

New Trends for Hydrogen Sulfide Scavenging Using Natural Compounds as Biogenic Amines

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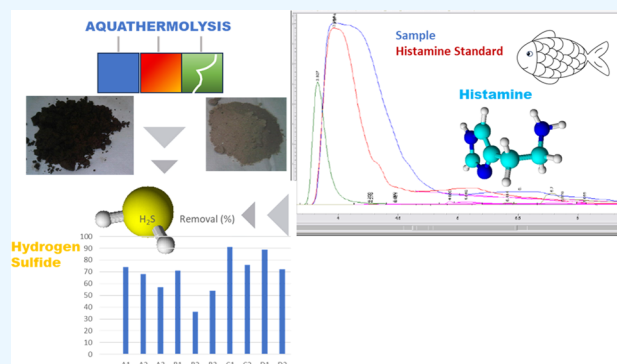


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ABSTRACT: Hydrogen sulfide (H_2S) mitigation through the use of additives in a laboratory-scale evaluation of steam injection in batch reactors was studied using extra heavy crude oil. For this purpose, additives based on biogenic amines from a fishing effluent were used with methanol and ethanol as solvents in a previous extraction of industrial fishmeal waste. The study of the extracts using high-performance liquid chromatography (HPLC) permitted the determination that the methanol-based extract with 48 h of decomposition had the highest biogenic amine content, totaling 1472 ppm. In addition, methanol extractions were more efficient, with an average biogenic amine content of 592 ppm. Subsequent evaluations were carried out for sand/oil/water/scavenging additive systems, where solutions of commercial organic compounds, analytical-grade histamine, and biogenic amine extracts were used. These evaluations were performed at a constant temperature of 247 °C and under an initial pressurization of methane gas of 215 psig, with a reaction time of 24 h. Characterization of gaseous effluents for each system allowed us to determine that the methods in which biogenic amine extracts were used with methanol were more effective in H_2S scavenging because they had the lowest gas concentration at the end of the reaction time. Within this group, the most effective was the C1 extract, with a H_2S reduction from 1700 to 150 ppm, representing 91% removal. The biogenic amine family produced by decomposition in conjunction with histamine has a synergistic effect in tests under vapor injection conditions when comparing the results with analytical-grade histamine solution-based additives and commercial additives. This study shows that using steam injection technology to use biogenic amines in H_2S mitigation is feasible.



1. INTRODUCTION

In implementing enhanced oil recovery (EOR) technologies, such as steam injection, a reduction in the temporary viscosity of crude oil is generated after several days of good closure because of the energy exchange between the injected steam and oil, thus increasing the production of hydrocarbons. This is the primary method used for the production of heavy oil reservoirs. These technologies have side effects, such as the production of acid gases (hydrogen sulfide and carbon dioxide), due to the aquathermolysis of heavy oil. Aquathermolysis is a group of chemical reactions between crude oil and water in a vapor or liquid state, so named by researchers.^{1,2} These reactions involve breaking down the compounds found in heavy crude oil, producing lighter compounds, improving the crude oil's characteristics (viscosity and API gravity), and the presence of acid gases. Various gaseous compounds, such as methane, nitrogen, mercaptans, water, carbon dioxide, and hydrogen sulfide, are produced during these reactions.

Hydrogen sulfide (H_2S) is a gas that, under environmental conditions, is characterized by high toxicity, putting the lives of working personnel and communities near the oil production area at risk. In addition, acid gas generates operational problems, damaging the installations, owing to pipe corrosion.

Therefore, eliminating these contaminants from the produced gas is necessary for commercialization. This is achieved through sweetening processes, where the gas is processed on the surface in operational centers and stations according to its pressure, richness, acidity, water content, and volume by employing solid and liquid scavengers.^{3,4} These compounds can absorb H_2S through a chemical reaction, making H_2S safer and more accessible to dispose of.

This study aims to formulate an H_2S scavenger that can be injected in conjunction with steam owing to the low thermal resistance of commercial scavengers to steam injection conditions. The active substances in this scavenger are biogenic amines that can absorb H_2S through a chemical reaction due to their high basicity and high thermal resistance. This study aimed to obtain these biogenic amines from fish, in

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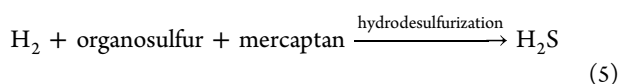
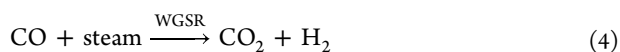
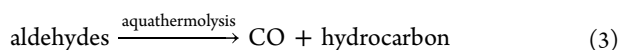
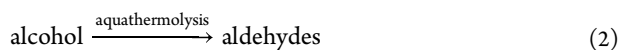
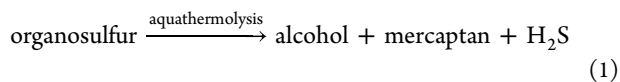


which high quantities are produced through post-mortem environmental degradation by extracting amines from industrial fish effluents. The reactions of the amines obtained were evaluated in steam injection simulation tests, where an eventual reduction in H₂S in the production gas is expected. To meet these objectives, a set of additives, including a commercial additive, analytical-grade biogenic amine (histamine) solutions, and biogenic amine extracts from fishmeals with different decomposition times, were evaluated using solvents, such as methanol and ethanol. For the characterization of the extracts obtained, analytical techniques such as high-performance liquid chromatography (HPLC) were used to quantify the biogenic amines present in the extracts. Subsequently, these additives were evaluated in a crude/sand/water/gas reaction system in batch reactors at an initial pressure of 215 psig of injected methane gas. The reactor temperature was maintained at 247 °C for 24 h. These gases were quantified by comparing the H₂S and CO₂ produced from the reaction, where the biogenic amine extracts, commercial additive, and histamine were used as hydrogen sulfide scavengers. Thus, the isolated behavior of histamine as a molecule within the reaction system can be evaluated as well as the performance of biogenic amine extracts in the final mitigation of H₂S.

