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Research Article

Performance of Different H_2S Scavengers in Crude Oil

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Abstract

The presence of H_2S in petroleum compromises the integrity of industrial equipment, affects the quality of by-products, and poses environmental and occupational challenges that increase costs and operational risks. A common solution to mitigate this contaminant is the continuous injection of liquid H_2S scavengers into the production stream. Most technical publications focus on H_2S scavengers for gaseous hydrocarbons and aqueous fluids at temperatures below 70°C, but there are few references regarding scavenger performance in liquid organic media at temperatures above 70°C. This article presents the results of a comparative study on the H_2S scavenging capacity of various concentrated active compounds and commercial products used in the petroleum industry. The methodology involves subjecting oils with different densities to a constant flow of gas with a known H_2S concentration at 33.1 kPa and 130°C. The H_2S concentration is measured in the gas phase using gas chromatography and in the liquid phase by potentiometric titration throughout the test period, after passing through the reaction system and before and after the introduction of a known aliquot of the H_2S scavenger. The methodologies employed allow for the evaluation and comparison of the H_2S scavenging capacity of the products analyzed. This enables classification according to efficiency, using tests that simulate conditions closer to field applications, with a predominantly organic environment, similar to new oil wells where the water content is less than 1 %(v/v). Among the commercial H_2S scavengers evaluated, the product based on ethoxylated compounds showed the best performance, while MEA-triazine and glyoxal-based scavengers exhibited lower performance, with glyoxal being slightly more effective than MEA-triazine. The zinc carboxylate-based scavenger demonstrated the lowest performance among the products tested. The study also showed that the mass of H_2S reacted is proportional to the product dosage, within the tested range of 500 mL/L to 1000 mL/L for all products. The information generated enables informed decisions regarding the best product for oil production, aiming for greater efficiency and a lower volume of injected scavenger. This approach supports operational safety, regulatory compliance, and minimal impact on oil refining stages due to residual scavengers and reaction products present in the produced oil.

Keywords

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

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1. Introduction

Oil exploration and production in Brazil have been advancing toward increasingly deeper reservoirs and greater water depths, creating significant technological challenges related to material selection and corrosion control. The presence of CO_2 and H_2S as contaminants in the produced fluids makes this scenario even more critical [1, 2]. Additionally, the produced water, which has a high potential for scaling and $CaCO_3$ deposition, represents 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 creates environmental and occupational issues [5, 6] that affect the entire production chain. One strategy to reduce the H_2S content in these fluids is the injection of liquid H_2S scavengers into the wells, which react with species in the H_2S equilibrium equation, converting them to less reactive forms. For H_2S scavengers used in oil and gas production, a high scavenging capacity and reaction speed are essential. The H_2S capture reaction should be irreversible and should not stabilize emulsions, form foam, gels, and precipitates. Additionally, these scavengers should exhibit low corrosivity and minimal environmental impact. Low cost and easy handling of raw products are also desirable, considering toxicity and viscosity. Various chemical substances are used for H_2S scavenging, including iron or zinc oxides and carboxylates, amines, triazines, aldehydes, ethoxylated compounds, and oxidizing agents [7-10].

There is a growing demand for increasingly efficient H_2S scavenger products with reduced process impact, as well as methods for determining the H_2S scavenging capacity that closely approximate conditions at the application site, including 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 reported in the literature as a way of evaluating H_2S scavengers, providing valuable information on the performance of these products under real application conditions. However, the considerable number of variables present in these tests often makes it difficult to obtain conclusive and reproducible observations. Furthermore, the impact of new products on processes downstream from the injection point complicates field testing, and conducting these tests carefully inevitably disrupts normal operation and production routine.

Most technical publications focus on H_2S scavengers for the treatment of gaseous hydrocarbons and aqueous fluids, at temperatures that do not exceed ambient temperatures by much. In contrast, there are still few references to the study of H_2S scavenger performance in liquid organic media, typically used in condensates of light petroleum compounds or organic fluids during well drilling operations, and generally at temperatures below 70 °C. We understand that the lack of information on the H_2S scavenging capacity at higher temperatures and/or in more complex organic fluids is related in most cases to the limitation of the test apparatus, the available analytical instrumentation and the risk of exposure to H_2S, despite the relevance of this type of information for the oil and gas industry [12].

