REDUCTION OF DISTILLATION UNIT FOULING

Applicant: ExxonMobil Research and Engineering Company, Annandale, NJ (US)

Inventors: Ashok UPPAL, Samia (CA); Gordon Bryce McGEARVEY, Samia (CA); Francis LEPINE, Counna (CA)

Appl. No.: 15/084,878

Filed: Mar. 30, 2016

Publication Classification

Int. Cl. C10G 75/04 (2006.01) C10G 75/02 (2006.01)

U.S. Cl. C10G 75/04 (2013.01); C10G 75/02 (2013.01)

Abstract

Basic components, including nitrogenous compounds, which lead to fouling in the overhead of petroleum refinery processing units, especially the crude unit, are removed by adsorbing the basic compounds on an adsorbent with acidic functionality. Suitable adsorbents include acidic functioning zeolites, ion-exchange resins and acidic amorphous solids such as alumina and solid acids such as solid phosphoric acid, tungstic acid and similarly functioning materials. The removal is typically affected by contacting a reflux stream from the distillation or other unit with a bed of the adsorbent.
Figure 1
REDUCTION OF DISTILLATION UNIT FOULING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application Ser. No. 62/152,228 filed Apr. 24, 2015, herein incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to a method for reducing the fouling tendencies of petroleum distillation units, especially the crude distillation unit.

BACKGROUND OF THE INVENTION

[0003] As the availability of conventional crudes declines, refiners are processing increasing amount of heavy crudes that are more sour (higher sulfur content) and contain higher concentrations of acidic components (measured as total organic acids). The refinery equipment, such as crude towers, are thus more susceptible to corrosive environments from these contaminants. The problem of corrosion in the crude unit has long been recognized. These acidic components can be native to crude or result from impurities/additives in the crude. Acid-induced corrosion, for example, frequently arises from chloride salts present in the originating crude usually from native salts from reservoir waters, including sodium chloride, calcium chloride and magnesium chloride. These salts are subject to varying degrees of hydrolysis in the crude unit furnace, with magnesium being the least heat stable most apt to hydrolyze to hydrogen chloride (HCl) at lower temperatures and sodium chloride being the most resistant until the higher temperatures of the vacuum tower are encountered and calcium chloride occupying an intermediate position in the ranking. While adequate desalter operation is capable of minimizing chloride salt carry-over, operation of the desalter unit tends to be erratic, resulting in chloride carry-over in an unpredictable manner.

[0004] Acidic corrosion induced by hydrogen chloride and other acidic components of the originating crude is for the most part, initially encountered in the upper portion of the atmospheric tower of the crude unit, especially in the tower overhead. To control acid corrosion, a common practice has been to adopt acid control measures as by the addition of caustic to the desalter effluent, by the addition of corrosion inhibitors such as amine neutralizers, e.g. imidazolines and other film forming agents into the overhead system where corrosion potential is the highest. When added in the crude overhead system, there is always some surplus which returns to the tower with the overhead/tower reflux streams. These neutralizers and film forming agents may, however, contribute to further problems by the formation of reaction products, which deposit on surfaces as foultants. These reaction products can also trap particulates present in the crude and/or corrosion products present in the tower, adding additional volume to the foultant. The overall product is a heavy, sticky, glue-like material that plugs the tray holes and disrupts fractionation. If the fouling persists, the tower has to be shut down and the trays need to be replaced/cleaned in order to make on-specification products. This tendency to form fouling deposits has been exacerbated in recent years with decreasing crude quality and the tendency to drop the tower top temperature to increase distillate production; with lower top temperatures, the conditions for introducing salt formation and other fouling mechanisms has become more prevalent. This has been noted by several authors including Payne et al., and Barletta et al.\(^1\).

\(^1\) Minimize corrosion while maximizing distillate", Hydrocarbon Processing March 2012, pp. 45-47; P IQ 3rd Quarter Issue, 2012, pp. 75-81. "Crude overhead system design considerations", Digitalrefining.com

[0005] Although a majority of the inhibitor lays down on the overhead equipment surface as a film to protect it, the remaining material returns to the distillation tower with the overhead reflux stream in an amine recycle loop as noted by Payne. The amine molecules which are basic in nature react with acidic components in the vapors rising in the tower; reaction pathways suggest that both acidic components and nitrogen molecules need to be present to cause fouling. Because the total amount of amines present in the reflux may arise not only from neutralizing amines added as corrosion inhibitors but also from other refinery sources including sour water strippers, amine wash units, their presence in largely unpredictable amounts makes foulant control problematic.