2. STEAM INJECTION

The enhancement of oil recovery during steam flooding is essentially based on the improvement in the flow properties of oil by heating. The decrease in viscosity with increasing temperature is particularly pronounced for heavy crude oil.^{5,6} Steam injection is a thermal recovery technique, where thermal energy is supplied to the reservoir by injecting steam. The steam injection process can be continuous or alternate. In continuous steam injection, steam is injected into several wells, whereas oil is produced in adjacent wells. The main mechanisms contributing to oil displacement in this process are the thermal expansion of reservoir fluids, the reduction of oil viscosity, and steam-distillation, the latter being the most significant. In addition to these mechanisms, gas thrust and solvent extraction effects have also been observed.⁶

2.1. Aquathermolysis. Aquathermolysis is the group of chemical reactions between high-temperature steam and at least some compounds of a mixture of heavy hydrocarbons.^{2,7–9} The aquathermolysis reactions are shown as follows:



These reactions compete with and influence the viscosity of heavy crudes in opposite directions. Once reactive species are generated by a rupture in the structures of the various C–S bonds, they can polymerize and increase the viscosity of the crude oil or initiate a series of consecutive reactions that result in the generation of products that can reduce its viscosity.

Therefore, acid polymerization is a possible chain reaction because of the connection between the reactive compounds generated during aquathermolysis.⁷ These reactive compounds are free radicals that react with unsaturated molecules in crude oil, generating new intermediaries that react in chains with other unsaturated molecules until the bond between two unsaturated carbonated chains occurs or an impurity stops the mechanism.

The reactions lead to a notable increase in the crude oil's average molecular weight and viscosity. On the other hand, there is the possibility of initiating a set of reactions that stimulate the generation of compounds of lower molecular weight, whose appearance in crude oil leads to an improvement in reducing its viscosity. These reactions involve decarboxylation processes that produce carbon monoxide and dioxide (CO and CO₂). In addition, hydrogen is generated, which consequently promotes hydrogenation and desulfurization reactions.^{1,10,11} The crude desulfurization reactions generate hydrogen sulfide from compounds, such as thioether and thiophene. This occurs because sufficient energy is supplied at temperatures greater than 200 °C to stimulate the breakdown of certain bonds, such as the C–S link. Hyne² outlined the temperature range in which there is evidence of chemical changes in crude oil due to the rupture of different bonds in its carbonated chains.

2.2. Location of Sulfur Causing H₂S Production. According to some studies, sulfur is obtained before aquathermolysis as follows:

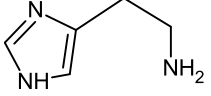
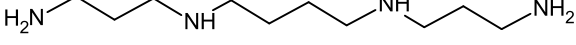
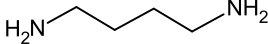
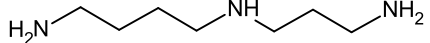
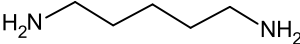
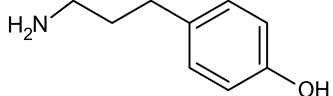
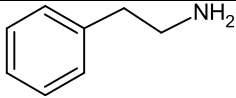
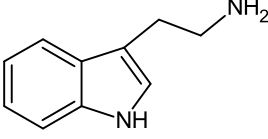
The residual organic phase indicates that sulfur is bound to the hydrocarbon matrix and is present in simple and complex sulfides, disulfides, thiols, and thiophenes. In contrast, in the inorganic phase, there are inorganic sulfides, mainly iron sulfides (FeS₂ or pyrite) and nonorganic sulfates (calcium and iron sulfates).

Studies have also been carried out after aquathermolysis to locate sulfur, which has been found in three phases: in the organic phase, such as saturated or aromatic compounds, resins, and asphaltenes; in the inorganic phase, as pyrite; and the gas phase, as H₂S.³ Other studies have concluded that sulfur is distributed in the producing sands in both inorganic and organic phases (the latter is in a more significant proportion). In addition, the sulfur content of the crude oil after aquathermolysis was greater than that of the original crude oil. The sulfur in the asphaltenes of the associated steam-stimulated crude oil is more significant than that in the original crude oil. Finally, sulfur in the resins of the associated crude oils, after aquathermolysis, is less than that in the original crude oil. This sulfur distribution behavior can be attributed to the desorption of the residual organic phase adsorbed on the porous medium.

