HYDROCARBON HYDROTREATING DEVICE AND METHOD FOR REMOVING CHLORIDE FROM A HYDROCARBON STREAM

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ABSTRACT

A method for processing hydrocarbons includes providing a hydrocarbon stream including chlorides from one or more of a crude, vacuum or coker column and contacting the provided hydrocarbon stream with an adsorbent capable of adsorbing the chlorides from the hydrocarbon stream. The dechlorinated hydrocarbon stream is then provided to a hydrotreater reactor.
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BACKGROUND OF THE INVENTION

[0001] Incremental shifts in crude oil demands have caused increases in diesel and jet fuel production, leading refineries to run their units in distillate mode and increasing demand for hydrotreaters. However, crude contaminants must be dealt with before the hydrotreating process. In particular, chloride contaminants including organic and inorganic chlorides must be mitigated.

[0002] Organic chloride content is not an intrinsic property of crude oil, but originates from accidental or unintentional contamination thereof. That is, the amount of organic chlorides found in the crude is not related to the location from which the crude originated or other physical properties of the crude oil. Accordingly, historic crude assays do not provide a reliable indication of future chloride levels. Thus, newly selected crude oils are always viewed as posing a high risk for chloride contamination in a hydrotreating device.

[0003] Conventionally, it is possible to run hydrotreaters that possess targeted halide removal systems. However, such hydrotreaters are expensive to operate and/or to maintain. Thus their operation is impractical. Other mitigation measures, including metallurgical upgradation and wash water, have limitations which prevent widespread use.

[0004] Spot sample analysis of crude oil received at certain refineries reflects a salt content that ranges from a PBT (Pounds per thousand barrels) of 10 to 300 (34 to 1,024 parts per million, by weight). In spite of desalter operations, most refinery data shows considerable quantities of both organic and inorganic chlorides in side cuts of crude, coker and/or vacuum column, particularly in light vacuum gas oil (LGO) from the vacuum column and light coker gas oil (LCGO) from the coker column. Thus, while the chloride content of the individual side cuts of these columns is relatively high, the typical chloride limit in most hydrotreating devices is relatively low, with an upper bound set at about 1 part per million, by weight.

[0005] Excess chlorides can lead to catastrophic failures, including chloride stress corrosion cracking (SCC). Presence of SCC phenomena can be somewhat mitigated through selection of materials during hydrotreater construction and/or reinforcing the pipes used throughout the hydrotreater. However, SCC-resistant materials are typically more expensive to purchase and maintain. Accordingly, there is a need for a relatively low cost process for removing both organic and inorganic chlorides from crude, coker and/or vacuum column distillates.

SUMMARY OF THE INVENTION

[0006] One aspect of the invention is a method for processing hydrocarbons, the method including providing a hydrocarbon stream including chlorides from a crude, vacuum and/or coker column. The provided hydrocarbon stream is contacted with an adsorbent capable of adsorbing the chlorides from the hydrocarbon stream. The dechlorinated hydrocarbon stream is then provided to a hydrotreater reactor.

[0007] Another aspect of the invention is a hydrocarbon hydrotreating device having: a crude, vacuum and/or coker column; an adsorbent bed disposed downstream of the crude, vacuum and/or coker column and in fluid communication therewith to contact a hydrocarbon stream from the crude, vacuum and/or coker column with an adsorbent in the adsorbent bed. The adsorbent bed is capable of adsorbing chlorides. A hydrotreater reactor is disposed downstream of the adsorbent bed and in fluid communication with the adsorbent bed to treat the hydrocarbon stream.

BRIEF DESCRIPTION OF THE DRAWING

[0008] The FIGURE illustrates one embodiment of the chloride adsorption process of the present invention before entering a hydrocarbon hydrotreating device.

DETAILED DESCRIPTION OF THE INVENTION

[0009] A process has been developed to remove organic and inorganic chlorides from a hydrocarbon stream before the stream enters a hydrotreater reactor.

