

- 1 -

VAPOR PHASE NEUTRALIZATION IN INTEGRATED SOLVENT DEASPHALTING AND GASIFICATION

FIELD OF THE INVENTION

5 The invention relates to the field of treatment of heavy oil that contains calcium and magnesium salts. Specifically, this invention relates to converting the salts to the non-corrosive oxides and then optionally removing these oxides from the heavy oil during deasphalting step.

BACKGROUND OF THE INVENTION

Crude oil is generally found in association with salt water. The salt water typically
10 contains sodium chloride as well as calcium and magnesium chlorides in varying proportion. The oil and water are subjected to a high degree of turbulence as they are produced. These actions form an emulsion in which water droplets are dispersed throughout the crude oil phase. The degree of mixing determines the size of the dispersed droplets and hence to some extent the stability of the emulsion, since the smaller the size of the droplets, the more difficult it is to
15 break the emulsion. The presence of indigenous surfactants in the crude oil also stabilizes the emulsion by forming a rigid interfacial layer which prevents the water droplets from contacting and coalescing with one another.

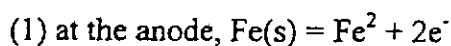
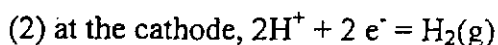
Thus, following production, crude oil can contain water to a greater or lesser extent, and this water must be removed. The action of water removal is termed crude oil dehydration. Some
20 emulsions may be broken down by heat alone but more often it is necessary to add a surface tension reducing chemical to achieve this end. Generally the application of heat and/or chemical is sufficient to reduce the water content, and more importantly the salt content, to an acceptable level but sometimes it is necessary to use electrostatic precipitation.

A dehydrated oil typically contains between 0.1 and 3.0% by vol. of water. However, if
25 the salinity of the remaining water is high, the salt content of the crude oil will also be high, e.g., between about 100 and 5000 parts per million by weight, even when such low quantities of water are present. Heavy crudes typically have water and salt contents that are in the upper end of these ranges. This salt is undesirable because the presence of salt reduces the value of the crude oil, leads to the corrosion and fouling of pipelines and downstream distillation columns,
30 and may poison catalysts used in downstream refining processes.

- 2 -

Hydrocarbon feedstocks such as petroleum crudes, gas oil, etc. are subjected to various processes in order to isolate and separate different fractions of the feedstock. In refinery processes, the feedstock is distilled so as to provide light hydrocarbons, gasoline, naphtha, kerosene, gas oil, etc. The lower boiling fractions are recovered as an over head fraction from a distillation column. The intermediate components are recovered as side cuts from the distillation column. The fractions are cooled, condensed, and sent to collecting and processing equipment. No matter what type of petroleum feedstock is used as the charge, the distillation equipment is subjected to the corrosive activity of acids such as H_2S , hydrochloric acid, organic acids, and H_2CO_3 .

Corrosive attack on the metals normally used in the low temperature sections of a refinery process system, (i.e. where water is present below its dew point) is an electrochemical reaction generally in the form of acid attack on active metals in accordance with the following equations:



The aqueous phase may be water entrained in the hydrocarbons being processed and/or water added to the process for such purposes as steam stripping. Acidity of the condensed water is due to dissolved acids in the condensate, principally hydrochloric acid, organic acids, H_2S , organic acids, and H_2CO_3 . Hydrochloric acid, the most troublesome corrosive material, is formed by hydrolysis of calcium and magnesium chlorides originally present in the brines.

It is often necessary to remove the salt from crude oil by washing with fresh water or a low salinity aqueous phase, imparting a degree of mixing to ensure adequate contact between high salinity water in the crude and low salinity wash water and then carrying out the separation process. This process is termed crude oil desalting.

Normally in desalting a small amount, i.e., about 5 volume percent of fresh water or water of low salinity is added to the dehydrated crude oil. When this is the case, a high degree of mixing is often required to induce good contact between saline droplets, non- or low-saline droplets and added demulsifier. Consequently, the emulsion produced is very stable with a low average droplet size.