3. ADDITIVES FOR HYDROGEN SULFIDE SCAVENGING

3.1. Hydrogen Sulfide Adsorption with Nonregenerable Liquids. Scavengers convert hydrogen sulfide into sulfur compounds, which are more accessible and safer to dispose of.¹² They are active-phase, nonregenerable amines, nitrites, triazines, or other nitrogen compounds. When the scavenger liquid possesses triazine (C₃H₆R₃N₃) as the active phase, the reaction mechanism suggests initial protonation of the nitrogen in the triazine ring by a hydrogen ion originating from the H₂S molecule.^{3,13} For economic reasons, H₂S scavenging is a

Table 1. Primary Amines Are Found in Fish Decomposition

Amine	Chemical Structure	Molecular Formula	Molecular Weight (g/mol)	Standard Boiling Point (°C)
Histamine		C ₅ H ₉ N ₃	111.2	209.5
Spermine		C ₁₀ H ₂₆ N ₄	202.3	150
Putrescine		C ₄ H ₁₂ N ₂	88.2	160
Spermidine		C ₇ H ₁₉ N ₃	145.3	180
Cadaverine		C ₅ H ₁₄ N ₂	102.2	179
Tyramine		C ₈ H ₁₁ NO	137.2	207
Phenyl-ethyl-Amine		C ₈ H ₁₁ N	121.2	195
Tryptamine		C ₁₀ H ₁₂ N ₂	160.2	137

technological alternative to natural gas containing less than 2000 ppm of H₂S.

3.2. H₂S Scavengers with Industrially Known Amines.

Monoethanolamine (MEA) is a primary, light-colored amine, the most reactive of the ethanolamines and the strongest base of all amines. It is preferably used in nonselective carbon dioxide and hydrogen sulfide removal processes. Low concentrations of CO₂ can be achieved using 4–5 mol % MEA but have problems with corrosion and foaming, thus limiting the concentration by 15% w/w.^{3,14} Diethanolamine (DEA) is a secondary amine that is a clear, hygroscopic, and viscous liquid at room temperature or higher. It has the most remarkable applicability in refinery gas treatment, where sulfurous compounds may degrade MEA. This amine is recommended for treating vapors with a high hydrogen sulfide content because it is much less corrosive than MEA. Still, the DEA solution becomes very viscous at high concentrations. The reaction of DEA with COS and CS₂ is slower than that of MEA with these sulfur compounds, and the reaction products are different, which causes lower amine losses when reacting with these gases.

Methyldiethanolamine (MDEA) is a tertiary amine that reacts slowly with CO₂. The best application is the highly effective and selective removal of H₂S in the presence of CO₂. The advantages of using MDEA include its low reaction heat with acidic gases, low energy requirements for regeneration,

and low degradability in gaseous currents containing H₂S and CO₂.^{3,14} Triethanolamine (TEA) is a slightly yellow and viscous liquid, and its most significant utility is its moisturizing capacity. It is a tertiary amine highly selective toward H₂S because the reaction with CO₂ is very slow. It can be used as an alkalization agent for long-chain fatty acids.^{3,14}

3.3. Biogenic Amines. Biogenic amines are produced in certain foods, such as blue fish (Scombridae) and fermented products, such as cheese, wine, or beer, by the action of microbial decarboxylase enzymes obtained from free amino acids in the food itself. The formation of certain biogenic amines is caused by a defect in the fermentation process or, in the case of fish, by hygiene deficiencies during the preservation process.^{15–17} Biogenic amines can accumulate in food at concentrations of up to 5000 ppm. These amines are formed in fish by improper handling and preservation, leading to proteolysis, which increases the levels of free amino acids in the muscle. The fish suffer an immediate deterioration after their capture and death due, in the first stage, to enzymes typically found in the muscle and subsequently to enzymes produced by microorganisms that quickly invade the fish. Generally, fish stored in places with poor hygiene and at temperatures above refrigeration for a long time are susceptible to the formation of large amounts of histamine.^{15,18}

The formation of biogenic amines is potentially increased when fish muscle and viscera are directly exposed to bacterial

action during evisceration and filleting operations.¹⁸ Some biogenic amines found during fish decomposition are listed in Table 1. These amines have appreciable thermal stability (boiling points greater than 150 °C) because of the number of carbons contained in the linear structure and benzene rings present.¹⁸

Among the amine-producing enzymes is L-histidine decarboxylase, which generates histamine from histidine. The consumption of histamine in high concentrations can be toxic to humans. The latter is a biogenic amine that is produced by the action of the enzymatic activity of certain bacteria, among which are *Escherichia coli*, *Salmonella* spp., *Lactobacillus* spp., and *Morganella morganii*.¹⁹

4. METHODS AND PROCEDURES

This study was divided into two parts; the first was the extraction of biogenic amines from fishmeal using methanol and ethanol as solvents. The content of biogenic amines, such as histamine, was determined in these extracts using HPLC. The second part involved studying biogenic amines as acid gas scavengers under steam injection conditions. It was decided to evaluate the extracts with commercial triazine-type H₂S scavenging additives and an analytical-grade histamine sample. The goal was to compare the efficiency of biogenic amines against high-temperature systems that reproduce acid gas mitigation conditions. To reproduce these conditions, the additives were placed in reaction systems by loading them with heavy oil/sand and steam at a constant temperature of 247 °C and a pressure of 1100 psig for 24 h.