[0010] Referring now to the FIGURE, a hydrotreater process including chloride adsorption is generally designated 10. A hydrocarbon stream containing organic and inorganic chlorides is provided from one or more of a vacuum column, a crude column, and a coker column through a line 12. The hydrocarbon stream preferably includes one or more of light vacuum gas oil, heavy vacuum gas oil, heavy atmospheric gas oil, heavy coker gas oil, light coker gas oil, light, light coker gas oil, vacuum column overhead, cracked naphtha, and straight run naphtha. One example hydrocarbon stream includes light vacuum gas oil, heavy vacuum gas oil, heavy coker gas oil and naphtha. The hydrocarbon stream leaving the column typically has a chloride content up to 40 parts per million, by weight. The line 12 is preferably split. A tankage line 14 allows the stream to be cooled using a cooling device 16, such as a fan-fan as shown in the FIGURE, and routed to tankage (not shown) when the downstream hydrotreater device is in shutdown mode. Additionally, a cracking line 18 optionally allows the stream to be routed to a cracker unit (not shown), bypassing the hydrotreater device. However, during normal operation, a hydrotreater line 20 routes the hydrocarbon stream to a hydrotreater device. Prior to entering the hydrotreater device, chloride content of the hydrocarbon stream should be mitigated to help prevent chloride buildup within the hydrotreater.

[0011] Downstream of the vacuum column, crude column, and/or coker column, and connected to the hydrotreater line 20, an adsorbent bed 22 is provided. The adsorbent bed 22 contains an adsorbent material that is preferably selected to adsorb both organic and inorganic chloride compounds. Preferably, the adsorbent material contained in the bed 22 allows for physical adsorption and/or chemisorption. Example materials for use in the bed 22 include adsorbents containing one or more of alumina, alumino-silicate, and a mixture thereof. In particular, adsorbents are capable of absorbing chloride compounds including, but not limited to, hydrochloric acid (HCl), ammonium chloride (NH₄Cl), sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), polychlorinated biphenyls (PCBs), 1-chloroheptane, 2-chloro-2-methyl hexane, and 2-chloro-2-methyl pentane. The adsorbent material preferably has an equilibrium chloride capacity of up to about 20 wt %, and more preferably in a range of about 10 wt % to about 20 wt %. A temperature of the hydrocarbon stream is preferably adjusted if necessary to enhance the effectiveness of the adsorbent. That is, the temperature of the hydrocarbon stream may be controlled by adding an optional heating or cooling device to the
hydrotreater line 20 so that the hydrocarbon stream entering the bed 22 has a temperature in a range from as low as ambient room temperature (e.g., approximately 20°C) to approximately 130°C. More preferably, the temperature of the hydrocarbon stream is approximately 125°C when the hydrocarbon stream enters the bed 22 and contacts the adsorbent. Those of skill in the art will recognize that other temperatures may be used with different adsorbent materials without departing from the scope of the invention.

The adsorbent bed 22 is preferably sized to provide a reasonable service life and to allow for sufficient flow of the hydrocarbon stream through the bed. For example, a bed having a volume of approximately 66 m³ is expected to have a service life of approximately 12 months. Additionally, the bed preferably accommodates a hydrocarbon stream flow rate of approximately 120 m³ per hour. Those of skill in the art will recognize that the bed size may be varied to accommodate differing flow rates and/or service lifetimes without departing from the scope of the invention.

After exiting the adsorbent bed 22, the organic and inorganic chloride content of the hydrocarbon stream is greatly reduced. Preferably, the chloride content of the hydrocarbon stream exiting the adsorbent bed 22 is less than 1 part per million, by weight. Even more preferably, the chloride content is less than 0.1 part per million, by weight. This chloride content advantageously mitigates SCC phenomena caused by the chlorides.

Once the service life of the adsorbent in the adsorbent bed 22 has elapsed, the adsorbent may be replaced. The used adsorbent may be regenerated, disposed of, or used in other capacities as is known in the art.