Desalting by mixing relatively large quantities of water, i.e., where the quantity of wash water employed is greater than 7.5% by volume of the crude oil, results in the formation of a less

stable emulsion and consequently less severe conditions are required to break it to recover the desalted crude oil. Often, gravity settling alone will be sufficient to effect separation. However, larger waste streams are produced.

Chemical demulsifiers are typically added to break the emulsions formed in desalting.

5 Electrical devices which charge the water drops to enhance separation are also used. The concentration of demulsifier added and temperature required will be lower than for a conventional desalting process. However, the emulsion can be destabilized and, assuming optimum mixing, the salt content can be reduced to as low as 6 parts per million for light oils. In order to desalt to such low levels, however, it is necessary to use conditions of high temperature,
10 a chemical demulsifier and often electrostatic separation. Demulsifiers usually comprise blends of surface active chemicals, e.g. ethoxylated phenolic resins, in a carrier solvent.

U.S. Pat. No. 4,806,231 describes a method for desalting crude oil wherein the salt content of the oil is reduced by washing crude oil containing residual salt water with washing water and allowing the resulting mixture to settle. This process forms an emulsion to transfer
15 salt from crude oil into the added water, and then teaches that the emulsion must be broken in a conventional manner, such as settling or through electrostatic means.

Up to about 90% of the salt can be removed with a single stage of water washing and separation. A second wash stage is commonly used to remove additional salt.

Salt removal effectiveness depends on the nature of the crude. Heavier oils are more
20 difficult to desalt than light crudes. One problem with processing heavy oils is the density of heavy oil is very close to the density of water. The emulsions are difficult to break, and even if broken the separation of the salt water and heavy crude is difficult. A cutter stock must be added to the crude to lower its density and decrease its viscosity so that the water can be admixed with the crude and then separated. Then the cutter stock must be stripped out of the oil and
25 recovered.

Caustic (NaOH) is commonly injected into the crude downstream of the desalter to reduce hydrogen chloride in the subsequent distilling operations. The caustic reacts with the magnesium and calcium chloride to form sodium chloride, which is more thermally stable and so will not hydrolyze. However, the quantity of caustic must be limited since caustic causes
30 furnace coking and induces operating problems in downstream units. New catalysts being used in downstream units in response to environmental control demands being imposed on refineries

- 4 -

are poisoned by caustic. In most instances, it is impractical to remove enough salt with desalters and/or caustic addition to completely eliminate hydrochloric acid corrosion.

Crude oil refineries typically include an atmospheric pressure distillation unit which fractionates the whole crude oil into various product fractions of different volatility, including gasoline, fuel oil, gas oil, and others. The lower boiling fractions, including naphtha, from which gasoline is derived, may be recovered from the overhead fraction. The fractions with intermediate volatility are then withdrawn from the tower as sidestreams. Sidestream products include kerosene, jet fuel, diesel fuel, and gas oil. The heaviest components are withdrawn in the tower bottoms stream.

In a typical crude oil atmospheric pipestill unit the crude is heated up to about 500° F to 700° F in a direct-fired furnace. The feed is then flashed into the atmospheric distillation unit which operates at a pressure between one and three atmospheres gauge pressure. The oil cools as it is flashed. Overhead tower temperature ranges typically from 200° F to 350° F.

The overhead and sidestream products are cooled and condensed and sent to other units to be processed into final products. The bottoms stream typically goes to a second distillation tower that operates under a vacuum. Even more light hydrocarbons are then distilled from the bottoms. Steam may be added to the bottom of the tower to promote stripping of light products from the bottoms. Also, water may be added to the top of the column to wash away soluble salts which often accumulate in the top trays and overhead components. The stripping steam and wash water coming into the system are substantial; the overhead naphtha gas stream coming off the top of the tower typically contains 20 to 40 mole % water.