4.1. Extracting Biogenic Amines from Fishmeal.

4.1.1. Generation of Various Matrices: Preparation of Fishmeal. Three different matrices were generated from the same effluent in which the content of biogenic amines could vary in each case depending on the exposure time to environmental conditions. The procedure for the latest technology in the industrial preparation of fishmeal for animal feed was adapted to the laboratory scale,²⁰ as follows:

The fish effluent was placed in a batch reactor with 200 mL of distilled water. It was then covered and heated to 121 °C. Once this temperature was reached, the heating was maintained for 45 min. Then, the mixture was left to cool to room temperature. Once cooled, the material was filtered through a Büchner flask connected to a vacuum line of -4.5 psig. The liquid entered the Büchner flask, and the solid accumulated on the filter paper, forming the pressing cake. The liquid was left to decant for approximately 12 h, and the remaining sample solids were added to the pressing cake. The remaining liquid was placed in a water bath at 75 °C for 1 h to evaporate most of the water. The solid was converted into a pressing cake and placed in an oven at 65 °C for 2 days to minimize moisture. Once the total humidity was reduced to a minimum, the solid was ground, obtaining a pulverized fishmeal with the characteristic smell of decaying fish and a humidity percentage of less than 5%. Table 2 presents the different fishmeals (matrices) studied, including two additional matrices corresponding to industrially acquired tuna and sardine flours.

4.1.2. Methanol/Ethanol Extraction. This procedure employed different solvents to extract biogenic amines from the parmesan cheese. These solvents were chosen for the generated matrices to determine the most efficient solvent for biogenic amine extraction.^{21,22} Four grams of the matrix sample and 20 mL of the solvent were mixed in a 150 mL

Table 2. Matrices Were Studied in Terms of Biogenic Amine Content

matrix	description
S24	sample prepared from fish after 24 h of decomposition
S48	sample prepared from fish after 48 h of decomposition
S72	sample prepared from fish after 72 h of decomposition
tuna	commercially purchased Scombridae family fishmeal
sardine	commercially purchased Clupeidae family fishmeal

container and shaken for 10 min. The solution was placed in a water bath at 60 °C for 15 min.¹⁷ The sample was cooled to room temperature and transferred to a 50 mL volumetric flask, which was then filled with a fresh solvent. After that, the sample was centrifuged for 10 min at 2500 rpm, and the supernatant was filtered through No. 1 filter paper.

A second extraction was performed using the same procedure. Finally, both extracts were collected in the same glass container and refrigerated to a temperature lower than 5 °C. Once the five matrices were extracted with methanol and ethanol were completed, 10 extracts were obtained and subsequently evaluated (see Table 3).

Table 3. Extracts Obtained from Methanol and Ethanol in Different Matrices

extract	description
M1	solvent: methanol and time: 24 h
M2	solvent: methanol and time: 48 h
M3	solvent: methanol and time: 72 h
M4	solvent: methanol and matrix: Clupeidae
M5	solvent: methanol and matrix: Scombridae
E1	solvent: ethanol and time: 24 h
E2	solvent: ethanol and time: 48 h
E3	solvent: ethanol and time: 72 h
E4	solvent: ethanol and matrix: Clupeidae
E5	solvent: ethanol and matrix: Scombridae

The methodology developed for determining biogenic amines in fish by HPLC and fluorescent detection was faithfully followed in this research.^{17,22,23}

4.2. Study of Biogenic Amines as Acid Gas Scavengers under Steam Injection Conditions. Figure 1 presents the general methodology used in this research for additive evaluation under steam injection conditions. This methodology is mainly based on the characterization of the components of the reaction (sand, oil, and additive) before and after a set of batch reactions using samples of heavy oil. The design of experiments and reaction conditions were selected following the information from the case study in Table 4.

4.2.1. Static Evaluation at Steam Injection Conditions. These tests were carried out on AISI 316 steel autoclaves of approximately 500 mL capacity, equipped with heating jackets and temperature controllers designed to withstand a maximum temperature of 350 °C and 3046 psig. All solutions evaluated in this section are listed in Table 5. The procedure is summarized: The reactors were loaded with sand, injection water, crude oil, and 5 mL of the scavenging additive, with a crude/water ratio of 1.3. After closing the reactors, this mixture was connected to a vacuum line at -4.5 psig for 30 min. Then, 215 psig of methane was injected into the reaction system. Finally, the controller was set at a temperature of 247 °C. The

