,25	2,07	0,4821

As shown in Figure 10, the mass of H_2S consumed, and consequently the percentage fraction consumed, is directly proportional to the dosage of the ETO-C product used, which is an H_2S scavenger based on ethoxylated compounds, considering the range of dosages studied. The regression using the least squares method allows for the determination of a line whose slope is related to the H_2S scavenging capacity of the product used.

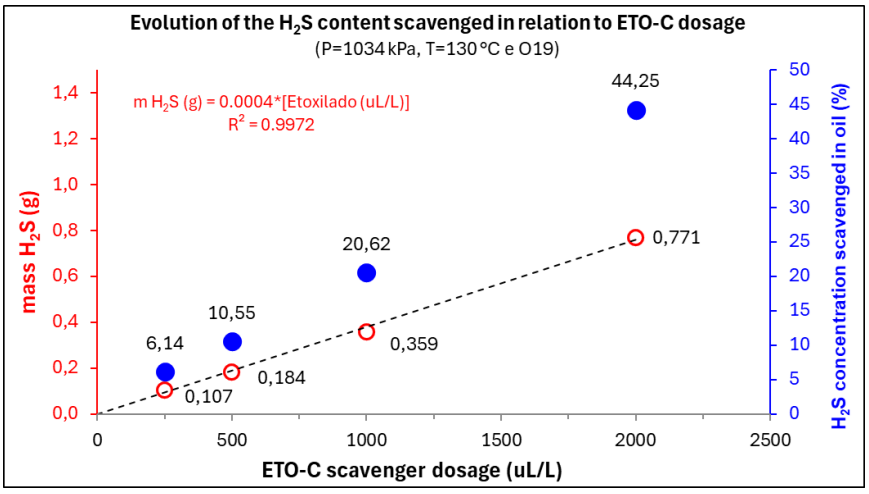


Figure 10. *Relationship Between the Dosage of Ethoxylated Scavenger Used and the Amount of H_2S Consumed.*

With these data, a relationship can be established between the mass or concentration of H_2S scavenged, monitored in the gas phase, and the dosage of the scavenger used in the oil:

$$m\ H_2S\ (g) = A \times ETO\text{-}C\ dosage\ (\mu L/L).$$

This relationship provides predictability between the dosage of the ethoxylated scavenger and the mass of H_2S consumed in laboratory tests conducted under the same experimental conditions. Based on the results, it is expected that a similar relationship will hold in fields application. By adapting to common parameters used for monitoring producing wells in the field, the following considerations can be made:

$$m_{H_2S}(kg/h) = \frac{C_{H_2S}(\mu L/L) \times Q_{GAS}(m^3/h) \times d_{H_2S}(mg/mL)}{10^6}$$

E,

$$SC\left(kg_{H_2S}/L_{SCAV}\right) = \frac{m_{H_2S}(kg/h)}{Q_{SCAV}(L/h)}$$

It follows that:

$$C_{H_2S}(\mu L/L) = \left(\frac{SC(kg/L) \times 10^6}{Q_{GAS}(m^3/h) \times d_{H_2S}(mg/mL)}\right) \times Q_{SCAV}(L/h)$$

Where,

C_{H2S} (µL / L), the concentration of H_2S consumed in the produced gas.

SC (kg_{H2S} / L_{SCAV}) H_2S Scavenger Capacity

Q_{gas} (m^3/ h), gas production flow rate

d_{H2S} (mg / mL), density of H_2S = 1,4167 mg/mL

Q_{SCAV} (L / h), scavenger flow rate

Naturally, this relationship must be validated through field tests to be effectively applied in optimizing the dosage of the ethoxylated scavenger. H_2S scavengers made from other active materials, such as triazine and glyoxal, may not follow the same relationship due to the distinct reaction mechanisms inherent to each and would require specific evaluations.

Beyond the technical aspect, the economic considerations play a critical role in industrial decisions regarding the use of chemical products. The price of a chemical product supplied to industry is subject to several factors, some of which are intangible, such as regulations, market opportunities, and economic conditions. Additionally, tangible factors like the availability of raw materials, logistics, and supply chain dynamics directly impact the final cost of the product at any given time. While calculating the cost-benefit ratio based on the H_2S scavenging capacity (SC) and the price of the H_2S scavenger ($) is beyond the scope of this study, it is likely the most effective approach to ensure the success of H_2S treatment in oil and gas production scenarios.