Hydrogen chloride is liberated from the crude in each of these steps. Said hydrogen chloride causes corrosion. Moreover, hydrogen chloride is liberated in subsequent treatment steps. For heavy crude oil, where desalting is not very effective, corrosion due to hydrogen chloride is a problem throughout much of the refining process.

SUMMARY OF THE INVENTION

The process of the invention is applicable to crude or as well as to partially processed oil streams. The greatest economic utility will be realized if the crude is a heavy crude that contains asphaltenes. The invention is a method of neutralizing acids present in crudes. The invention is also the integration of gasification, solvent deasphalting, and vapor phase neutralization that results in particularly efficient and economical advantages.

- 5 -

In this invention the heavy oil is heated to from about 300° F to about 600° F, preferably from about 350° F to about 550° F, more preferably from about 400° F to about 500° F. The crude is beneficially heated in one or more stages utilizing high and optionally medium pressure steam that is a product of gasification of an asphaltene-rich hydrocarbonaceous fraction that is subsequently separated from the crude.

The crude is maintained at this temperature range about 350° F to about 550° F and gases are flashed off the crude. Salts such as magnesium chloride and calcium chloride react with water in the crude to form metal hydroxides and hydrochloric acid. Water, in either its liquid or its vapor form, may be advantageously admixed with the crude. Again, medium or high pressure steam advantageously obtained from the gasification process can supply both the heat and the water. Said steam generation from the waste heat of gasification is known to the industry.

The steam is advantageously admixed with the heated crude to provide additional water and heat, as well as to carry away the hydrochloric acid. The hydrochloric acid is gaseous at the temperature and pressure of the crude. The hydrochloric acid is separated from the crude in a flash drum.

To the extent there is sufficient water in the crude to react with the precursors of acids, no water need be added, and heat could be added via a heat exchanger.

The remaining calcium and magnesium hydroxides, plus other salts and solids, are subsequently advantageously removed from the crude during deasphalting. Deasphalting involves admixing solvent with the crude. These salts can be removed by filtering after sufficient solvent has been admixed to reduce the viscosity of the crude, or alternatively the salts can be allowed to precipitate with the asphaltenes. The asphaltenes are then advantageously gasified, providing steam as a by-product. Said steam is useful in the process of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The process of the invention is applicable to crude oil, heavy crude oil, and very heavy crude oil, as well as to partially processed oil streams. As used herein, the terms "crude oil", "heavy oil", "heavy crude", "very heavy crude", and "oil" are used interchangeably to denote a hydrocarbon stream that has a viscosity greater than about 20 centipoise at ambient conditions.

The greatest utility will be realized if the crude is a heavy crude that contains asphaltenes. A very heavy crude typically has a viscosity in the range 200 to 250,000, typically

- 6 -

2,000 to 250,000, mPa.s at the processing temperature. Said heavy crudes have asphaltenes, typically in the range of 5 to 40 percent by weight. A partially processed oil stream may also be used in place of the heavy crude oil. For example, the process is applicable to an oil stream wherein a fraction of the light ends have been removed by, for example, moderate temperature stripping.

Heavy crudes are being utilized more in refineries because they are lower priced than lighter crudes. When refined the heavy crudes produce more residual oil that contains a significant amount of asphaltenes. To maximize the value of residual oils, light oils are separated from the asphaltene components in the oil. The light components are recovered using solvent extraction and sold as valuable products. The asphaltene-rich component is separated and converted in gasification units into products such as hydrogen, carbon monoxide, and combustion turbine fuel.

Heavy crude oils are typically diluted with lighter hydrocarbon fractions such as condensate or light crude oil before dehydration and desalting. The purpose of this is to reduce the viscosity and density of the oil phase to facilitate oil-water phase separation. While such dilution may facilitate processing by reducing the viscosity, it is not necessary to the present invention.

The heavy crude oil may be partially desalted prior to undergoing the process of this invention. One method is to mix about 50 to 98%, preferably 80 to 95%, by volume of a heavy crude oil with 2 to 50%, preferably 5 to 20%, by volume of an aqueous solution of an emulsifying surfactant or an alkali, percentages being expressed as percentages by volume of the total mixture. With such a high water content the mixing can be effected under low shear conditions in the range 10 to 1,000, preferably 50 to 500, reciprocal seconds.