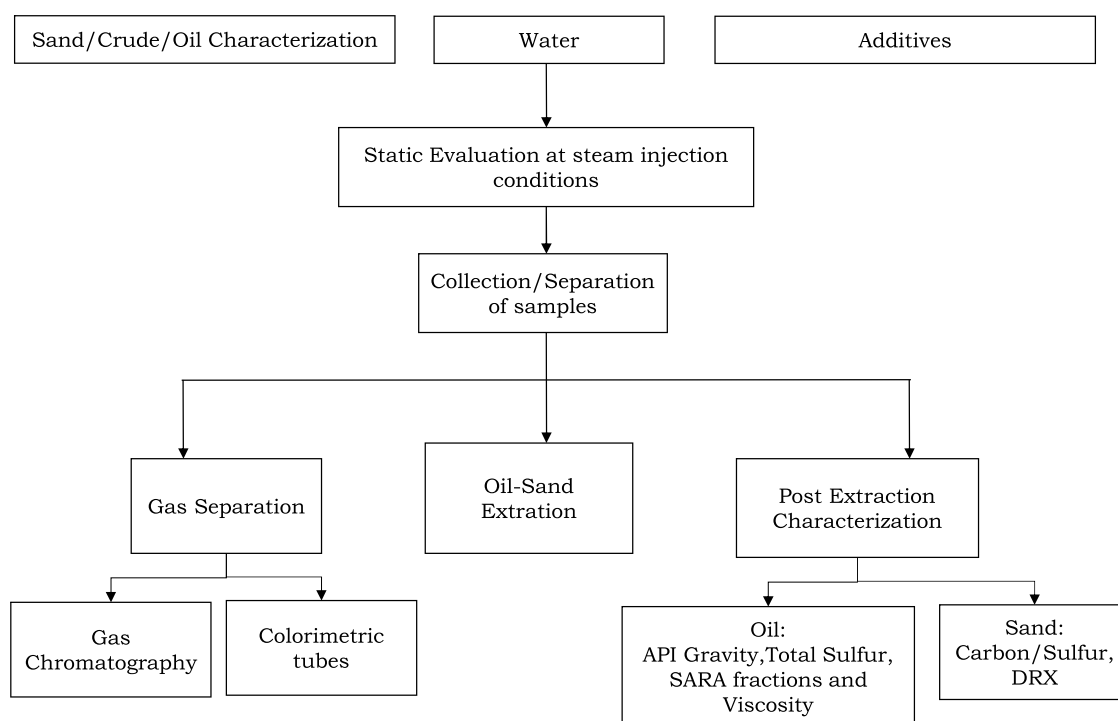


Figure 1. Experimental scheme.

Table 4. Properties and Operational Conditions of Extra Heavy Crude Oil Reservoir

properties	value
porosity, \emptyset , vol %	27
crude oil saturation, SOR, vol %	73
steam temperature, °C	247
reservoir pressure, psig	900

Table 5. Solutions Were Evaluated during Testing under Steam Injection Conditions

solution	description
A1	histamine solution at 1% w/w analytical grade
A2	histamine solution at 0.5% w/w analytical grade
A3	histamine solution at 0.2% w/w analytical grade
B1	commercial scavenger at 1% w/w
B2	commercial scavenger at 0.5% w/w
B3	commercial scavenger at 0.2% w/w
C1	biogenic amine extract from methanol and 48 h
C2	biogenic amine extract from methanol and 72 h
D1	biogenic amine extract from ethanol and 48 h
D2	biogenic amine extract from ethanol and 72 h

reaction system was left for 24 h when the desired conditions were reached.

4.3. Experimental Techniques and Water Preparation. Table S1 presents a summary of the experimental techniques used in the characterization of compounds before and after aquathermolysis reactions. These essays were carried out twice.^{14,24,25}

Injection water was prepared following the recommended practice for analysis of oil-field waters.²⁶ The characteristics of the injection water are summarized in Table S2.

5. RESULTS

5.1. Determination of Histamine in Extracts Obtained through HPLC. The chromatographic method was used to evaluate the histamine contents in the different extracts. Peak areas were measured in the chromatograms obtained for each extract, and the concentrations of histamine were calculated from a standard calibration curve using histamine samples of known concentration, obtaining the following linear equation¹⁷

$$\text{area} = 53.1 \times \text{concentration (ppm)} + 440.6 \quad (6)$$

Quantification was performed by duplicate. These values had an error of approximately 20%. Figure 2 shows the amount of histamine found in each extract.

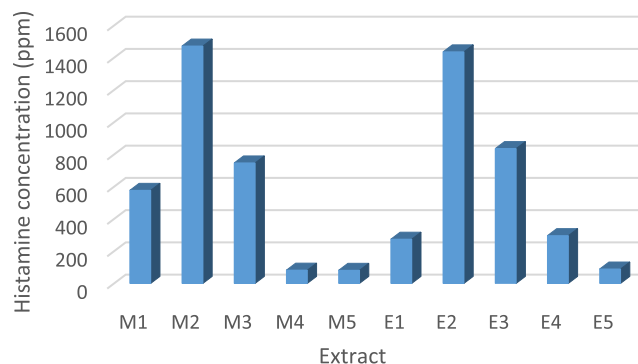


Figure 2. Final histamine concentration for each of the extracts.

As expected, the extracts with the highest histamine content were M2 and E2. The reason is that they come from a fish effluent matrix, where the largest generation of biogenic amines is presumed to exist. Both had a very similar histamine concentration, so the solvents used in extraction did not show a marked difference in these extracts. Extracts M3 and E3 had

similar histamine concentrations. However, for M1 and E1, the extraction efficiency was greater with methanol.²¹

5.2. Analytical-Grade Histamine and Commercial Organic Compound Solutions. Analytical-grade histamine solutions were prepared at 1, 0.5, and 0.2% w/w concentrations. Similarly, solutions of commercial organic compounds were prepared at the same concentrations. These solutions are shown in Table 5.