This article presents comparative results on the H_2S scavenging capacity of commercial products, based on different active ingredients used in the oil industry, applying a methodology initially developed as a prototype through a partnership between Petrobras and CCTechnologies-DNV (USA) [16] and later refined and standardized at the Petrobras Research Center/CENPES [12]. This methodology, described in more detail by Bonfim [12, 13], is employed to study, compare and rank 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, under conditions resembling 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, 13]. The information generated allows decisions to be made regarding the best product to be used in the oil production scenario, aiming for greater efficiency and a smaller volume of injected H_2S scavenger. Successful treatment primarily reduces the risk of material failure due to H_2S exposure, ensures compliance with legal and operational requirements, and minimizes the impact on oil refining stages from both residual scavengers and their reaction products that remain in the oil.

2. Experimental

2.1. Headings

Four commercial H_2S scavengers samples (C) used in oil and gas production environments, each containing different active ingredients, were evaluated alongside three concentrated samples (P) of their respective active ingredients. Among the concentrated samples, only the product (ethylenedioxy) dimethanol (CAS 112-27-6), equivalent to the commercial ethoxylated compounds, was not available for testing (Table 1).

Table 1. *Commercial H_2S scavenger products evaluated and their respective active ingredients.*

Samples	Active compounds	CAS Number
Commercial (C)		
TRI-C	Hexahydro-1,3,5-tris (hydroxyethyl)-s-triazine or MEA-triazine	4719-04-4
ETO-C	Ethoxylated compounds	3586-55-8 [1]
GLI-C	Ethanedial or glyoxal	107-22-2
ZIN-C	Zinc carboxylate	Not determined
Concentrated (P)		
TRI-P	Hexahydro-1,3,5-tris (hydroxyethyl)-s-triazine	4719-04-4
GLI-P	Ethanedial	107-22-2
ZIN-P	Zinc caprylate	557-09-5

[1] CAS number representing one of the major molecules that make up the commercial product.

2.2. Oils

H_2S scavengers were evaluated in a °API 19 (O19) crude collected in Brazilian producing fields with the physical-chemical characteristics presented in Table 2.

Table 2. *Physical-chemical characteristics of the oil used in the performance evaluation tests of H_2S scavengers.*

Tested oil	O19
Density °API	18,9
Density 20 °C / 4 °C	0,9372
Water content (%m/m)	0,97
Total sulfur (%m/m)	0,744
Kinematic viscosity (mm2/s) at 20 °C	608,2
Kinematic viscosity (mm2/s) at 30 °C	293,0
Kinematic viscosity (mm2/s) at 50 °C	90,76
Dynamic viscosity (mPa.s) at 20 °C	570,3
Dynamic viscosity (mPa.s) at 30 °C	272,8
Dynamic viscosity (mPa.s) at 50 °C	83,37
Saturates (%m/m)	39,5
Aromatics (%m/m)	32,5
Resins (%m/m)	24,9
Asphaltenes (%m/m)	3,1

2.3. Experimental Setup

The experimental apparatus (Figure 1) consisted of a one liter Hastelloy© C22 autoclave equipped with mechanical stirring and instrumentation for monitoring and controlling temperature, pressure, and gas flow within the reaction system.

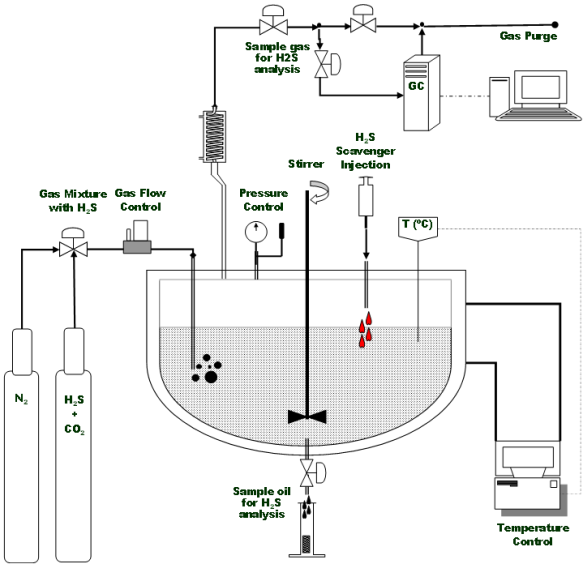


Figure 1. *Schematic diagram of the H_2S scavenger performance evaluation apparatus.*

In this experimental setup, a Varian® Micro-GC chromatograph model CP-4900 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 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 standard gas mixture containing 3.2 %(v/v) H_2S and 96.8 %(v/v) CO_2.

A Metrohm 785 DMP Titrino© automatic potentiometric titrator equipped with a silver-silver sulfide indicator electrode and an Ag/AgCl reference electrode was used to determine the H_2S content dissolved in the oil. The analysis was performed on 5 mL aliquots of oil, collected from the reaction system during the test and transferred into recipients containing isopropanol, toluene, and ammonium hydroxide. A 0.01 N silver nitrate titrant solution was used to obtain the titration curve, and calibration was performed periodically with a standard sodium chloride solution as described in UOP Standard 163 [14, 15].