A suitable mixer is a vessel having rotating arms. Suitably the speed of rotation is in the range 500 to 1,200 rpm. Below 500 rpm mixing is relatively ineffective and/or excessive mixing times are required.

The resulting emulsion can be partially broken by conventional means and the phases separated. The resulting mixture is a layer of relatively salt-free oil and a layer of relatively salt enhanced water. An intermediate layer comprising an emulsion may still be present.

- 7 -

Preferably a demulsifier is added to assist in breaking the crude oil/water emulsion. Suitable demulsifier concentrations are in the range 1 to 500, preferably 1 to 100, parts per million.

U.S. Pat. No. 4,806,231 describes a method for desalting crude oil wherein the salt
5 content of the oil is reduced by washing crude oil containing residual salt water with washing water and allowing the resulting mixture to settle. This process forms an emulsion to transfer salt from crude oil into the added water, and then teaches that the emulsion must be broken in a conventional manner, such as settling or through electrostatic means.

While such desalting processes may be performed on the crude oil, one advantage of the
10 current invention is that such processes are not necessary to remove the hydrochloric acid-generating salts from the crude oil.

The crude is advantageously dehydrated, especially if a desalting process was performed. Crude is typically dehydrated prior to transport. However, secondary dehydration at the refinery is often beneficial. Dehydration of oil-in-water emulsions is typically carried out in washing
15 tanks of various configuration, wherein the emulsified oil is introduced into the tank and passed through a water cushion wherein a washing process takes place due to the physical-chemical similarity of the phases. Separation is completed by gravity, and emulsions are broken by chemical emulsion breakers, heat, and/or electric or magnetic fields. Gravity separation of a heavy crude is difficult, in part because the viscosity of the crude is so high, and in part because the density of heavy crudes can be the same as the density of water.

For heavy crude oils it is necessary to use conditions of high temperature, a chemical demulsifier and often electrostatic separation to adequately dehydrate the mixture. Demulsifiers usually comprise blends of surface active chemicals, e.g. ethoxylated phenolic resins, in a carrier solvent. Heating is preferably carried out at a temperature in the range 200° to 320° F.

25 In the desalting and dehydrating of crude oil, water-insoluble solids such as rust, iron sulfide, silt, clay, drilling mud components, etc., contained in the crude accumulate in an interfacial emulsion layer or cuff between the desalted crude and water phases. The major portion of this cuff is typically recycled to the crude feed and the remainder is typically mixed with a light diluent oil to break the emulsion and then settled to separate the crude and the water,
30 where the water-insoluble solids separate with the water. The separated oil phase may be combined with the desalted and/or dehydrated crude. However, in the process of this invention

- 8 -

the cuff can be processed with the oil. The water is removed in the heating and flashing step, and the solids can be recovered at the point where the calcium and magnesium oxides are recovered.

Crude oils contain salts dissolved in water entrained from the production well and from saltwater picked up during tanker shipment. Less typically, solid salt particles are suspended in the crude. Generally, the chloride salts are sodium chloride, magnesium chloride, and calcium chloride. Depending on the source of the saltwater, the amount of each salt in the crude can vary considerably. The dehydrated heavy crude oil may contain from about 0.1 to about 5 percent by volume water, and from between about 50 to about 8000 parts per million salts, more typically from about 400 to about 4000 parts per million salts. If the crude was partially desalted, the salt content will be at the lower end of this range, and the crude oil/water will be at an elevated temperature. This aids the next step in the process, in which the crude oil and remaining water are then heated.

While these desalting and secondary dehydrating pre-treatment steps are beneficial, one important aspect of this invention is that such pre-treatments are not necessary to the process of the invention. The process of this invention removes both water and corrosive acids from the crude.

To the extent added water from steps such as prior desalting is not present, water or steam may need to be added to obtain a mixture, or a reaction mass, until the mixture has been exposed to about 5% by weight water, where a fraction of the water is preferably steam.