4. Conclusions

The methodologies presented, both with monitoring of H_2S levels in the gas phase (Methodology A) and in the oil phase (Methodology B), enabled the evaluation, comparison, and differentiation of the H_2S scavenging capacity of various commercial H_2S scavengers used in the oil industry. This approach enables their classification in terms of efficiency.

The methodology consolidates, in a single test, conditions that closely resemble field application, which have been relatively uncommon in laboratory settings. In this study, 100 %(v/v) crude oil was used; however, the methodology and apparatus are versatile enough to evaluate mixtures of water and oil in proportions ranging from 0 to 100 %(v/v), aqueous solutions with salinity up to 200 g/L in NaCl, temperatures between 30°C and 250°C, and pressures ranging from atmospheric pressure up to 1034 kPa.

Additionally, the proposed methodology provides not only the H_2S scavenging capacity per volume of scavenger used (kg H_2S scavenged/L product) but also insights into the reaction time and rate required to minimize H_2S content in both gas and liquid phases. This information can guide the optimization of treatment protocols for oil platforms (onshore and offshore), subsea and topside operations, as well as terminals, tanks, and pipelines.

Among the commercial H_2S scavengers evaluated in this study, the product based on ethoxylated compounds (ETO-C) demonstrated superior compared to the MEA-triazine-based product (TRI-C) under identical experimental conditions.

The study also showed that, using this methodology, the mass of H_2S scavenged is proportional to the amount of product dosed. For the ethoxylated product, a linear relationship was observed between 250 µL/L and 2000 µL/L of the dosed product.

In this set of tests, the type of crude oil used as the reaction medium did not significantly affect the scavenging capacity of the commercial product ETO-C when monitoring H_2S levels in the gas phase. This behavior may also be influenced by other characteristics of the crude oil, such as the distribution of polar and non-polar compounds in each type; however, exploring this correlation lies beyond the scope of this work.

Abbreviations

AAS	Atomic Absorption Spectrometry
BSW	Basic Sediment and Water
CAS	Chemical Abstracts Service Registry Number
DMSO	Deuterated Dimethyl Sulfoxide
GC/MS	Gas Chromatography coupled with Mass Spectrometry
MEA	Monoethanolamine
MEG	Monoethylene Glycol

NMR	Nuclear Magnetic Resonance
PPQ	Poraplot Q chromatographic column
RGL	*Gas/Liquid Ratio*
RGO	Gas/Oil Ratio
RSD	Relative Standard Deviation
Scav	Scavenger
SC	Scavenging Capacity
TCD	Thermal Conductivity Detector

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Author Contributions

Andre Luiz Castro Bonfim: Conceptualization, Formal Analysis, Investigation, Methodology, Resources, Writing – original draft

Alvaro Augusto Oliveira Magalhaes: Writing – review & editing

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Data Availability Statement

The data supporting the outcome of this research work has been reported in this manuscript.

Conflicts of Interest

The authors declare no conflicts of interest.

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Biography

Andre Luiz Castro Bonfim graduated in Industrial Chemistry and holds a Master's degree in Materials Engineering and Corrosion from the Federal University of Rio de Janeiro. He has experience in the petrochemical industry, where he was involved in quality control activities for basic petrochemical inputs and fuels, as well as R&D activities aimed at optimizing petrochemical processes. Currently, he is a researcher at the Petrobras Research Center – CENPES, specializing in corrosion within the oil and gas industry, with a focus on R&D of chemicals for corrosion mitigation and failure analysis. Furthermore, he coordinates projects related to H_2S scavengers, corrosion inhibitors, and the corrosivity of biofuels, oil, and derivates.

Research Field

Andre Luiz Castro Bonfim: Corrosion in the Oil and Gas Industry and Chemical Mitigation Strategies

Alvaro Augusto Oliveira Magalhães: Corrosion Control and Monitoring in Oil and Gas Industry

[1] Due to the high viscosity of oil O12, the viscosity parameter was measured at temperatures different from those of the other oils listed in Table 2.

[2] μL/L corresponds to ppm_v, parts per million by volume.

[3] Test Condition: P = 1034 kPa; T = 130°C; Oil °API 19; 1000 μL/L of H_2S Scavenger.