2.4. Performance Evaluation Methodology for H_2S Scavengers

Two methodologies were used, the first monitoring the concentration of H_2S present in the gas phase maintained at constant flow (*Methodology A*), and the second monitoring the concentration of H_2S in the oil phase with the test apparatus closed, therefore 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 to evaluate the evolution of the H_2S content in the gas and oil phases throughout the tests after 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, 13, 16]. 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 at room 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 each stage of the procedure (1) Deaeration with N2, (2) Saturation with H_2S, (3) H_2S scavenging and (4) Area equivalent to the mass of H_2S reacted per volume of scavenger used (kg H_2S /L Scav). For the tests evaluating the H_2S scavenging capacity, N2 with of 99.999 %(v/v) purity was used in the deaeration step to remove the oxygen present in the reaction system at the beginning of the test 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.

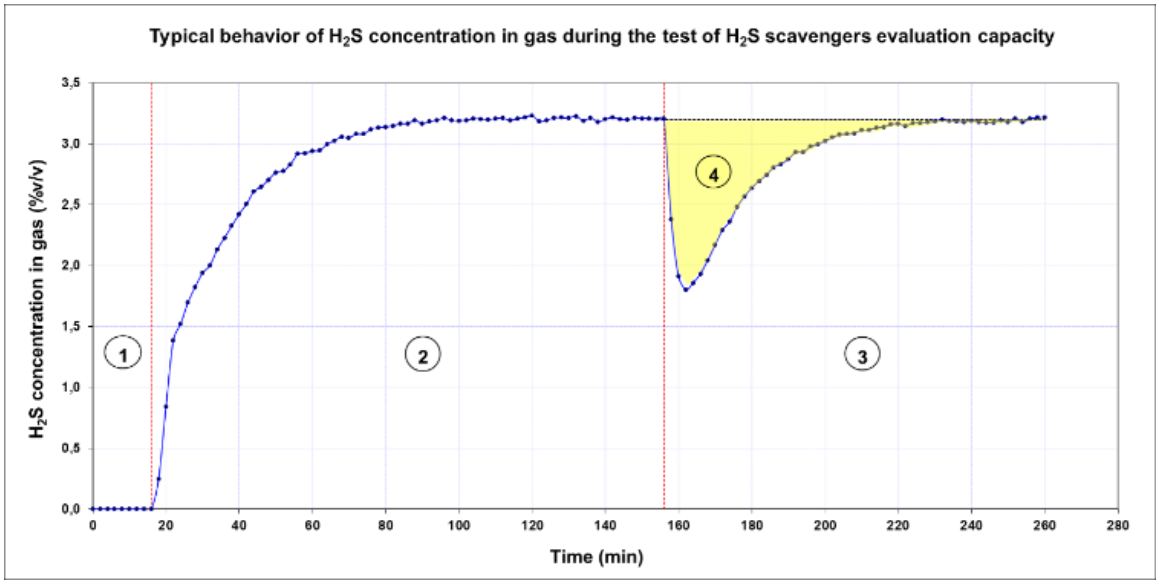


Figure 2. *Typical profile of H_2S concentration in the gas phase over the test time, determined by gas chromatography: ① Deaeration with N2, ② Saturation with H_2S, ③ H_2S scavenging and ④ Mass of H_2S reacted per volume of scavenger used (kg H_2S / L Scav).*

The mass of H_2S reacted by the product added to the fluid is calculated by determining the area of the curve indicated by the region ④. Using conventional spreadsheets, the area as a function of time can be calculated by integration for each product evaluated (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 (1), (2), and (3), the volume in liters of H_2S scavenged, Vg ^{H2S} (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;

$Area$, 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 (5), 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 (6):

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

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 (7), that is, the volume of scavenger needed to reduce 1 kg of H_2S (L of Scavenger / kg of H_2S). Thus, SCv can be calculated by:

$$SC\ \left(\frac{L}{kg}\right) = \frac{V^{Seq}}{m^{H2S}} = \frac{\text{Volume of H2S scavenger } (Liter)}{\text{Mass of H2S scavenged } (kg)} \quad (1)$$

