Abstract:

Title: THE USE OF ACID BUFFERS AS METAL AND AMINE REMOVAL AIDS

A process for reducing contaminants during a desalting process is disclosed. The process may comprise providing an acid buffer solution; providing a contaminated stream; and mixing the acid buffer solution with the contaminated stream.
THE USE OF ACID BUFFERS AS METAL AND AMINE REMOVAL AIDS

FIELD OF THE INVENTION

[0001] The present invention relates to the use of acid buffers to reduce contaminants in crude oil. More specifically, the acid buffers are used to reduce metals and amines from crude oil in a refinery desalting process.

BACKGROUND OF THE INVENTION

[0002] Liquid hydrocarbon mediums, such as crude oils and crude fractions, including naphtha, gasoline, kerosene, jet fuel, fuel oil, gas oil and vacuum residuals, often contain contaminants that can be deleterious to either refinery processing or product quality. The contaminants can contribute to corrosion, heat exchanger fouling, furnace coking, catalyst deactivation and product degradation in refinery and other processes. The contaminants are broadly classified as salts, bottom sediment and water, solids and metals. The amounts of these impurities vary depending upon the particular crude and its processing.

[0003] Desalting is a process that is used to remove contaminants, primarily inorganic salts, from crude oils prior to refining. The desalting step is provided by adding and mixing with the crude a few volume percentages of fresh water to contact brine and salt. Desalting provides benefits to the processing or refining of crude oils, including, reducing crude unit corrosion; reducing crude preheat system fouling; reducing the potential for distillation column damage; reducing energy costs; and reducing downstream process and product contamination.

[0004] Other contaminants that are not desirable in the processing of crude oils are metals. It is intended that metals referred to in this invention include, but are not limited to, are those of Groups IIA, IIB, VIIA, VIIIB, and IVA of the Periodic Table (CAS version). Exemplary metals include, but are not limited to, calcium, iron, zinc, silicon, nickel, sodium, potassium, vanadium and combinations thereof.
In crude oil desalting, an emulsion of water in oil is intentionally formed with the water admitted being on the order of about four (4) to about ten (10) percent by volume based on the crude oil. Water is added to the crude and mixed intimately to transfer the impurities in the crude to the water phase. Separation of the phases occurs due to coalescence of the small water droplets into progressively larger droplets and eventual gravitational separation of the oil and underlying water phase.

Acids, including citric acid, are frequently added to the wash water as a metals sequestering agent. The wash water containing the metals is then separated in the desalter. Citric acid, however, forms a citrate salt with the calcium present in the caide oil. Calcium citrate has limited solubility in water; therefore at concentrations above around 200 ppm as calcium, a dispersant is required.

After leaving the desalter, the crude enters a distillation tower and subsequently, enters the condensers. Water may be entrained in the hydrocarbons being processed and/or water added to the process for such purposes as steam stripping. The acidity of the condensed water may be very high, leading to corrosion. The high acidity is due to dissolved acids in the condensate, principally HCl, organic acids, H₂S, and ¾Cl¾. HCl, the most troublesome corrosive material, is formed by hydrolysis of calcium and magnesium chlorides originally present in the brines.

Amines are frequently added at various points in hydrocarbon refining processes in an attempt to control the corrosiveness of condensed acidic materials. Amines may be added in pure form or as an aqueous solution. Their high alkalinity serves to raise the pH of the initial condensate rendering it less corrosive. Optimally, the amines are added in amounts sufficient to raise the pH of the liquid at the point of initial condensation to above a pH of 6.0.

Depending on relative boiling points, certain alkyl amines for instance, can remain in the crude oil after desalting and distill up the atmospheric tower. HCl salts of these amines can lead to deposition and to very aggressive under-deposit corrosion or molten salt corrosion. Corrosion rates of greater than 1000 mpy (mils per year penetration of corrosion) have been identified.
BRIEF DESCRIPTION OF THE INVENTION

[0010] It was surprisingly discovered that adding an acid buffer solution during a desalting process would effectively reduce contaminants in crude oil while maintaining a pH suitable for downstream crude oil distillation and condensation processes. In addition, the acid buffer would increase the solubility of calcium citrate, minimizing or eliminating the need to add dispersants to the desalter.

[0011] Accordingly, a process for reducing contaminants during a desalting process is disclosed. The process may comprise providing an acid buffer solution; providing a contaminated stream; and mixing the acid buffer solution with the contaminated stream. The contaminated stream may be an aqueous or hydrocarbon stream, or a mixture thereof. In another embodiment, the desalter is in a crude oil refinery.

[0012] In another embodiment, the acid buffer solution may further comprise at least one acid selected from the group consisting of citric acid, glycine, 2(N-methylol)ethanesulfonic acid, methanesulfonic acid, acetic acid, formic acid, and phosphoric acid.

[0013] In another embodiment, the acid buffer solution may comprise at least one counter-ion selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, and ammonium. In yet another embodiment, the acid buffer solution may comprise citric acid and sodium citrate.

[0014] Another embodiment is disclosed wherein the acid buffer solution may have a pH ranging from about 3.0 to 7.4. Alternatively, the pH may be about 6.5.