Downstream of the adsorbent bed 22, the dechlorinated hydrocarbon stream is provided to the hydrotreater device. In particular, the dechlorinated stream is preferably routed through line 24 to be joined with a combined gas oil stream 26 to form a joined stream 32. The combined gas oil stream 26 includes hydrocarbons from other sources, including a hot feed 28 and a cold feed 30 that is warmed using a heat exchanger 31. Each of which may include one or more of light vacuum gas oil, heavy vacuum gas oil, heavy atmospheric gas oil, heavy coker gas oil, light coker gas oil, light light coker gas oil, vacuum column overhead, cracked naphtha, and straight run naphtha. The heat exchanger 31 used to warm the cold feed 30 preferably receives high pressure steam (HPS) as an input. The HPS cools within the heat exchanger 31, and exits the heat exchanger as high pressure condensate (HPC) 31b. The mixing of the dechlorinated stream in line 24 and the combined gas oil stream 26 forms the joined stream 32. The joined stream 32 is then provided through one or more filters 34 to a feed surge drum 36 as is known in the art.

The output of the feed surge drum 36 passes through a charge pump 38 and one or more preheaters 40 to a combined feed heater 42. Then, after heating, the stream is routed to a reactor 44. The reactor effluent is routed through the preheaters 40 to provide heat to the hydrocarbon stream. The preheaters 40 are preferably heat exchangers. Thus, in addition to heating the stream entering the combined feed heater, the preheaters 40 also help to cool the reactor effluent. The reactor effluent is then provided to a further cooling unit 46, such as an air cooler, and provided to a high pressure separator 48 to separate the liquid and gaseous portions of the stream. The gaseous portion of the hydrocarbon stream exits the separator 48 and is provided to a recycle gas scrubber 50 for removal of impurities. The scrubbed gas is then routed to a compressor 52, and recycled as inputs to both the combined feed heater 42 and the reactor 44. The high pressure separator also produces, as a byproduct, sour water, which exits the separator 48 through line 49. The sour water is wastewater containing waste products such as hydrogen sulfide and ammonia.

The liquid portion of the hydrocarbon stream exits the high pressure separator 48 and enters a stripper 54 to further separate liquid and gaseous components. Gaseous components are removed from the stripper 54 as off-gas 55, and liquid stripper effluent is routed to fractionator 56, to divide the hydrocarbon stream into various hydrocarbon outputs, including naphtha 56a, kerosene 56b, diesel 56c, and vacuum gas oil bottoms 56d. That is, low pressure steam enters the fractionator 56 through input line 57, and the input hydrocarbon stream is divided into its various component outputs 56a-56b based upon their differing boiling points, as is known in the art. The naphtha output 56a of the fractionator 56 is cooled before entering a receiver 58, and the output hydrocarbon liquid is then divided so that a portion is recycled into the fractionator, and a portion is output as a hydrocarbon output. Sour water is removed from the receiver 58 through line 59.

The reduction in chlorides in the hydrotreater allows for reduction in the amount of wash water used throughout the hydrotreating process. In particular, less wash water is required in upstream and downstream process line of the air cooler 46. This leads to a commensurate reduction in the amount of sour water produced during hydrotreating.

Light vacuum gas oil (LVGO) is the component of the hydrotreating process that is most vulnerable to chloride contamination. Accordingly, it follows that the LVGO stream is the primary target for chloride adsorption, as is shown in the figure. However, those of skill in the art will recognize that this chloride adsorption process can be adapted for use on other hydrocarbon streams either in place of or in addition to its use on the LVGO stream, without departing from the scope of the invention.

While at least one exemplary embodiment has been presented in the foregoing detailed description, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment is merely an example, and is not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those of skill in the art with a convenient road map for implementing an exemplary embodiment of the invention. It will be understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.

What is claimed is:

1. A method for processing hydrocarbons, the method comprising:
   providing a hydrocarbon stream including chlorides from one or more of a crude, vacuum or coker column;
   contacting the provided hydrocarbon stream with an adsorbent capable of adsorbing the chlorides from the hydrocarbon stream; and
   providing the dechlorinated hydrocarbon stream to a hydrotreater reactor.