SUMMARY OF THE INVENTION

[0006] According to the present invention we propose to remove basic components, including nitrogenous compounds, which lead to the fouling from the reflux stream in the crude unit or another process unit by adsorbing the basic compounds on an adsorbent with acidic functionality. Suitable adsorbents include acidic functioning zeolites, ion-exchange resins and acidic amorphous solids such as alumina and solid acids such as solid phosphoric acid, tungstic acid and similarly functioning materials. The processing scheme is preferably augmented to treat a reflux stream from the unit by passing it in whole or in part over an adsorbent bed prior to returning to the unit. The nitrogen compounds, essential for the fouling mechanism are thus removed or reduced and fouling can be controlled or eliminated.

[0007] The present method is particularly applicable to reducing the fouling which takes place as described above in the overhead of a distillation unit such as the crude atmospheric tower.

DRAWINGS

[0008] The single Figure of the accompanying drawings shows a simplified schematic of a petroleum refinery crude unit with amine treating unit in the overhead reflux loop.

DETAILED DESCRIPTION

[0009] The Figure depicts the initial processing units encountered by the incoming crude oil. The oil passes from storage tank 10 by way of line 11 to desalter 12 and the desalted hydrocarbon effluent enters atmospheric tower 13 at an appropriate level according to its composition in the conventional way. The tower overhead passes out from the low temperature end of the tower through line 14 through air cooler and heat exchanger equipment 15 to receiver 16 with the accumulated water passing out from boot 17. The hydrocarbon reflux passes to adsorption vessel 18 in which the residual basic compounds in the reflux stream are removed by adsorption on a bed of acidic-functioning solid before returning as reflux to tower 13. Neutralizing amine is added to the overhead in line 14 from supply drum 19. The removal of the basic components including nitrogen com-
pounds from the reflux stream reduces or eliminates fouling in the tower and associated equipment as well as in downstream processing units.

[0010] In the present method of reducing fouling in refinery process units such as the atmospheric distillation tower as well as other units in which a reflux stream is recirculated to a heated vessel or distillation column, the presence of polar and/or basic nitrogen compounds is reduced by passing the stream in contact with a solid porous adsorbent having acidic functionality accessible to the nitrogen compounds present in the stream. The method is particularly applicable to distillation units which typically have a high temperature end in the lower portion of a distillation column or tower and lower temperature end at the upper end of the tower. The references here to the “high temperature end” and “low temperature end” therefore refer to the relative temperatures at the two ends of the tower; absolute values are not implied as the tower is run at temperatures appropriate to the feed being processed and the fractions to be separated from it. The actual temperatures at the high and low temperature ends of the tower are therefore selected in accordance with the operating requirements as experience dictates. An overhead or reflux stream is circulated in a loop at the low temperature end of the tower to maintain control over the temperature profile of the column and it is in this overhead that corrosion inhibitors are usually added. According to the present invention, this reflux loop is also the location in which the adsorbent for removing the basic nitrogenous compounds which react with acidic components in the process stream is most suitably located.

[0011] The adsorbent is selected to have acidic groups on the adsorbent react chemically with the amino or other basic groups on the nitrogen compounds present in the circulating stream and under the prevailing conditions, bind to the acidic sites on the adsorbent, effectively removing it from the circulating stream by a process of chemisorption. Generally the adsorbent will be a porous solid with pores adequately large to permit access to the interior pore structure of the adsorbent when the bulk of the active sites exist so that optimal contact of the basic compounds with active sites on the adsorbent is assured.

[0012] Suitable solid adsorbent can typically be classified as solid metal oxides or high molecular weight organic polymers. Metal oxides may be either amorphous or crystalline. Amorphous solid adsorbents typically include oxides of metals such as aluminum, silica, magnesium, titanium, thorium, although the more common oxides including alumina, silica and silica-alumina will be preferred on grounds of cost. Many forms of alumina and silica-alumina exist with varying degrees of acidity and porosity and are commonly used as catalyst support materials. Activated alumina with its higher surface area is attractive as an adsorbent.

[0013] Crystalline materials such as the zeolites are particularly effective as they are known to possess high surface areas and can be synthesized with varying degrees of controlled acidity depending on the ratio of the oxides in the zeolite, for example, alumina to silica in the aluminosilicates, boron to silica in borosilicates, iron to silica in ferrosilicates and so on. The aluminosilicates are the most common and will generally be preferred for the present purpose. The aluminosilicates exhibit a wide range of pore structures with pore sizes ranging upwards from about 2 Å with small pore 8-oxygen ring zeolites such as erionite and zeolite A having pores of about 4 Å and the intermediate pore size zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35 and ZSM-48 having pore openings defined by 10-member oxygen rings with pore openings in the range of about 5 Å, larger pore size zeolites such as ZSM-4, ZSM-12 may have 12-membered ring systems with pores about 6 Å. Dual pore systems are also known, e.g., as in mordenite.