This methodology can be used to evaluate single-phase or multiphase systems (gas, oil, and water) under constant mechanical agitation, under different experimental conditions of BSW, RGO, and/or RGL, as well as to monitor and control the parameters of temperature, pressure, H_2S concentration, and scavenger dosage. 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 saturated with an H_2S -containing gas mixture until the H_2S concentration in the oil stabilizes. After saturation, the gas flow is stopped, and the system remains sealed for 30 minutes under continuous stirring. A precise dose of H_2S scavenger is then injected, with oil samples collected at 1 minute, 10 minutes, 20 minutes, 30 minutes, and 40 minutes afterward. Samples are drawn from the reaction vessel's bottom through a small, coiled tube maintained at 15 °C, flowing directly into containers with a titration solvent mixture (isopropanol, toluene, and ammonium hydroxide). These samples are immediately analyzed using an automatic potentiometric titrator to determine the H_2S concentration in the oil. To maintain system equilibrium between gas and liquid phases, sample volumes are limited to approximately 5 mL, resulting in minimal pressure changes of only 3.4 kPa per collection. Titration curves are analyzed following UOP Method 163 [14].

Figure 3 shows representative results obtained using this methodology with a gas mixture of 3.2 %(v/v) H_2S in CO_2 at atmospheric pressure and ambient temperature. The graph displays H_2S content in oil samples collected during both the saturation phase and after H_2S scavenger injection.

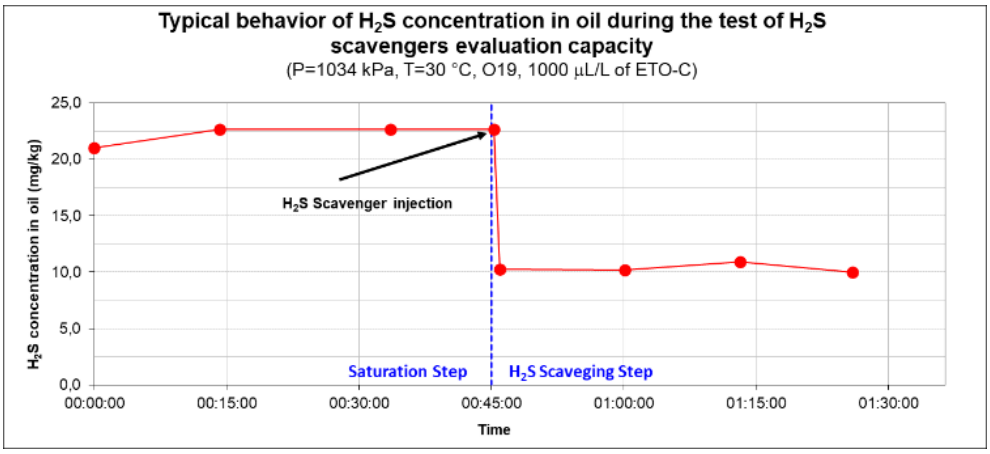


Figure 3. *Typical profile of H_2S concentration in oil determined by potentiometric titration throughout a test, saturated with a gas mixture containing 3.2 %(v/v) H_2S, with 500 µL/L of product.*

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: O19

Water Cut: < 1 %(v/v) (original sample content)

Gas Flow Rate: 0.6 L/min

H_2S Content in Gas: 3.2 %(v/v) (balance in CO_2)

Scavenger Dosage: 500 µL/L and 1000 µL/L

Commercial Scavenger: TRI-C, GLI-C, ETO-C and ZIN-C

Concentrated Scavengers: TRI-P, GLI-P and ZIN-P

The repeatability of the methodology for evaluating the scavenging capacity of H_2S scavengers was evaluated in order to determine the degree of agreement between the results of successive tests carried out under the same measurement conditions where the relative standard deviation (RSD) was less than 10 % for the products tested, confirming good agreement between the results [12].

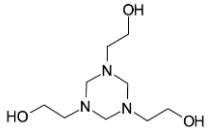
3. Results and Discussion

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

3.1. Chemical Characteristics of the H_2S Scavengers Evaluated

The H_2S scavengers evaluated were characterized based on the type and content of active compounds by means of Nuclear Magnetic Resonance (13C NMR), gas chromatography coupled to mass spectrometry (GC/MS) and Atomic Absorption Spectrometry (AAS). The water content was determined using the Karl Fischer coulometric method. For the 13C NMR, deuterated dimethyl sulfoxide (DMSO-d6) was used to lock the magnetic field and as a chemical shift reference. The molecular structure obtained from the active compounds is presented in Table 3, while the concentration of the mapped components is presented in Table 4.