2. The method of claim 1, wherein the provided hydrocarbon stream comprises one or more of light vacuum gas oil,
heavy vacuum gas oil, heavy atmospheric gas oil, heavy coker gas oil, light coker gas oil, light light coker gas oil, vacuum column overhead, cracked naphtha, straight run naphtha, and mixtures thereof.

3. The method of claim 2, wherein the hydrocarbon stream comprises light vacuum gas oil, heavy vacuum gas oil, heavy coker gas oil and naphtha.

4. The method of claim 1, wherein the provided hydrocarbon stream has a chloride content up to 40 parts per million by weight, and the de-chlorinated stream has a chloride content in a range of less than 1 part per million, by weight.

5. The method of claim 1, wherein said adsorbent includes one or more of alumina, alumino-silicate, and a mixture thereof.

6. The method of claim 1, wherein said step of contacting comprises contacting the provided hydrocarbon stream with the adsorbent while the hydrocarbon stream is at a temperature greater than or equal to ambient room temperature and up to 130°C.

7. The method of claim 6, wherein said temperature is approximately 125°C.

8. The method of claim 1, where the hydrocarbon stream includes organic chlorides and inorganic chlorides.

9. A hydrocarbon hydrotreating device comprising:
   a) a crude, vacuum and/or coker column;
   b) an adsorbent bed disposed downstream of said crude, vacuum and/or coker column and in fluid communication with said crude, vacuum and/or coker column to contact a hydrocarbon stream from said crude, vacuum and/or coker column with said adsorbent bed, said adsorbent bed capable of adsorbing chlorides; and
   c) a hydrotreater reactor disposed downstream of said adsorbent bed and in fluid communication with said adsorbent bed.

10. The hydrocarbon hydrotreating device of claim 9, wherein the hydrocarbon stream includes one or more of light vacuum gas oil, heavy vacuum gas oil, heavy atmospheric gas oil, heavy coker gas oil, light coker gas oil, light light coker gas oil, vacuum column overhead, cracked naphtha, straight run naphtha, and mixtures thereof.

11. The hydrocarbon hydrotreating device of claim 9, wherein the hydrocarbon stream includes light vacuum gas oil, heavy vacuum gas oil, heavy coker gas oil and naphtha.

12. The hydrocarbon hydrotreating device of claim 9, wherein the downstream of said adsorbent bed is combined with a gas oil combined feed prior to entering said hydrotreater reactor.

13. The hydrocarbon hydrotreating device of claim 9, wherein said adsorbent bed contains an adsorbent including one or more of alumina, alumino-silicate and a mixture thereof.

14. The hydrocarbon hydrotreating device of claim 9, wherein the hydrocarbon stream enters said adsorbent bed having a chloride content up to 40 parts per million by weight, and leaves said adsorbent bed having a chloride content in a range of less than 1 part per million, by weight.

15. The hydrocarbon hydrotreating device of claim 9, wherein the hydrocarbon stream enters said adsorbent bed at a temperature equal to or greater than ambient room temperature and up to 130°C.

16. The hydrocarbon hydrotreating device of claim 15, wherein said temperature is approximately 125°C.

17. The hydrocarbon hydrotreating device of claim 9, where the hydrocarbon stream includes organic chlorides and inorganic chlorides.

18. A hydrocarbon hydrotreating device comprising:
   a) a crude, vacuum and/or coker column;
   b) an adsorbent bed containing an adsorbent including one or more of alumina, alumino-silicate and a mixture thereof and disposed downstream of said crude, vacuum and/or coker column, so that said adsorbent contacts a hydrocarbon stream from said crude, vacuum, and/or coker column; and
   c) a hydrotreater reactor disposed downstream of said adsorbent bed and in fluid communication with said adsorbent bed.

19. The hydrocarbon hydrotreating device of claim 18, wherein the hydrocarbon stream includes organic chlorides and inorganic chlorides, and enters said adsorbent bed at a temperature equal to or greater than ambient room temperature and up to 130°C.

20. The hydrocarbon hydrotreating device of claim 18, wherein the downstream of said adsorbent bed is combined with a gas oil combined feed prior to entering said hydrotreater reactor.