PROCESS FOR REMOVING HYDROGEN SULFIDE IN CRUDE OIL

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ABSTRACT

A method for reducing the amount of hydrogen sulfide present in crude oil includes adding a hydrogen sulfide scavenger composition to the crude oil to capture the hydrogen sulfide, migrating the captured sulfides to an aqueous phase and removing the aqueous phase from the crude oil. The hydrogen sulfide scavenger composition includes glyoxal and a quaternary ammonium salt.
PROCESS FOR REMOVING HYDROGEN SULFIDE IN CRUDE OIL

FIELD OF THE INVENTION

[0001] This invention relates generally to methods for removing hydrogen sulfide and more particularly, to removing hydrogen sulfide from crude oil.

BACKGROUND OF THE INVENTION

[0002] Crude oil may contain hydrogen sulfide, which is highly corrosive in the presence of water and poisonous in very small concentrations. The risk of exposure to hydrogen sulfide from handling crude oil is a health and safety concern during storage, transportation (shipping, truck or pipeline) and processing of the crude oil.

[0003] Hydrogen sulfide scavengers are used to remove hydrogen sulfide from the crude oil. Typical hydrogen sulfide scavengers are triazines and aldehydes. However, triazines release amines into the liquid hydrocarbon media and residual triazines thermally decompose to release additional amines into the liquid hydrocarbon media and may pose additional health concerns. The free amines can form salts, which deposit on the processing equipment and cause corrosion. Aldehydes can have slower reaction kinetics and may have incomplete hydrogen sulfide scavenging.

[0004] What is needed is an improved scavenger for removing hydrogen sulfide from crude oil.

BRIEF DESCRIPTION OF THE INVENTION

[0005] In one embodiment, a method for reducing the amount of hydrogen sulfide present in crude oil includes adding a hydrogen sulfide scavenger composition to the crude oil to capture the hydrogen sulfide, migrating the captured sulfides to an aqueous phase and removing the aqueous phase from the crude oil, wherein the hydrogen sulfide scavenger composition includes glyoxal and a quaternary ammonium salt.

[0006] The various embodiments provide an improved hydrogen scavenging process for crude oil that quickly captures hydrogen sulfide and does not generate amine byproducts.

DETAILED DESCRIPTION OF THE INVENTION

[0007] The singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. The endpoints of all ranges reciting the same characteristic are independently combinable and inclusive of the recited endpoint. All references are incorporated herein by reference.

[0008] The modifier “about” used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., includes the tolerance ranges associated with measurement of the particular quantity).

[0009] “Optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, or that the subsequently identified material may or may not be present, and that the description includes instances where the event or circumstance occurs or where the material is present, and instances where the event or circumstance does not occur or the material is not present.

[0010] In one embodiment, a method for reducing the amount of hydrogen sulfide present in crude oil includes adding a hydrogen sulfide scavenger composition to the crude oil to capture the hydrogen sulfide, migrating the captured sulfides to an aqueous phase and removing the aqueous phase from the crude oil, wherein the hydrogen sulfide scavenger composition includes glyoxal and a quaternary ammonium salt.

[0011] The crude oil may be any type of crude oil containing hydrogen sulfide. Any amount of hydrogen sulfide the crude oil may be reduced and the actual amount of residual hydrogen sulfide will vary depending on the starting amount. In one embodiment, the hydrogen sulfide levels are reduced to 150 ppm by weight or less, as measured in the vapor phase, based on the weight of the crude oil. In another embodiment, the hydrogen sulfide levels are reduced to 100 ppm by weight or less, as measured in the vapor phase, based on the weight of the crude oil. In another embodiment, the hydrogen sulfide levels are reduced to 50 ppm by weight or less, as measured in the vapor phase, based on the weight of the crude oil. In another embodiment, the hydrogen sulfide levels are reduced to 20 ppm by weight or less, as measured in the vapor phase, based on the weight of the crude oil.

[0012] The hydrogen sulfide scavenger composition is added to the crude oil in any conventional manner. In one embodiment, the scavenger composition is injected into the crude oil by a conventional in-line injection system and may be injected at any point in-line suitable to allow the scavenger to mix with the crude oil, such as in a pipeline or in a tank. The scavenger composition can be added to the crude oil in a continuous manner or can be added in one or more batches and repeated additions may be made.

[0013] The scavenger composition is added to the crude oil in any amount sufficient to reduce the levels of hydrogen sulfide in the crude oil. In one embodiment, the scavenger composition is added in an amount of from about 1 ppm to about 3000 ppm by weight, based on the weight of the crude oil. In another embodiment, the scavenger composition is added in an amount of from about 10 ppm by weight to about 2000 ppm by weight, based on the weight of the crude oil. In another embodiment, the scavenger composition is added in an amount of from about 50 ppm by weight to about 1500 ppm by weight, based on the weight of the crude oil. In another embodiment, the scavenger composition is added in an amount of from about 100 ppm by weight to about 1200 ppm by weight, based on the weight of the crude oil.