Table 3. *Molecular structure of the main active compounds in the samples evaluated.*

H_2S Scavengers	Structure of the Majority Active Compounds	CAS Number
TRI-C, TRI-P	 Hexahydro-1,3,5-tris (hydroxyethyl)-s-triazine	4719-04-4

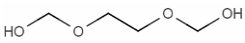
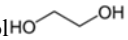
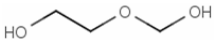
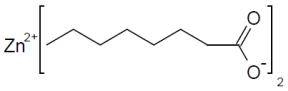
H_2S Scavengers	Structure of the Majority Active Compounds	CAS Number
ETO-C	 2-(hydroxymethoxy) ethoxymethanol  1,2-Ethanediol (MEG)  2-(Hydroxymethoxy) ethanol and other homologous compounds	3586-55-8 107-21-1 13149-79-6
GLI-C, GLI-P	 Ethanedial and oligomers	107-22-2
ZIN-C, ZIN-P	 Zinc caprylate	557-09-5

Table 4. *Characteristics of commercial H_2S scavengers and active compounds evaluated.*

H_2S Scavengers	Active Matter Content	Water Content
TRI-C	57 %(m/m)	43 %(m/m)
GLI-C	46 %(m/m)	54 %(m/m)
ETO-C	92 %(m/m)	7,2 %(m/m)
ZIN-C	1,2 %(m/m) as Zn	0,27 %(m/m)
TRI-P	(16,5 %(m/m) as Carboxilate)	33 %(m/m)
GLI-P	67 %(m/m)	53 %(m/m)
ZIN-P	47 %(m/m)	< 0,01 %(m/m)

The results presented in Table 3 and Table 4 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. In GLI-C, the active matter observed was a mixture of molecules formed from glyoxal (CAS 107-22-2), oligomers, around 46 %(m/m) and water with a content of around 54 %(m/m). In ETO-C, the analyses indicate that the active matter consists of glycols, such as 2-(hydroxymethoxy) ethoxymethanol (CAS 3586-55-8), and a series of homologous polyglycols with the addition of monoethylene glycol (MEG) units. The total glycol content of ETO-C was estimated at 92 %(m/m) and water content of 7.2 %(m/m). ZIN-C presented 1.2 %(m/m) of Zinc, 15.3 %(m/m) of organic salt (carboxylate) and approximately 83.5 %(m/m) of organic solvent consisting of alkyl-benzenes, paraffins, naphthalenes and methyl esters of acids, with chains of 10 to 18 carbons. The water content found was 0.27 %(m/m). Among the concentrated (pure) samples, TRI-P presents the active substance 1,3,5-tri (2-hydroxyethyl) hexahydro-triazine at a content of 67 %(m/m) and water with approximately 33 %(m/m). In GLI-P, as in GLI-C, a mixture of oligomers formed from glyoxal with a content of 47 %(m/m) and 53 %(m/m) of water was observed. The ZIN-P sample presented 1.12 %(m/m) of zinc caprylate (CAS 557-09-5), corresponding to 0.2 %(m/m) of zinc and organic solvent composed of a mixture of esters, this sample was free of water.

3.2. Performance of Different Active Ingredients used as H_2S Scavengers

Initially, we compared the H_2S scavenging capacity among the concentrated active ingredient samples (TRI-P, GLI-P, and ZIN-P) typical of H_2S scavengers. Figure 4 shows the monitoring of the H_2S content in the gas phase after the injection of each product evaluated at a dosage of 1000 µL/L, calculated in relation to the total volume of liquid evaluated. The *Methodology A*, mentioned in 2.4, for monitoring the H_2S

content in the gas phase allowed the differentiation of the scavenging capacity (SC) of the H_2S scavenger products.

Table 5 shows the mass of H_2S consumed by each product evaluated, calculated from the curves shown in Figure 4, with TRI-P presenting a higher scavenging capacity than GLI-P and both much higher than ZIN-P.

H_2S Scavenging Capacity rating scale:
TRI-P > GLI-P >> ZIN-P

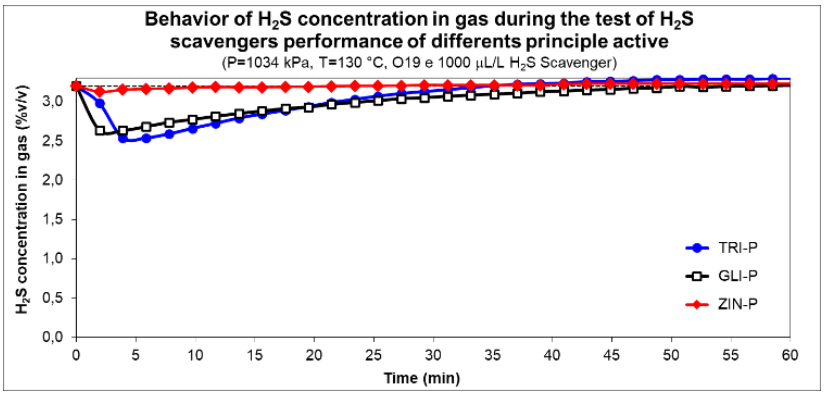


Figure 4. *Monitoring of H_2S content in the gas phase after the injection of 1000 µL/L of concentrated active compounds from typical H_2S scavengers.*

