

EMULSIFICATION OF HYDROCARBON GAS OILS TO INCREASE EFFICACY OF WATER BASED HYDROGEN SULFIDE SCAVENGERS

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates generally to processing heavy oil, and more particularly, to methods for removing hydrogen sulfide in heavy oil with an aqueous-based scavenger/oil emulsion.

Description of Related Art

[0002] Fossil products, and notably heavy oil, often contain significant quantities of hydrogen sulphide, H₂S, which is a toxic, highly corrosive, inflammable and explosive gas. The risk of exposure to hydrogen sulfide from handling heavy oil is a health and safety concern during storage, transportation (shipping, truck or pipeline) and processing.

[0003] Hydrogen sulfide scavengers can be used to remove hydrogen sulfide from heavy oil. It is known to be possible to reduce the hydrogen sulphide content present in aqueous mediums by using aqueous solutions of aldehydes such as formaldehyde, glyoxal, and glutaraldehyde (see for example the U.S. Pat. Nos. 4,680,127 and 5,284,635). However, simple addition of water-based hydrogen sulfide scavengers to heavy oil provides poor results. Additionally, when dispersed in a heavy oil, water-based scavengers such as glyoxal will eventually settle out of the heavy oil into an acidic aqueous phase and settle to the bottom of processing equipment. This aqueous phase may run along the bottom of the processing or refinery equipment as small tributaries in pipelines or stagnate at the bottom of holding tanks. This acidic aqueous phase is highly corrosive and can cause troughing in the processing or refinery equipment.

[0004] What is needed is an improved method for removing hydrogen sulfide from hydrocarbon media without causing corrosion to processing equipment.

SUMMARY OF THE INVENTION

[0005] In one aspect, the invention is directed to a method for reducing the amount of hydrogen sulfide present in heavy oil and reducing the amount of corrosion in processing equipment contacting the heavy oil. The method includes the steps of adding an aqueous-based scavenger containing one or more aldehydes to the heavy oil using a static mixer injection system and creating an aqueous-based scavenger/heavy oil emulsion using a high shear/high velocity pump. In one embodiment, the method further includes diverting a portion of the heavy oil into a scavenger addition branch, adding the aqueous-based scavenger to the portion of the heavy oil and forming the emulsion in the addition branch, and adding the aqueous-based scavenger/oil emulsion to the heavy oil in the processing equipment. In one desirable embodiment, the aqueous-based scavenger is glyoxal. The various embodiments provide an improved hydrogen sulfide scavenging process for heavy oil that reduces hydrogen sulfide while minimizing corrosion to processing equipment.

[0006] The present invention and its advantages over the prior art will become apparent upon reading the following detailed description and the appended claims with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The above mentioned and other features of this invention will become more apparent and the invention itself will be better understood by reference to the following description of embodiments of the invention taken in conjunction with the accompanying drawings, wherein:

[0008] FIG. 1 is a schematic diagram of an aqueous-based scavenger addition system for use with hydrocarbon media processing equipment.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The invention will now be described in the following detailed description with reference to the drawings, wherein preferred embodiments are described in detail to enable practice of the invention. Although the invention is described with reference

to these specific preferred embodiments, it will be understood that the invention is not limited to these preferred embodiments. But to the contrary, the invention includes numerous alternatives, modifications and equivalents as will become apparent from consideration of the following detailed description.

[0010] 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.

[0011] 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).

[0012] “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.

[0013] Turning now to Figure 1, a hydrogen sulfide scavenger addition system 10 is fluidically connected to processing equipment 12 for hydrocarbon media. The scavenger system 10 reduces the amount of hydrogen sulfide present in the hydrocarbon media, such as heavy oils, by adding an aqueous-based scavenger in a manner so as to desirably avoid causing significant corrosion to processing equipment 12. Aqueous-based scavengers are useful for the elimination of hydrogen sulphide present in various fluids and notably are particularly effective at eliminating the hydrogen sulphide present in heavy oils which can exist in the form of water in oil or oil in water emulsions. The processing equipment 12 in contact with the heavy oil may be any type of equipment that can be used for processing the hydrocarbon media, such as pipelines and holding tanks. Processing equipment 12 subject to corrosion is generally processing equipment made of carbon steel, but any type of processing equipment may be protected. The heavy oil may be any type of heavy oil containing hydrogen sulfide. In one embodiment, the heavy oil includes, but is not limited to, gas oil, naphtha, FCC slurry, diesel fuel, fuel oil, jet fuel, gasoline, kerosene or vacuum residua. In one embodiment,

the heavy oil may be at an elevated temperature to aid in transport in the processing equipment 12. For example, the heavy oil may be at a temperature of from about ambient to about 150 °C. Typically, the temperatures required to move the heavy oil in the processing equipment 12 is about 80 °C.