[0014] The hydrogen sulfide scavenger may be added neat or diluted with water or solvent and may be formulated or blended with other suitable materials or additives.

[0015] The hydrogen sulfide scavenger composition captures and neutralizes hydrogen sulfide in the crude oil by incorporating the sulfur into an inert ringed compound. The ringed compound is non-hazardous and is attracted to the water phase and migrates to a water phase away from an oil phase.

[0016] The hydrogen sulfide scavenger composition comprises glyoxal and a quaternary ammonium compound. Glyoxal is a water-soluble aldehyde and may include oligomers of glyoxal. Glyoxal is commercially available. The glyoxal is catalyzed with a quaternary ammonium salt, which improves the efficacy of the scavenger composition and enhances removal of hydrogen sulfide. The catalyst may be any suitable quaternary ammonium salt. In one embodiment, the catalyst has formula:  

$$\text{R}_1 \text{R}_2 \text{R}_3 \text{R}_4 \text{N}^+ \text{X}^-$$

wherein $\text{R}_1$, $\text{R}_2$ and $\text{R}_4$ are each independently an alkyl group having from 1 to 30 carbon atoms, an aryl group having from 6 to 30 carbon atoms or an arylalkyl group having from 7 to 30 carbon atoms; and $\text{X}$ is a halide, sulfate, nitrate or carboxylate. The alkyl groups and the aryl groups may be substituted or unsubstituted.

[0017] In one embodiment, $\text{R}_1$ is an alkyl group having from 1 to 24 carbon atoms. In one embodiment, $\text{R}_2$ is an alkyl
having from 1 to 24 carbon atoms, an aryl group having from 6 to 24 carbon atoms or an arylalkyl group having from 7 to 24 carbon atoms.

[0018] In one embodiment, R\textsuperscript{3} and R\textsuperscript{4} are each, independently, an alkyl group having from 1 to 24 carbon atoms. In another embodiment, R\textsuperscript{3} and R\textsuperscript{4} are each, independently, an aryl group having from 1 to 4 carbon atoms.

[0019] The alkyl group includes, but is not limited to, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, decyl or dodecyl. The aryl group may be phenyl. The arylalkyl group include may be benzyl. The halide may be chloride, bromide or iodide. The sulfite may be a methyl sulfate. The nitrate may be a bisulfite nitrate. The carboxylate may be acetate.

[0020] In one embodiment, the quaternary ammonium salt is alkyl benzyl ammonium chloride or benzyl cocaoyl (C\textsubscript{12}–C\textsubscript{18}) dimethylammonium chloride. In another embodiment, the quaternary ammonium salt includes, but is not limited to dicocaoyl (C\textsubscript{12}–C\textsubscript{18}) dimethylammonium chloride, didecamethylenedimethylammonium chloride, di(dihydrated tallow alkyl) dimethyl quaternary ammonium methyl chloride, methyl bis(2-hydroxyethyl cocaoyl (C\textsubscript{12}–C\textsubscript{18}) quaternary ammonium chloride, dimethyl(2-ethyl) tallow ammonium methyl sulfite, n-dodecylbenzyl dimethylammonium chloride, n-octadecylbenzyl dimethylammonium chloride, n-dodecyltrimethylammonium sulfite, soya alkyltrimethylammonium chloride or hydrogenated tallow alkyl (2-ethyl-hexyl) dimethyl quaternary ammonium methylsulfate.

[0021] In one embodiment, the quaternary ammonium salt is present from about 0.01 to about 15 percent by weight based on the amount of glyoxal. In another embodiment, the quaternary ammonium salt is present from about 1 to about 10 percent by weight based on the amount of glyoxal.

[0022] The scavenger composition is attracted to an aqueous phase and the captured sulfides will migrate into an aqueous phase. If an emulsion is present, the captured sulfides can be migrated into the aqueous phase from the crude oil and removed with the aqueous phase. If no emulsion is present, a water wash can be added to attract the captured sulfides. In one embodiment, the hydrogen sulfide scavenger composition is added before the crude oil is treated in a desalter, which emulsifies the hydrocarbon media with a water wash to extract water soluble contaminants and separates and removes the water phase from the crude oil.

[0023] In one embodiment, a water wash is added in an amount suitable for forming an emulsion with the crude oil. In another embodiment, the water wash is added in an amount of from about 1 to about 50 percent by volume based on the volume of the emulsion. In another embodiment, the wash water is added in an amount of from about 1 to about 25 percent by volume based on the volume of the emulsion. In another embodiment, the water wash is added in an amount of from about 1 to about 10 percent by volume based on the volume of the emulsion. In one embodiment, the amount of crude oil is present in an amount of from about 50 to about 99 percent by volume based on the volume of the emulsion. In another embodiment, the crude oil is present in an amount of from about 75 to about 99 percent by volume based on the volume of the emulsion. In another embodiment, the crude oil is present in an amount of from about 90 to about 99 percent by volume based on the volume of the emulsion.