Table 5. *H_2S scavenging capacity of active compounds at a dosage of 1000 µL/L.*

H_2S Scavengers	Mass of H_2S consumed (mg)	SC_v (V Scav /m H_2S gas) (L / kg)	SC (m H_2S gas / V Scav) (kg / L)
TRI-P	0,1343	5,96	0,168
GLI-P	0,1020	7,85	0,127
ZIN-P	0,0045	177,69	0,006

3.3. Performance of Commercial H_2S Scavengers with Different Active Ingredients

Monitoring of H_2S in the gas phase - The commercial H_2S scavenger samples, TRI-C, GLI-C, ETO-C and ZIN-C, were compared in terms of H_2S scavenging capacity using Methodology A. Figure 5 and Figure 6 present the monitoring of the H_2S content in the gas phase after the injection of each product tested at two different concentrations: 1000 µL/L and 500 µL/L. The dosage was calculated based on the volume of liquid to be treated. This methodology enabled a clear differentiation in performance between the H_2S scavenger products at both concentrations.

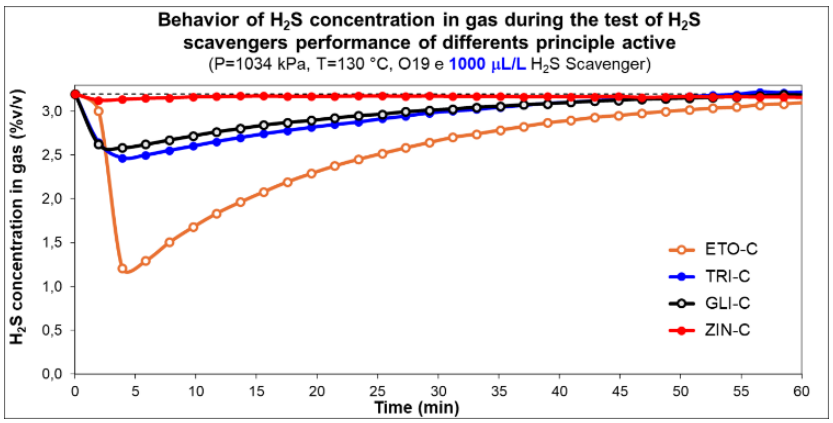


Figure 5. *Monitoring of H_2S content in the gas phase after the injection of 1000 µL/L of H_2S scavengers with different active compounds.*

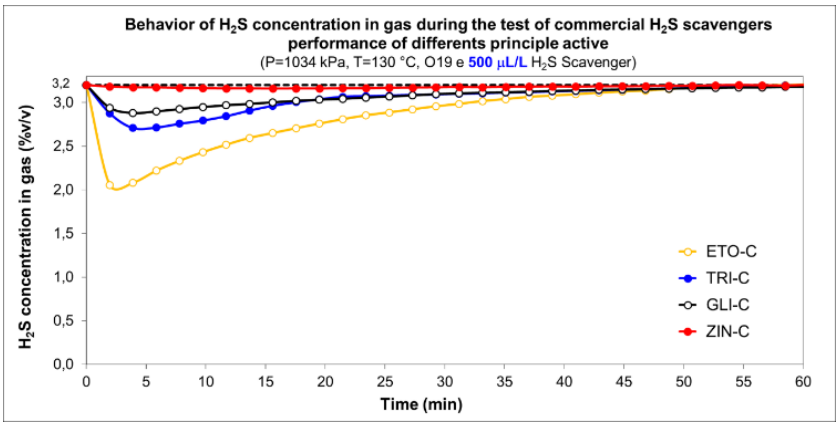


Figure 6. *Monitoring of H_2S content in the gas phase after the injection of 500 µL/L of H_2S scavengers with different active compounds.*

Table 6 presents the mass of H_2S consumed by each evaluated product, calculated from the previous curves at the two concentrations mentioned. It also shows the percentage reduction relative to the original H_2S mass (1.584 g) for each product, at the two dosages used.