5.3. Gas Characterization after Reactions. The volatile compounds (from ethane to heptane) and H₂S come mainly from the reaction of organic compounds contained in crude oil with water. H₂S formation is connected to CO, CO₂, and light hydrocarbon formation.^{1,27} Figure 3 shows that extracts with

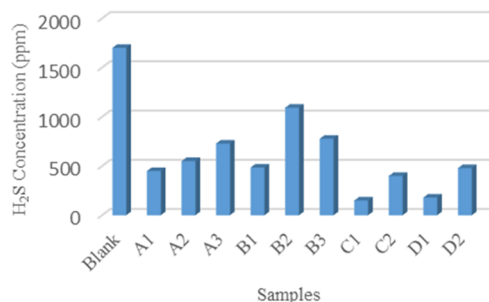


Figure 3. Influence of solutions on H₂S production.

methanol and ethanol were generally more effective at scavenging H₂S than those treated with commercial organic compounds or histamine solutions. This occurs due to a group of biogenic amines obtained in matrices prepared from decaying fish. These amines can include histamine, cadaverine, putrescine, and agmatine. They enhance the scavenging effect of H₂S as a scavenger amino group, contrary to histamine-prepared solutions, in which the impact of a single amine is available and, therefore, has less scavenging capacity. To verify this, note that in systems where A1, A2, and A3 are present, H₂S was reduced by 74–57% concerning the blank system value. However, these solutions differ in histamine concentration from C1 and D1 samples. The C1 and D1 solutions have a histamine concentration of 1472 and 1436 ppm, and H₂S was reduced by 91 and 89%, respectively. This fact shows that this concentration of amines for the extract is not just histamine, but a possible group of amines.

C1 and D2 extracts are obtained from the matrix prepared from the fishing effluent, with 48 h of decomposition. So, it is deduced that this matrix has a higher concentration of biogenic amines than the other matrices.

5.4. Effect of Additives on Gases from the Reaction. Equations 1–5 show that during the aquathermolysis reaction, the C–S bond of the S-containing organic molecule of heavy oil ruptured, resulting in H₂S, CO₂, and H₂ in the gas products.^{9,14,17} In all systems, there is a higher production of CO₂ compared with the light compounds produced. This CO₂ may be produced by different paths, such as the decarboxylation of carboxylic derivatives or the water gas shift reaction (WGSR):



According to some researchers,^{1,2,10,27,28} this reaction is critical because the thermodynamic equilibrium is shifted to the right side at temperatures above 200 °C, being promoted by the mineral compounds contained in the system. This could

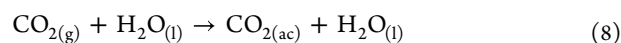
be considered a low-temperature WGSR between 150 and 280 °C. Industrially, the LT-WGSR is carried over Cu–Al–Zn catalysts.²⁷ Let us remember that minerals can catalyze these reactions at downhole conditions.

The initial rupture of the sulfur–carbon bond from aquathermolysis generates carbon monoxide, which participates in this reaction, producing CO₂ and molecular hydrogen, the presence of the latter suggesting the possibility of crude oil upgrading through hydrogenation. Since crude oil compounds and their associated minerals can catalyze the water gas shift reaction, CO₂ can be expected to predominate over CO in the gases produced. Only CO₂ is observed in some cases.² A possible hydrogenation can be interpreted at least on the gas side. Table 6 shows very low or undetectable amounts

Table 6. Gas Compositions from Reactions

gas (% molar) system	H ₂	CO ₂	CH ₄	C ₂ –C ₅ ⁺	CO	H ₂ S (ppm)	H ₂ S removal (%)
blank	0.05	2.96	96.80	1.21	0	1700	
A1	0.00	2.66	97.27	1.19	0.01	450	74
A2	0.00	2.91	96.95	0.83	0.01	550	68
A3	0.09	4.18	95.61	3.45	0.02	729	57
B1	0.00	2.39	97.55	0.42	0	486	71
B2	0.15	3.34	94.13	0.21	0.02	1093	36
B3	0.00	1.83	96.99	0.01	0	777	54
C1	0.00	2.04	96.82	0.01	0	150	91
C2	0.00	2.28	96.32	0.01	0	400	76
D1	0.04	2.14	94.37	0.01	0	180	89
D2	0.00	2.57	95.94	0.01	0.01	480	72

of CO. This means that the CO generated during the aquathermolysis reactions eventually became CO₂. However, amounts of CO₂ produced by different paths during aquathermolysis reactions limit the water gas shift reaction, displacing the equilibrium to the left CO and H₂O sides, thus reducing hydrogen production. Furthermore, the CO₂ produced could tend to acidify the aqueous system as follows:



In this way, the medium is acidified, promoting the catalysis of polymeric reactions between the different fragments generated during the breakdown of the organosulfur compounds in the aquathermolysis reaction. In addition, Table 6 shows that the percentage of CO₂ produced decreases for methanol extracts concerning the blank more than the systems treated with analytical-grade histamine and the commercial organic compound, whereas in some cases, these percentages, instead of decreasing, increase. This indicates that less acidic conditions are being generated in the systems treated with methanol, possibly due to the formation of the group of amines that react with CO₂, producing, under these conditions, compounds such as carbonates, carbamates, and bicarbonates.^{15,17} This limits polymeric reactions, thus resulting in the formation of heavier compounds in crude oil. In this way, it can be noted that the overall effect of amines makes it possible not only to reduce H₂S but also to decrease the overall amount of CO₂. Amines react with organic and inorganic acids (neutralization reaction), resulting in crystalline and stable salts.²⁷