[0024] The water wash and crude oil are emulsified by any conventional manner. In one embodiment, the water wash and crude oil are heated and thoroughly mixed to produce an oil-in-water emulsion. In one embodiment, the water wash and crude oil are heated at a temperature in a range of from about 90°C to about 150°C. The water wash and crude oil are mixed in any conventional manner, such as an in-line static mixer or an in-line mix valve with a pressure drop of about 0.2 to about 2 bar depending on the density of the crude oil. The emulsion is allowed to separate, such as by settling, into an aqueous phase and an oil phase. In one embodiment, the aqueous phase is removed. In another embodiment, the aqueous phase is removed by draining the aqueous phase.

[0025] Demulsifiers may be added to aid in separating the water from the crude oil. In one embodiment, the demulsifiers include, but are not limited to, oxalkylated organic compounds, anionic surfactants, nonionic surfactants or mixtures of these materials. The oxalkylated organic compounds include, but are not limited to, phenolformaldehyde resin ethoxylates, alkoxylated polyols and amides, such as Phronic® block co-polymers. The anionic surfactants include alkyl or aryl sulfonates, such as dodecyl benzene sulfonate. These demulsifiers may be added in amounts to contact the water from about 1 to about 1000 ppm by weight based on the weight of the crude oil. Combinations of additives may be used, but the total amounts of additives added should be in the range of from about 1 to about 1000 ppm by weight based on the weight of the crude oil.

[0026] In order that those skilled in the art will be better able to practice the present disclosure, the following examples are given by way of illustration and not by way of limitation.

EXAMPLES

Example 1

[0027] Hydrogen sulfide scavenging tests were performed on a crude oil containing 500 ppm hydrogen sulfide in the liquid phase from a Texas refinery in Valero. Testing was performed using the modified ASTM 5705-95 test that measures vapor phase H\textsubscript{2}S two hours after treatment (140°F) via dragger tube. Results are shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H\textsubscript{2}S Scavenger (1000 ppm)</th>
<th>Residual H\textsubscript{2}S (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE-1</td>
<td>MEA\textsuperscript{a} triazine</td>
<td>400</td>
</tr>
<tr>
<td>CE-2</td>
<td>Triazine 8411C\textsuperscript{b}</td>
<td>120</td>
</tr>
<tr>
<td>CE-3</td>
<td>MMA\textsuperscript{c} triazine + Catalyst\textsuperscript{d}</td>
<td>200</td>
</tr>
<tr>
<td>CE-4</td>
<td>MEA\textsuperscript{a} triazine + Catalyst\textsuperscript{d}</td>
<td>200</td>
</tr>
<tr>
<td>CE-5</td>
<td>Glyoxal</td>
<td>950</td>
</tr>
<tr>
<td>1</td>
<td>Glyoxal + Catalyst\textsuperscript{d}</td>
<td>140</td>
</tr>
</tbody>
</table>

\textsuperscript{a}MEA is monoethanolamine

\textsuperscript{b}Triazine 8411C is available commercially from Clearwater, Inc as Stealth-Clear 8411C.

\textsuperscript{c}MMA is monomethylamine

\textsuperscript{d}Catalyst is cocaoyltrimethylbenzyl ammonium chloride (Arcapal® DMCH-80) at 1.6% by weight treatment level (actives basis) based on the weight of the triazine or glyoxal.

[0028] Sample 1 has comparable results to the use of a triazine in reducing hydrogen sulfide, but the catalyzed glyoxal can be removed in an aqueous phase; whereas, the triazine remains with the oil and can generate amines upon further processing. The catalyzed glyoxal sample shows significant improvement over glyoxal; whereas, catalyzing the triazine does not improve the performance of the triazine.

Example 2

[0029] The concentration of the hydrogen sulfide in the vapor phase was determined at different levels of treatment dosages after 1 hour and 2 hours for samples 1 and comparative examples CE-1 and CE-3, as shown in Table 2.
The samples reduce and control the hydrogen sulfide level. Sample 1 has comparable results to CE-1 and CE-3. However, Sample 1 can be removed in a aqueous phase and does not remove amine like the triazine samples will.

Example 3

5 g of H₂S was bubbled into a 2 L flask containing 1 L of a commercially available raw crude sample containing <25 μg/ml of hydrogen sulfide initially. The flask was equipped with a mechanical stirrer and a condenser with a caustic trap. The crude oil was stirred at room temperature for 1 hour. The H₂S concentration in the H₂S-infused crude was 3940 μg/ml.