[0014] Mesopore materials including the zeolitic materials of the M(41)S series such as MCM-41 and MCM-48 are characterized by pores in the range of about 20-30 Å and by a very high specific surface area which, by reason of the larger pores is highly accessible by many species in refinery streams. The mesoporous solid oxide materials are therefore particularly well suited to act as adsorbents in the present method. Macroporous materials having even larger pores are generally amorphous in type and with a greater pore size distribution are, however, quite suitable for use as adsorbents of the basic nitrogen compounds in the pump-around circuits of the various refinery units.

[0015] The adsorbent may have its own intrinsic acidity conferred by chemistry, depending on its composition, e.g., the silica-alumina ratio in the zeolites. Alternatively, adsorbents may be made by using a solid support with an acidic material impregnated onto it or even grafted onto it by chemical reaction. Support materials may again be amorphous or crystalline solid metal oxides or mixtures of oxides e.g., silica, alumina, silica-alumina with the acidic function impregnated into it. A suitable material of this kind is generally known as Solid Phosphoric Acid (SPA) which is typically prepared by combining a phosphoric acid with the selected support/carrier and drying the resulting material. In particular, it can be prepared by mixing the support with phosphoric acid, extruding the resulting paste, and calcining the extruded material. The activity of a solid phosphoric acid catalyst can be related to the amount and/or chemical composition of the phosphoric acid component which may be comprised, for example, of ortho-phosphoric acid (H₃PO₄), pyro-phosphoric acid (H₂P₂O₇), tri-phosphoric acid (H₃P₃O₁₀), tetra-phosphoric acid (H₄P₄O₁₃), or the like, or any combinations of them. Each of the various phosphoric acids has a unique acid strength, and, accordingly, the acidic activity of a given sample of solid phosphoric acid catalyst can depend on the P₂O₅/H₂O ratio of the phosphoric acid deposited on the support. Support materials for impregnated acids may typically include one or more oxides of silicon, boron, aluminum, zirconium, titanium, or zinc, with silicon supports being preferred. Although non-oxygen support materials may be used, for example, activated charcoal with an impregnated acid, they will not normally be preferred as they are not as robust as the metal oxide materials under refinery conditions.

[0016] Another useful class of solid adsorbents comprises the ion-exchange resins, in this case of the cation exchange type. These resins typically comprise macrotetrical, porous, high molecular weight organic polymers typified by polystyrene, usually cross-linked with divinylbenzene (DVB). The acidic functionality may be categorized as either strongly acidic as in the cation exchange resins containing sulfonic acid groups or the corresponding salts or weakly acidic as in the cation exchange resins containing carboxylic acid groups or the corresponding salts. The pore size of the resins will be determined by the polymerization conditions and the ratio of styrene to DVB in the resin. Macroporous resins, with their high effective surface area,
facilitate the ion exchange process. Also, they give access to the exchange sites for larger ions and are suitable for use in refinery hydrocarbon streams at refinery conditions. The resins are generally in the form of rigid beads, facilitating handling in bed preparation. Resins with various pore sizes are readily available commercially, such as the Amberlyst™, Amberlyst-15™ and Dowex™ resins of Dow Chemical.

[0017] The adsorptive capacity of the bed will, at some point, become exhausted at which time the adsorbent will need to be discarded or regenerated. Metal oxide adsorbents may be regenerated by exposure to temperatures high enough to drive off the organic amines; ion exchange resins may be regenerated by treatment with an acid which will react with and displace the amine moieties attached to the resin. Monitoring of the amine content of the circulating stream should be carried out to determine when amine breakthrough is likely to occur. The volume of the bed or beds (typically, a plurality of beds will be used in the adsorption vessel) and its inherent sorptive capacity should be adjusted according to the level of nitrogen compounds known to circulate in the stream, including both the corrosion inhibitors and amines from other refinery sources, usually referred to as "trump amines".

EXAMPLE

[0018] This example illustrates the effectiveness of several commercially available adsorbents in removing corrosion inhibitor from a hydrocarbon stream.