5.5. Characterization of Crude Oil after Reactions.

5.5.1. Viscosity. Figure 4 shows that for most of the solutions

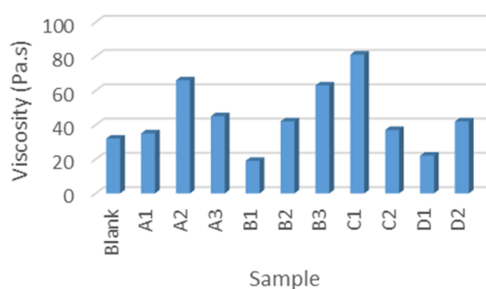


Figure 4. Viscosity of crude oil in the various post-reaction systems at 50 °C.

treated with analytic histamine and the organic compound, the viscosity of the crude oil increases in comparison with the blank, except the mixture treated with analytical-grade histamine solution at 2000 ppm (A3), whose final viscosity decreases. On the other hand, in the A3 and C2, the oil viscosity reduced notably. When oil is exposed to conditions favorable for aquathermolysis, the primary mechanism comprises reactions between vapor/water and organic sulfides in heavy crude oil.^{2,7,8,10} Under these injection conditions, the C–S bonds in the sulfides are easily broken. In addition, other bonds, such as C–N and C–O, are affected. Reactive species from aquathermolysis, probably organ-sulfurized compounds, can polymerize or react with water to produce smaller fragments involved in subsequent reactions considered an essential part of the total aquathermolysis process. Acid polymerization produces unwanted viscosity increases due to free radicals formed through aquathermolysis, which generate much longer molecules.

Thus, for the systems shown in Figure 4, those treated with analytical-grade histamine, the commercial organic compound, as well as the methanol and ethanol extracts, besides producing smaller molecules by aquathermolysis, acid polymerization reactions are also favored, resulting in an increased viscosity in the crude oil.

5.5.2. API Gravity. Figure 5 shows that no significant changes in API gravity were observed after the reaction for the

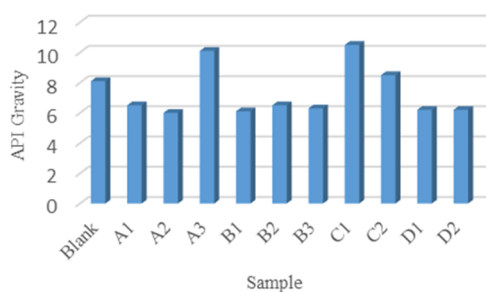


Figure 5. API gravity in oil samples after the reaction.

group of samples. Differences were only observed in samples A3, C1, and C2. The API gravity values increase, which means that there is an improvement in the crude oil and a decrease in viscosity compared with the virgin crude oil (percentages of viscosity reduction compared with the blank test).

5.5.3. Saturated, Aromatic, Resin, and Asphaltene Fraction. When comparing SARA fractions of the original

crude and the blank product with all reaction products, there was an increase in saturated, aromatic, and asphaltene fractions, accompanied by a decrease in resin content. According to Lamoureux-Var et al.,²⁹ resins are long-chain branched structures with diverse linear and aromatic functional groups throughout their composition. Due to molecular rearrangement, the resin fraction ultimately leads to the production of saturated and aromatic fractions. Therefore, the reduction in resin fraction and the conversion of certain cyclic hydrocarbons could cause increased aromatics in the overall set of samples (see Table 7).

During this molecular reorganization in the aquathermolysis reaction, there were breakages in bonds involving heteroatoms, mainly in sulfur bonds. This phenomenon leads to more branched and complex compounds, such as asphaltenes. This observation aligns with the assertions of Hyne,² who proposed that variations in viscosity could also result from changes in molecular shape and conformation. Many authors assert that the formation of H₂S after the reaction is presumed to originate from the resin fraction in the crude, as both the resin and asphaltene fractions contain heteroatoms along their lengthy structure, including sulfur (resins can contain up to 45% sulfur).^{14,29} As shown in Table 7, the resin content significantly decreases in all cases, as discussed earlier, involving the organosulfur compounds present in the crude.

There were instances where the generation of H₂S was low, such as in the case of additives C1 (150 ppm) and D1 (180 ppm), which also exhibited a substantial decrease in resin content after the reaction (from 47 to 21% for C1; from 47 to 23% for D1). More concentrated scavenging additives were used in these reactions. This high reduction in resin content indicated that there was also a breakdown of organosulfur compounds in the crude oil for this series of reactions, along with the subsequent release of typical sulfur compounds such as mercaptans and H₂S. A slight increase in the saturated fraction was noticeable; however, in some cases, this rise was insufficient to solubilize the produced asphaltene content fully. Since the latter constitutes the heaviest fraction of crude and harbors many heteroatoms, this results in an upsurge in crude viscosity. Thus, the predominant factor contributing to the viscosity increase for most employed additives was the expansion of the asphaltene structure in each respective case, proving to be more influential than the saturated production and aromatics concerning crude viscosity effects.

