Fuel 216 (2018) 681–685

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

# Spectroscopic evaluation of commercial $H_2S$ scavengers

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## ARTICLE INFO

*Keywords:*
Crude oil
Scavengers
Hydrogen sulfide
PCA

## ABSTRACT

The presence of hydrogen sulfide ($H_2S$) poses many challenges in the production of petroleum at all stages of crude oil refinement and processing. Injection of an $H_2S$ scavenger into the hydrocarbon stream is most commonly used to reduce the concentration of $H_2S$. Several $H_2S$ scavengers are commercially available, but each one must be examined to determine its suitability in terms of efficiency for capturing sulfide in petroleum. Therefore, in the present work, we proposed a system and process (hereinafter denoted as experimental setup/design) to test various $H_2S$ scavengers for their ability to efficiently capture sulfide in petroleum. To accomplish this, 46 samples of commercial $H_2S$ scavengers were tested using spectroscopy in the infrared region in association with Principal Component Analysis. It was concluded that samples with extreme pH and absorbance band intensity at 1175 $cm^{-1}$ greater than 0.095 showed the best efficiency for capturing sulfide in petroleum and that success of competing scavengers could be predicted based on these parameters.

## 1. Introduction

The presence of sulfur compounds in petroleum, especially hydrogen sulfide ($H_2S$), may cause damage at several stages of petroleum production and refinement. $H_2S$, a gas known for its rotten egg odor, is colorless and inflammable. It is an environmental contaminant and harmful to health at concentrations as low as 50 parts per million (ppm). The effects on human health from exposure to $H_2S$ are irritation and asphyxia, depending on the concentration and time of exposure [1]. This gas is soluble in water where it behaves like a weak acid. It reacts with iron to form iron sulfide, a very corrosive product that is insoluble and adheres to steel surface, leading to clogging of equipment [2,3]. $H_2S$ is a contaminant commonly present in the production streams in oil and gas fields and must be removed from the oil to reduce environmental pollution, protect workers' health and avoid corrosion and clogging of pipes and equipment [4,5].

Petroleum companies commonly inject scavengers into crude oil to remove or reduce $H_2S$ [6–8]. $H_2S$ scavengers are commercial formulations whose compounds have the ability to react with and capture sulfide in crude oil. Thus, products based on triazines, ethanolamines and aldehydes are frequently used [9,10]. $H_2S$ scavengers may be added to drilling fluids or to oil and gas production processes [11]. However, the performance of these products has never been fully evaluated or understood [12–14].

Therefore, the improvement of efficiency in petroleum treatment calls for strategies to optimize these evaluative processes, including, for example, the use of chemometric tools. Such tools combined with technological and instrumental development make it possible to apply multivariate analysis to chemical data. In exploratory analysis, some methods have applied function curves that typically represent the largest possible amount of information contained in a set of analytical data. Among those methods, Principal Component Analysis (PCA) is most frequently applied. It is a chemometric tool used for identification of a smaller number of uncorrelated variables known as principal components from a larger set of data. Essentially, PCA reduces the dimension of original data to so-called principal components, or PCs, thus allowing the natural grouping of the data and facilitating the identification of more important variables in a determined system (detection and evaluation). From PCs, two new datasets are generated and denoted as scores (**T**) and loadings (**P**), as

$$\boldsymbol{X} = \boldsymbol{T}\boldsymbol{P}^T + \boldsymbol{E} \tag{1}$$

where **X** is spectral matrix, and **T** and **P** provide, respectively, information on samples and variables [15,16]. **E** is a residual matrix. When analyzing the scores, it is possible to more carefully study the data without the loss of relevant information [17,18].

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https://doi.org/10.1016/j.fuel.2017.12.021
Received 12 July 2017; Received in revised form 29 November 2017; Accepted 4 December 2017
0016-2361/