A demulsifier was added to the H₂S-infused crude oil in the amounts shown in Table 3.

5% by volume wash water was mixed with glyoxal and cocouallydimethylbenzyl ammonium chloride, as shown in Table 3, and added to the H₂S-infused crude oil. The wash water was mixed with the H₂S-infused crude oil at 4000 ppm for 2 seconds, grids on, and heated to 130° C, at a pressure of 4 psi to form an emulsion.

The emulsion was allowed to sit for 30 minutes to separate the water phase from the crude oil. A water drop reading was performed to test the emulsion separation and is shown in Table 4. The water phase was removed from the separated emulsion and observed for clarity as shown in Table 3.

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Demulsifier (ppm)</th>
<th>Treatment² (ppm)</th>
<th>Mean Water Drop (ml)</th>
<th>Separated water Clarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>0</td>
<td>2.73</td>
<td>Clear</td>
</tr>
<tr>
<td>CE-8</td>
<td>6</td>
<td>0</td>
<td>4.50</td>
<td>Clear</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>100</td>
<td>4.50</td>
<td>Slightly cloudy</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>100</td>
<td>4.48</td>
<td>Slightly cloudy</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>250</td>
<td>4.75</td>
<td>Cloudy</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>250</td>
<td>4.70</td>
<td>Cloudy</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>500</td>
<td>4.75</td>
<td>Cloudy</td>
</tr>
<tr>
<td>7</td>
<td>12</td>
<td>500</td>
<td>4.75</td>
<td>Cloudy</td>
</tr>
</tbody>
</table>

¹Demulsifier is an alkoxylated alkylphenol formaldehyde available commercially from General Electric Company.
²Does not indicate an oleum total volume.
³Treatment is glyoxal and cocouallydimethylbenzyl ammonium chloride at 1.6% by weight treatment level (active basis) based on the weight of the glyoxal.

Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>1 min (ml)</th>
<th>2 min (ml)</th>
<th>4 min (ml)</th>
<th>8 min (ml)</th>
<th>16 min (ml)</th>
<th>32 min (ml)</th>
<th>Mean water drop (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.4</td>
<td>1.8</td>
<td>2.7</td>
<td>3.5</td>
<td>4</td>
<td>4</td>
<td>2.73</td>
</tr>
<tr>
<td>CE-8</td>
<td>1.8</td>
<td>4</td>
<td>4.7</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>4.50</td>
</tr>
<tr>
<td>2</td>
<td>1.8</td>
<td>4</td>
<td>4.7</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>4.50</td>
</tr>
</tbody>
</table>
7. The method of claim 4 wherein the arylalkyl group is benzyl.

8. The method of claim 4 wherein the halide is selected from the group consisting of chloride, bromide and iodide.

9. The method of claim 1 wherein the catalyst is alkyl benzyl ammonium chloride or benzyl cocaalkyl (C_{12}-C_{18}) dimethylammonium chloride.

10. The method of claim 1 wherein the catalyst is selected from the group consisting of dioctoalkyl (C_{12}-C_{18}) dimethylammonium chloride, benzyl cocaalkyl (C_{12}-C_{18}) dimethylammonium chloride, ditafoowdimethyldimonium chloride, di(hydrogenated tallow alkyl) dimethyl quaternary ammonium methyl chloride, methyl bis[2-hydroxyethyl] cocooalkyl (C_{12}-C_{18}) quaternary ammonium chloride, dimethyl(2-ethyl) tallow ammonium methyl sulfate, n-dodecylbenzyldimethylammonium chloride, n-octadecylbenzyldimethyl ammonium chloride, n-dodecyltrimethylammonium sulfate, soya alkyltrimethylammonium chloride and hydrogenated tallow alkyl (2-ethylhexyl) dimethyl quaternary ammonium methyl sulfate.

11. The method of claim 1 wherein the quaternary ammonium salt is present from about 0.01 percent by weight to about 15 percent by weight based on the weight of the glyoxal.

12. The method of claim 11 wherein the quaternary ammonium salt is present from about 1 percent by weight to about 10 percent by weight, based on the weight of the glyoxal.

13. The method of claim 1 wherein the crude oil is treated in a desalter.

14. The method of claim 13 wherein a water wash is added to the crude oil.

15. The method of claim 14 wherein the water wash is added in an amount of from about 1 percent by volume to about 10 percent by volume based on the volume of the emulsion.

16. The method of claim 14 wherein the water wash is added in an amount of from about 1 percent by volume to about 25 percent by volume of the emulsion.

17. The method claim 14 wherein the water wash and crude oil are emulsified by heating and mixing the crude oil and water wash.

18. The method of claim 14 wherein the crude oil and water wash are heated to a temperature in a range of from about 90° C. to about 150° C.

19. The method of claim 14 wherein the wash water is removed by draining.

* * * * *