Table 6. *Performance of scavengers with different active compounds at concentrations 1000 µL/L and 500 µL/L, at P=1034 kPa and T=130 °C.*

H_2S Scavenger	**Dosage (µL/L)**	**H_2S consumed (mg)**	**H_2S consumed (%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
TRI-C	500	0,0842	4,8	4,75	0,211
GLI-C	500	0,0677	3,9	5,91	0,169
ZIN-C	500	0,0114	0,7	35,21	0,028
ETO-C	1000	0,3594	20,6	2,23	0,449
TRI-C	1000	0,1423	8,2	5,62	0,178
GLI-C	1000	0,1228	7,0	6,51	0,154
ZIN-C	1000	0,0183	1,1	43,68	0,023

As observed, ZIN-C exhibited the lowest performance under the tested conditions. TRI-C and GLI-C demonstrated better performance than zinc carboxylate, with results closely aligned. Considering a test variability of 10% [12, 13], there is no statistically significant difference between TRI-C and GLI-C. ETO-C showed the highest efficiency, resulting in the greatest reduction of H_2S content in the gas phase compared to the initial concentration, and thus the highest mass of H_2S reacted over time.

These results also indicate that the mass of H_2S reacted is proportional to the quantity of product dosed, since the H_2S consumption at a dosage of 500 µL/L was approximately half of that observed at 1000 µL/L of each product. Based on the curves obtained, a performance rating scale of H_2S scavenging capacity can be established under the evaluated conditions, expressed as mass of H_2S consumed per volume of H_2S scavenger used (i.e., kg H_2S gas / L Scavenger). The results allow us to rank the various products as presented below:

Performance rating scale:

Ethoxylate > Triazine ≡ Glyoxal > Metal Carboxylate

Naturally, the observed H_2S scavenging capacities are specific to the evaluated commercial products. Other commercial products may present different performance levels depending on their composition and active compounds content. However, the proposed methodology provides a reliable means to classify them and to verify the consistency of their specification and quality control over the time in field applications.

It is also noted that the H_2S scavenging capacity of the products was independent of the concentration used (500

µL/L or 1000 µL/L), as the scavenging capacities (expressed per kg H_2S gas / L Scavenger) remained consistent across dosages.

Finally, when comparing the behavior of the commercial H_2S scavenger (C) and its respective active compounds (P), a similar performance profile was observed, as shown in Table 7. This convergence can be attributed to the comparable active compounds content in both the commercial products and their corresponding pure active compounds, as previously presented in Table 4.

Table 7. *Comparison between H_2S scavenger products and active compounds used.*

H_2S Scavengers	Active Matter Content (%m/m)	Water Content (%m/m)	SC (m H_2S /V Scav) (kg/L)
TRI-C	57	43	0,178
TRI-P	67	33	0,168
TRI-C	57	43	0,178
GLI-C	46	54	0,154
GLI-P	47	53	0,127
ZIN-C	1,2 (as Zn)	0,27	0,023
ZIN-P	0,2 (as Zn)	< 0,01	0,006
ETO-C	92	7,21	0,449

Monitoring of H_2S *in the oil phase* - A second set of tests was performed following Methodology B, described in 2.4. In this procedure, after saturating the oil with a gas mixture containing 3.2 %(m/m) of H_2S, the system was sealed, and the gas flow stopped. After an equilibrium period of 30 minutes, small volumes of oil samples were sampled and analyzed. The average content of H_2S dissolved in the API 19 (O19) oil before the addition of the H_2S scavengers was 225.5 ± 6.8 mg/kg of H_2S, corresponding to a mass of 0.1674 g of H_2S in the volume of oil used.

Following saturation, in order to evaluate the effect of the scavengers in reducing the dissolved H_2S content, 1000 µL/L of each of the products previously tested were injected. The H_2S content in the oil was monitored for approximately 40 min, and the reduction in its content after the injection of each product is shown in Figure 7.