[0014] In the illustrated embodiment, a portion of the heavy oil flowing through the processing equipment 12 is diverted from the processing equipment 12 into the scavenger addition system 10 via a scavenger addition branch 14. A static mixer 16 is used to initially mix the scavenger with the portion of heavy oil flowing through the system 10. In one embodiment, the static mixer 16 comprises an injection quill dispersion system 18. The scavenger is added to the diverted heavy oil flow in a continuous manner with the injection quill 18 located generally at the center of the addition branch 14 in the direction of the heavy oil flow. The injection quill 18 desirably has an open-ended tube (not shown) cut at about a 45° angle with a slot. It utilizes the turbulence created to achieve distribution of the injected scavenger into the heavy oil flow in the addition branch 14. The scavenger injection rate is controlled with an injection pump 20 or shut-off valve 22 in addition line 24. A suitable injection quill 18 is available from Metal Samples Corrosion Monitoring Systems of Munford, AL. Alternately, the scavenger may be injected into the heavy oil by any conventional in-line injection system and may be injected at any point in-line suitable to allow the scavenger to mix with the heavy oil.

[0015] After addition of the scavenger to the heavy oil, an aqueous-based scavenger/oil micro-emulsion is formed using a high shear/high velocity mixer or pump 30. In one embodiment, an inline high shear pump 30 such as one available from Silverson Machines, Inc. of East Longmeadow, MA. The diverted portion of the heavy oil flow in the scavenger addition system 10, now containing the micro-emulsion, is then returned to the heavy oil flow in the processing equipment 12. Alternately, the scavenger may be added to the heavy oil flowing through the processing equipment without diverting a portion of the flow such that the entire heavy oil flow flows through the scavenger addition system 10.

[0016] According to the invention, the scavenger is a dispersed aqueous phase containing about 20 to 70% of one or more aldehydes chosen from the group constituted

by formaldehyde, glyoxal, glutaraldehyde, glycolaldehyde or glyoxylic acid. In one desirable embodiment, the water-based scavenger added to the heavy oil to reduce the hydrogen sulfide is Glyoxal. Glyoxal is a water-soluble aldehyde and may include oligomers of glyoxal. Glyoxal is commercially available as a 40 weight percent aqueous solution. The scavenger may also contain an enhancing additive to catalyze the reaction of actives with the hydrogen sulfide. In one embodiment, the enhancing catalyst is a quaternary ammonium salt. The quaternary ammonium salt desirably is added in an amount of about 2.5 wt %.

[0017] The glyoxal is added to the heavy oil in an amount sufficient to reduce the levels of hydrogen sulfide in the heavy oil. In one embodiment, glyoxal may be added in an amount of from about 1 ppm to about 2000 ppm, and desirably between about 1 ppm and about 500 ppm by volume, based on the velocity of the heavy oil through the processing equipment and the concentration of hydrogen sulfide. In another embodiment, glyoxal may be added in an amount of from about 10 ppm to about 200 ppm by volume. Any amount of hydrogen sulfide in the heavy 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 volume or less, as measured in the vapor phase, based on the volume of the heavy oil. In another embodiment, the hydrogen sulfide levels are reduced to 100 ppm by volume or less, as measured in the vapor phase, based on the volume of the heavy oil. In another embodiment, the hydrogen sulfide levels are reduced to 50 ppm by volume or less, as measured in the vapor phase, based on the volume of the heavy oil. In another embodiment, the hydrogen sulfide levels are reduced to 20 ppm by volume or less, as measured in the vapor phase, based on the volume of the heavy oil. It is believed that emulsification of the water-based scavenger in the hydrocarbon media greatly increases the surface area of the aqueous phase. This increased surface area in combination with the temperature required to move the hydrocarbon media in the pipeline allows for efficient transfer of actives into the hydrocarbon phase. This effective application of the scavenger reduces the amount of chemical that is needed to be added to the hydrocarbon media. Additionally, aided by turbulent flow in the pipeline, the water-based scavenger/oil micro-emulsion takes several hours to separate. Typically, this allows

sufficient time for the heavy oil to flow through the processing equipment 12 and into a suitable storage facility, thus, reducing any corrosion effects on the processing equipment 12.

[0018] While the disclosure has been illustrated and described in typical embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions can be made without departing in any way from the spirit of the present disclosure. As such, further modifications and equivalents of the disclosure herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the scope of the disclosure as defined by the following claims.

What is claimed is:

CLAIMS

1. A method for removal of hydrogen sulphide present in heavy oil in hydrocarbon media processing equipment, the method comprising the steps of:
adding an aqueous-based scavenger containing one or more aldehydes to the heavy oil using a static mixer injection system; and
creating an aqueous-based scavenger/heavy oil emulsion using a high shear/high velocity pump.
2. The method of claim 1 further comprising diverting a portion of the heavy oil into a scavenger addition branch, adding said aqueous-based scavenger to the portion of the heavy oil and forming the emulsion in the addition branch, and adding the aqueous-based scavenger/oil emulsion to the heavy oil in the processing equipment.
3. The method of claim 1 wherein the static mixer uses a dispersion quill.
4. The method of claim 1 wherein the aqueous-based scavenger is glyoxal.
5. The method of claim 1 wherein the processing equipment comprises a pipeline.