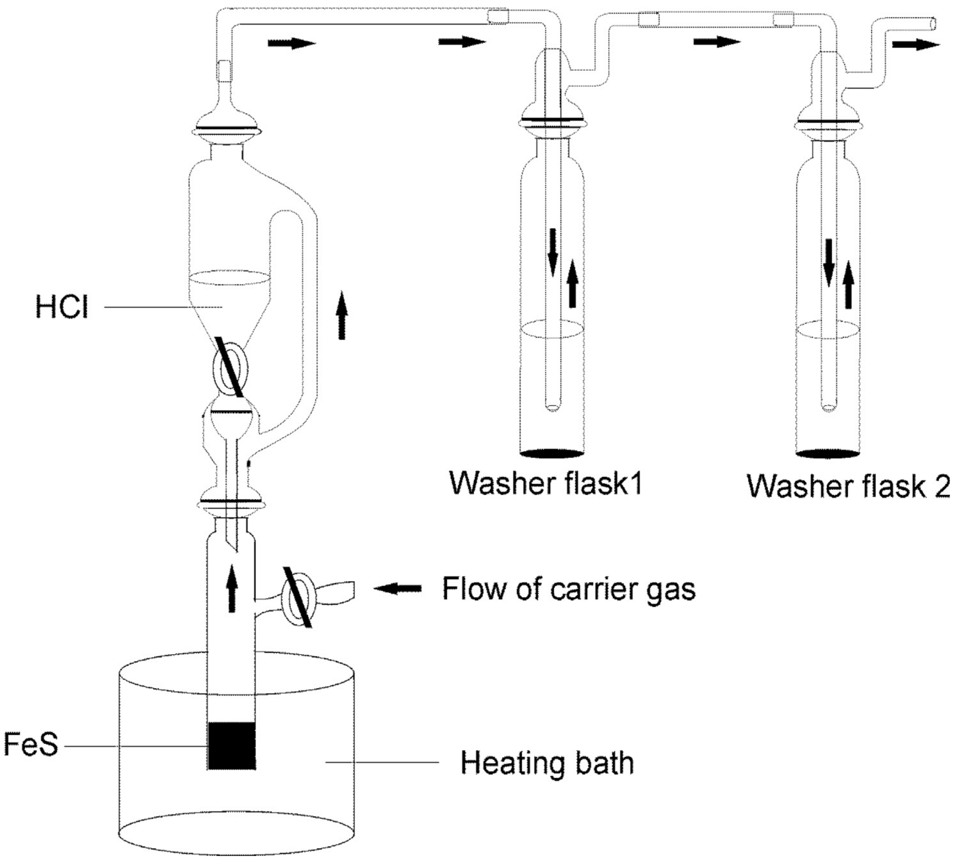

**Fig. 1.** Experimental system to produce and capture $H_2S$.

Thus far, no studies have evaluated and compared the relative efficiency of various commercially available $H_2S$ scavengers in terms of their ability to react with and capture sulfide in crude oil. Therefore, in the present work, we propose an experimental setup designed to test various $H_2S$ scavengers for their ability to efficiently capture sulfide in petroleum at laboratory scale, using spectroscopy in the infrared region in association with PCA.

## 2. Experimental

In this paper, 46 samples of commercial scavengers of $H_2S$ were tested for their performance in capturing sulfide in petroleum. The crude oil came from a field in a sedimentary basin on the coast of Espírito Santo, Brazil.

### 2.1. Experimental design for testing $H_2S$ scavengers

The proposed experimental design (Fig. 1) included a glassware setup connected with a spherical joint and seal between the pieces with apertures just in the entry of the carrier gas and in the outlet of the flow. First, $H_2S$ is formed and then passed through the scavenger sample emulsified in petroleum. The amount of sulfide captured by each scavenger is determined at the same operational conditions. When $6.0\,mol{\cdot}L^{-1}$ hydrochloric acid (HCl) reacts with iron sulfide II (FeS), we know that $H_2S$ has been formed (Reaction (2)) in the generator flask inside the system. Thus, by opening the funnel tap, separation allows HCl to react slowly with FeS within 2 min. The sulfur content in the composition of the standard FeS sulfide is then verified by elemental analysis. The generator flask is connected to a carrier gas to inject $H_2S$ bubbles into washer flasks 1 and 2 during 60 min. These flasks respectively contain the mixture of 2 wt% of commercial $H_2S$ scavenger in petroleum and a solution of $5\,mol{\cdot}L^{-1}$ sodium hydroxide (NaOH). In the experiment, the process continued as follows. The generator flask of $H_2S$ was placed in a heating bath at a temperature of 65 °C ( ± 1 °C). Argon gas (Ar) was used as the carrier gas to ensure that the formed $H_2S$ was bubbled into the mixture of $H_2S$ scavenger and petroleum. Hence, washer flask 1 contained that part of the sulfide captured by the scavenger emulsified with petroleum, while flask 2 contained the part that was not (Reaction (3)). The efficiency of the $H_2S$ scavengers depends on the amount of sulfide captured.

$$2HCl_{(aq)} + FeS_{(s)} \rightleftharpoons H_2S_{(g)} + FeCl_{2(aq)} \tag{2}$$

$$H_2S_{(g)} + 2NaOH_{(aq)} \rightleftharpoons Na_2S_{(aq)} + 2H_2O_{(l)} \tag{3}$$

Sulfide captured in each flask was quantitated by potentiometric titration according to the UOP (Universal **Oil** Products) method 163 [19]. Scavenger efficiency was evaluated based on the captured sulfide concentration in the mixture of scavenger and oil. Thus, sulfide concentration captured by the $H_2S$ scavenger emulsified in petroleum correlates with the efficiency of the particular product such that higher sulfide concentration, as determined by potentiometric titration of flask 1's contents, represents increased efficiency.

Washer flask 2 contains the sulfide not captured in washer flask 1, as noted above, thus ensuring that the quantitation of this remnant, essentially because potentiometric titration should have detected the capture of whole sulfide by the scavenger, observing the sums of sulfide captured in flasks 1 and 2, when compared to the calibration value.

To verify the percentage of sulfide produced that was captured and quantified by the experimental system, calibration was performed using only the solution flask containing $5\,mol{\cdot}L^{-1}$ NaOH. The calibration procedure was repeated six times in order to obtain an average representative of six different days.

### 2.2. The prediction test of sulfide capture efficiency in petroleum

A PCA model was implemented using data acquired from middle infrared spectra of the scavengers. The spectral range used in the