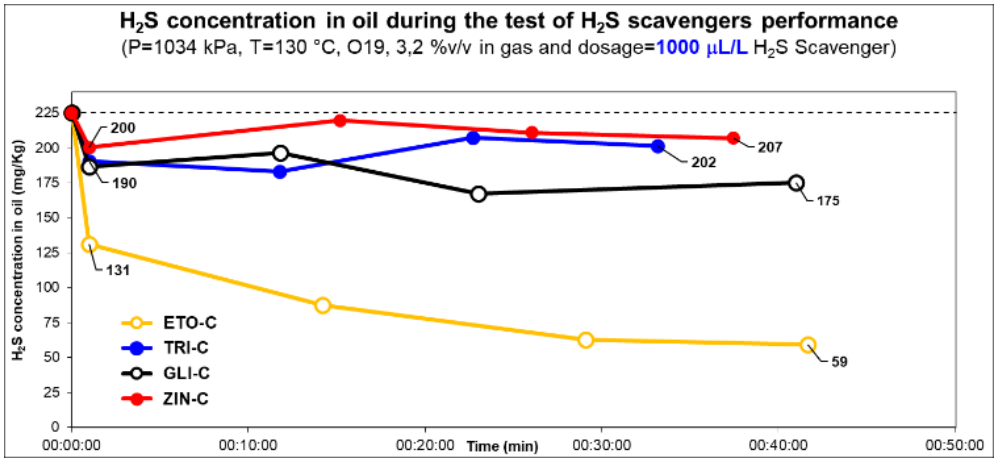


Figure 7. *H_2S concentration after H_2S scavengers injection.*

The ethoxylated product ETO-C reduced the dissolved H_2S content to the lowest levels and did so rapidly. As observed in the gas phase tests, the carboxylate-based product ZIN-C showed the lowest performance. Once again, the glyoxal-based scavengers GLI-C and MEA-triazine-based scavengers TRI-C showed similar performance, particularly during the initial reaction period.

The H_2S concentrations in the oil at 1 min and 40 min after

the injection of each commercial H_2S scavengers is highlighted in Figure 7. These two time points allow for the evaluation of both the reaction kinetics and scavenging capacity of each product, considering that after 40 minutes all the injected product is assumed to have reacted with the H_2S.

The mass of H_2S consumed and the equivalent percentage fraction relative to the original H_2S content are presented in Table 8, which also includes the performance results from the oil-phase monitoring for each evaluated scavenger. The observed performance ranking was consistent with that obtained in the gas-phase tests. Therefore, both methodologies are suitable for evaluating and distinguishing the performance of H_2S scavengers under the tested conditions.

Performance Ranking:

Ethoxylated > *Glyoxal* ≡ *Triazine* > *Metal Carboxylate*

Table 8. *Performance of the products evaluated in O19 oil at a dosage of 1000 μL/L.*

H_2S Scavenger	Time (min)	H_2S in oil (mg/kg)	H_2S consumed (mg)	H_2S consumed (%m/m)	SC_v (Vol Scav / m H_2S oil) (L/kg)	SC (m H_2S oil / Vol Scav) (kg/L)
ETO-C	1	131	70	42	-	-
ETO-C	40	59	123	74	6,49	0,154
GLI-C	1	187	28	17	-	-
GLI-C	40	175	37	22	21,52	0,046
TRI-C	1	190	26	15	-	-
TRI-C	40	202	17	10	45,77	0,022
ZIN-C	1	200	18	11	-	-
ZIN-C	40	207	13	8	58,31	0,017

The economic aspect also influences industry decisions on use chemical products. The price of these products depends on numerous factors, such as regulations, market conditions, raw material availability, and logistics. These factors impact the final product cost. While this work does not focus on it, calculating the cost-benefit ratio based on H_2S scavenging capacity (SC) and the price of H_2S scavengers is crucial for successful H_2S treatment in oil and gas production wells.

4. Conclusions

The methodology used is capable of evaluating, comparing, and differentiating the performance of different H_2S scavenger products used in the oil industry, bringing together in a single test conditions that are closer to field application and, until now, uncommon in the laboratory, which include the presence of oil, temperatures above 100°C and pressures of up to 150 psi (1034 kPa). Monitoring H_2S levels in both gas and oil phases enabled the comparison of different products' performance, allowing classification by 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.

Among the commercial H_2S scavengers evaluated, the one based on ethoxylated compounds ETO-C exhibited the highest performance. The TRI-C and GLI-C scavengers performed similarly, both showing lower performance compared to ETO-C. The ZIN-C scavenger demonstrated the lowest performance among the products evaluated.

The study showed that the mass of H_2S reacted is proportional to the amount of products dosed for all products evaluated, at dosages ranging from 500 μL/L to 1000 μL/L.

The H_2S scavenging capacities depend on the commercial products evaluated. Other products may perform differently based on their formulation and active content. This methodology helps classify these products and verify their specifications and quality over time.

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

Jose Antonio da Cunha Ponciano Gomes: Writing – review & editing

Alvaro Augusto Oliveira Magalhaes: Writing – review & editing

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Data Availability Statement

The data supporting the findings of this research are presented 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 H2S scavengers, corrosion inhibitors, and the corrosivity of biofuels, oil, and derivates.

Research Field

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

Jose Antonio da Cunha Ponciano Gomes: Corrosion

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