[0019] Reagent grade dodecane, a C12 paraffin, was selected to represent a typical reflux stream in a distillation tower with kerojet side draw. The concentration of corrosion inhibitor in the reflux stream may, based on literature and vendor information, range from about 10 to about 20 mg/L, measured as total nitrogen. Accordingly, dodecane was dosed with a commercial amine type corrosion inhibitor (Baker Hughes BPR81202™ that contains amine derivative/amide imidazolines) equivalent to 12.6 mg/L of nitrogen. This dodecane was then treated with several adsorbents for 22 hrs in a laboratory shaker at room temperature. At the end of the experiment, the adsorbent/dodecane mixture was filtered to separate the adsorbent. The filtrate (treated dodecane) was tested to determine the effectiveness of the adsorbent in removing corrosion inhibitor (measured by nitrogen removal). The results are presented in Table 1 below. These data show that the adsorbents are very effective in removing the corrosion inhibitor. As little as 0.014 gms of MCM-41 were required to remove 92 percent of nitrogen.

What is claimed:
1. A method of reducing fouling in a petroleum refinery process unit in which basic nitrogen compounds are present in a circulating stream of petroleum hydrocarbons, which method comprises passing the stream in contact with a solid, porous adsorbent having acidic functionality to adsorb the basic nitrogen compounds on the adsorbent.
2. A method according to claim 1 in which the basic nitrogen compounds are adsorbed on the adsorbent by reaction with acidic sites on the adsorbent.
3. A method according to claim 1 in which the solid adsorbent comprises a porous, acidic metal oxide.
4. A method according to claim 1 in which the solid adsorbent comprises an amorphous, acidic metal oxide.
5. A method according to claim 1 in which the solid adsorbent comprises a porous, acidic crystalline zeolite.
6. A method according to claim 1 in which the solid adsorbent comprises a porous, acidic cation exchange resin.
7. A method according to claim 1 in which the stream of petroleum hydrocarbons is circulating in a recirculation loop of a refinery unit operating at elevated temperature.
8. A method according to claim 1 in which the stream of petroleum hydrocarbons is circulating in a reflux loop of a distillation unit.
9. A method according to claim 1 in which the stream of petroleum hydrocarbons is circulating in a reflux loop of a crude oil atmospheric distillation unit.
10. A method according to claim 1 in which the stream of petroleum hydrocarbons is circulating in a reflux loop of a crude oil atmospheric distillation unit and is contacted with the solid, porous adsorbent in the reflux loop.
11. A method of reducing fouling in a low temperature end of a refinery distillation tower having a low temperature end and a high temperature end in which basic nitrogen compounds are present in a circulating reflux stream of petroleum hydrocarbons at the low temperature end, which method comprises passing the circulating reflux stream in contact with a solid, porous adsorbent having acidic functionality to adsorb the basic nitrogen compounds on the adsorbent.
12. A method according to claim 11 in which the circulating reflux stream of petroleum hydrocarbons is circulating in a reflux loop of a crude oil atmospheric distillation unit.
13. A method according to claim 12 in which the stream of petroleum hydrocarbons is circulating in the reflux loop of the crude oil atmospheric distillation unit and is contacted with the solid, porous adsorbent in the reflux loop.
14. A method according to claim 13 in which the stream of petroleum hydrocarbons is circulating in the reflux loop of the crude oil atmospheric distillation unit comprising a cooler connected to the low temperature end of the tower, a receiver to receive a cooled stream from the cooler and a bed of solid, porous adsorbent located in the reflux loop between the receiver and the tower.
15. A method according to claim 13 in which the reflux loop includes means for adding a corrosion-inhibiting basic nitrogenous compound to the circulating reflux stream.
16. A method according to claim 13 in which the reflux loop includes means for adding a corrosion-inhibiting basic nitrogenous compound to the circulating reflux stream between the low temperature end of the tower and the receiver.

| TABLE 1 |
| Nitrogen Removed by Adsorption |
|------------------|------------------|------------------|------------------|
| Adsorbent Type   | MCM-41 Zeolite   | Amberlyst™ Ion-Exchange Resin | Anaphous™ Alumina | Polyvinyl™Phosphoric Acid |
| Adsorbent Amount (g/45 ml dodecane) | 0.014 | 0.13 | 0.13 | 0.008 |
| Product          | 1 | 1 | 1.8 | 1.1 |
| Nitrogen (mg/L)  | 92 | 92 | 85.7 | 91 |
17. A method according to claim 11 in which the stream of petroleum hydrocarbons is circulating in the reflux loop of a crude oil atmospheric distillation unit.

18. A method according to claim 11 in which the stream of petroleum hydrocarbons is circulating in the reflux loop of a vacuum distillation unit.