5.6. Mass Balance in Sulfur Content. The sulfur values for each of the crude oils treated are listed in Table 8. According to Hyne,² the amount of H₂S generated during the steam injection process correlates well with the amount of organic sulfur in crude oil. Consequently, during the decomposition of organosulfur compounds of crude oil derived from their hydrolysis, the sulfur content in the crude oil decreases, affecting its physical characteristics. Thus, the percentage of sulfur in the systems studied decreases concerning that contained in the original crude oil since H₂S is produced, indicating organosulfur compounds' decomposition. So, it is essential to highlight the role of the scavenging effect of the extracts since the amount of H₂S expected from the desulfurization of crude oil is not obtained. This strengthens the fact that sulfur compounds are generated from the H₂S and amine compounds during the aquathermolysis of heavy crude.

In addition, Table 8 shows a marked decrease of sulfur in the crude oil for the cases of C2 and D2 (10 and 13%), whereas

Table 7. Crude Oil Characterization before and after the Reaction

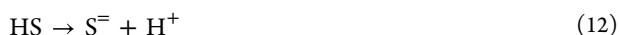
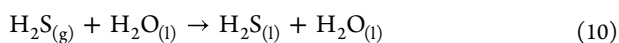
	saturated (% w/w) ± 1	aromatic (% w/w) ± 1	resin (% w/w) ± 1	asphaltene (% w/w) ± 1	sulfur (% w/w) ± 0.14	API gravity ± 0.6	viscosity at 50 °C (Pa·s) ± 1
original oil	7	35	47	11	3.48	8.4	32
blank	10	48	23	19	3.21	8.1	35
A1	14	43	27	16	3.44	6.5	66
A2	14	43	27	16	3.4	6	45
A3	11	39	35	15	3.41	10.1	19
B1	12	46	23	19	3.33	6.1	42
B2	13	45	25	17	3.06	6.5	63
B3	12	47	21	20	3.17	6.3	81
C1	16	50	21	13	3.4	10.5	37
C2	18	47	21	14	3.15	8.5	22
D1	13	47	23	17	3.35	6.2	42
D2	13	51	20	17	3.01	6.2	37

Table 8. Sulfur Mass Balance for Various Reactions (Weight)

system	before reaction			post-reaction				total
	sulfur in crude	sulfur in sand	total sulfur	sulfur in crude	sulfur in sand	sulfur in gas	total sulfur	general balance
blank	0.479	0.179	0.658	0.442	0.060	0.003	0.505	0.153
A1	0.458	0.179	0.637	0.452	0.219	0.001	0.673	0.000
A2	0.457	0.179	0.637	0.447	0.189	0.001	0.637	0.000
A3	0.456	0.179	0.636	0.447	0.179	0.002	0.628	0.007
B1	0.460	0.179	0.640	0.440	0.100	0.001	0.541	0.099
B2	0.457	0.179	0.637	0.402	0.090	0.003	0.494	0.142
B3	0.458	0.179	0.638	0.418	0.130	0.002	0.549	0.089
C1	0.458	0.179	0.637	0.447	0.080	0.001	0.528	0.109
C2	0.458	0.179	0.637	0.414	0.100	0.001	0.515	0.122
D1	0.457	0.179	0.637	0.440	0.070	0.001	0.511	0.126
D2	0.456	0.179	0.636	0.395	0.279	0.002	0.676	0.000

the percentage decrease of sulfur for the blank was lower (8%). Therefore, it is expected that since the reduction of the sulfur content is more significant for C1 and C2, more H₂S is generated during the aquathermolysis reaction. In most cases, the amounts of sulfur before and after the reaction do not coincide, i.e., the input and output are unequal. This is because the amount of sulfur present in the injection water added to the system is not considered and compounds containing sulfur generated from histamine, biogenic amines, or even H₂S itself may be dissolved in this medium.

There is a difference between the sulfur content before and after the reaction. It can be attributed to the separation process between sand and oil when the spectrometry atomic emission method is carried out. The H₂S formed at low pressures is dissolved in water, forming HS⁻ and H⁺, according to the following equations^{14,27}



The H₂S formed can be dissolved in the aqueous phase, but it cannot be physically accounted for due to the small amount of water used; in addition, H₂S is usually lost during subsequent separations between sand and treated crude oil.

6. CONCLUSIONS

The sample prepared from a fish effluent with 48 h of decomposition had a higher content of biogenic amines than

those obtained from the same fish effluent with 24 and 72 h of decomposition, as well as those prepared from tuna and sardine flours.

Methanol is the most effective solvent in the extraction of biogenic amines, with an average extraction of 592 ppm of these amines for the five matrices evaluated.

Using biogenic amines in H₂S mitigation due to steam injection technology is feasible since a lower concentration in an alcohol solution has a combined H₂S scavenging action as effective as that of aqueous solutions of analytic-grade histamine with higher concentrations.

Extracts prepared from fish effluent with 48 h of decomposition in methanol proved the most effective in H₂S scavenging and, generally, in acid gas reduction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c09235>.

Experimental techniques for component characterization pre- and postaquathermolysis reactions covering heavy oil, sand mineralogy, and gas composition; composition of synthetic injection water according to API RP 45 standards, detailing ion concentrations; and comprehensive characterization of oil and sand samples, including chemical compositions, viscosity, API gravity, and mineral content (PDF)

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<https://pubs.acs.org/10.1021/acsomega.3c09235>

Notes

The authors declare no competing financial interest.

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