[0015] In another embodiment, the acid buffer solution may be present in a range of from about 1 to about 6,000 ppm of the contaminated stream. In yet another embodiment, the acid buffer solution may be present in a range of from about 100 to about 4,000 ppm. Alternatively, the acid buffer solution may be present in a range of from about 500 to about 2,000 ppm.
Another embodiment discloses a method wherein the contaminants reduced are metals and amines.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

It was surprisingly discovered that adding an acid buffer solution during a desalting process would effectively reduce contaminants in crude oil while maintaining a pH suitable for downstream crude oil distillation and condensation processes. In addition, the acid buffer would increase the solubility of calcium citrate, minimizing or eliminating the need to add dispersants to the desalter.

Accordingly, a process for reducing contaminants during a desalting process is disclosed. The process may comprise providing an acid buffer solution; providing a contaminated stream; and mixing the acid buffer solution with the contaminated stream. This process is suitable for use in a variety of desalting applications, including, but not limited to, wastewater treatment and crude oil refining. Accordingly, the contaminated stream may be an aqueous or hydrocarbon stream, or a mixture thereof. In another embodiment, the desalter is in a crude oil refinery.

In another embodiment, the acid buffer solution may comprise at least one acid selected from the group consisting of citric acid, glycine, 2(N-morpholino)ethanesulfonic acid, methanesulfonic acid, acetic acid, formic acid, and phosphoric acid.

The acid buffer solution may comprise at least one ion to maintain electric neutrality; i.e., a counter-ion. Suitable counter-ions include, but are not limited to, alkali metals or ammonium. Accordingly, in another embodiment the acid buffer solution further comprises a counter-ion selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, and ammonium. In yet another embodiment, the acid buffer solution may comprise citric acid and sodium citrate.

Another embodiment is disclosed wherein the acid buffer solution may have a pH ranging from about 3.0 to 7.4. Alternatively, the pH may be about 6.5.
In another embodiment, the acid buffer solution may be present in a range of from about 1 to about 6,000 ppm of the contaminated stream. In yet another embodiment, the acid buffer solution may be present in a range of from about 100 to about 4,000 ppm. Alternatively, the acid buffer solution may be present in a range of from about 500 to about 2,000 ppm.

Another embodiment discloses a method wherein the contaminants reduced are metals and amines.

EXAMPLES

COMPARATIVE EXAMPLE 1

For Comparative Example 1, an aqueous solution saturated with tricalcium citrate was prepared and heated to 120 °C. The concentration of calcium citrate was measured at 103 ppm as calcium using inductively coupled plasma ("ICP") mass spectrometry.

EXAMPLE 1

For Example 1, 1000 ppm of a citric acid sodium citrate buffer was added to the aqueous solution saturated with tricalcium citrate and heated to 120 °C. The pH of the citric acid sodium citrate buffer was about 6.5. This time, the concentration of tricalcium citrate was measured at 230 ppm as calcium using ICP mass spectrometry.

This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to practice the invention, including making and using any devices or systems and performing any incorporated methods. The patentable scope of the invention is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

What is claimed is:
CLAIMS

1. A process for reducing contaminants during a desalting process comprising:
   (a) providing an acid buffer solution;
   (b) providing a contaminated stream; and
   (c) mixing said acid buffer solution with said contaminated stream.

2. The process of claim 1, wherein said desalting process is in a crude oil refinery.

3. The process of claim 1, wherein said acid buffer solution comprises at least one
   acid selected from the group consisting of citric acid, glycine, 2(N-mophos)ethanesulfonic acid, methanesulfonic acid, acetic acid, formic acid, and phosphoric acid.

4. The process of claim 3, wherein said acid buffer solution further comprises at
   least one counter-ion selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, and ammonium.

5. The process of claim 4, wherein said acid buffer solution comprises citric acid and
   sodium citrate.

6. The process of claim 1, wherein said acid buffer solution has a pH ranging from
   about 3.0 to 7.4.

7. The process of claim 6, wherein said acid buffer solution has a pH of about 6.5.

8. The process of claim 1, wherein said acid buffer solution is present in a range of
   from about 1 to about 6,000 ppm of said contaminated stream.
9. The process of claim 8, wherein said acid buffer solution is present in a range of from about 0 to 4,000 ppm of said contaminated stream.

10. The process of claim 9, wherein said acid buffer solution is present in a range of from about 500 to about 2,000 ppm of said contaminated stream.

11. The process of claim 1, wherein said contaminants comprise metals and amines.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

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According to International Patent Classification (IPC) or to both national classification and IPC.

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

**CIOG**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>FR 2 937 563 AI (GE ENERGY PRODUCTS FRANCE SNC [FR]) 30 April 2010 (2010-04-30) examples 1-3</td>
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Further documents are listed in the See patent family annex.

**Date of the actual completion of the international search**

30 May 2013

**Date of mailing of the international search report**

05/06/2013

**Name and mailing address of the ISA/ European Patent Office, P.O. 5618 Patentlaan 2 NL-2280 HV Rijswijk Tel. (31-70) 340-2040, Fax (31-70) 340-3016**

**Authorized officer**

Bernet, Olivier
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