In this invention the crude is heated to from about 300° F to about 600° F, preferably from about 350° F to about 550° F, more preferably from about 400° F to about 500° F, and even more more preferably from about 450° F to about 500° F. The heat may come from one or more of heat exchangers, furnaces, or by contact with steam.

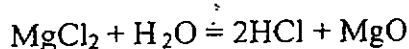
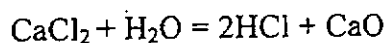
It may be advantageous to preheat the crude under pressure to minimize boiling and to realize more efficient heat transfer. Such preheating may be to a temperature above the ranges stated above. When the pressure is lowered and petroleum and water flash off, the crude will cool. Preheating to a temperature of between 400° F and about 700° F is advantageous in many situations.

The crude is then flashed in a flash drum to remove gases. The pressure on the crude during the flash may range from a vacuum of about 3 psia to over 20 atmospheres of pressure. It

- 9 -

is preferred that the pressure be between about 1 and about 10 atmospheres. It may be necessary to heat the crude in the flash drum as water and hydrocarbons vaporize. It is often particularly advantageous to heat the crude, or to keep the temperature from dropping below about 300° F, by admixing medium or low pressure steam to the crude. Medium or high pressure steam is advantageously obtained from a gasification process. The steam is admixed with the heated crude to provide additional water and heat, as well as to carry away the hydrochloric acid.

The salts such as magnesium chloride and calcium chloride react with water in the crude to form metal oxides and hydrochloric acid. The chloride salts begin to hydrolyze at temperatures in the range of 300° F to 450° F, which may occur in the preheat exchangers. Sodium chloride is stable and does not hydrolyze significantly in the atmospheric crude tower system. Hydrochloric acid is released when $MgCl_2$ and $CaCl_2$ are hydrolyzed by water present in crude oil:



The calcium and magnesium oxides are essentially inert solids during subsequent processing of the oil, in that they do not promote corrosion and that they do not poison many catalysts. These solids, plus other solids such as sodium chloride, iron, and clays, may be advantageously removed by filtering after solvent is admixed with the heavy crude in subsequent deasphalting steps. The solvent lowers the viscosity of the heavy crude to the point where solids removal by, for example, filtering or gravity separation, is technically feasible. It is advantageous to remove sodium chloride and other solids with the calcium and magnesium oxides during solvent deasphalting.

Or, the solids may be allowed to precipitate with the asphaltenes in subsequent deasphalting steps.

The crude may also contain low molecular weight carboxylic acids (acetic, propionic, butyric acids) which will generally follow the hydrochloric acid.

The hydrochloric acid is gaseous at the temperature and pressure of the crude in the flash drum. The hydrochloric acid is separated from the crude and proceeds to a wash column on the top of the flash drum.

Corrosion may occur on the metal surfaces of fractionating towers such as crude towers, trays within the towers, heat exchangers, etc. The most troublesome locations for corrosion are

- 10 -

tower top trays, overhead lines, condensers, and top pump around exchangers. It is usually within these areas that water condensate is formed or carried along with the process stream. The top temperature of the fractionating column is usually, but not always, maintained at about or above the dew point of water. The aqueous condensate formed contains a significant concentration of acid. The pH of the condensate is highly acidic and corrosive. Accordingly, neutralizing treatments are used to render the pH of the condensate more alkaline to thereby minimize acid-based corrosive attack.

The gaseous hydrochloric acid is contacted with aqueous base, typically ammonia. The base reacts with the acid to form a salt, i.e., the ammonia reacts with the hydrochloric acid to form NH_4Cl . Other bases, especially metal oxides and hydroxides can also be used. The water is captured in a chimney tray so that it does not fall into the oil. There is an excess of NH_3 in the water stream. Ammonia is effective for increasing the pH of the overhead bulk water to within a safe pH range, which is greater than about 5.5, preferably greater than about 6.5, and more preferably greater than about 7.5.

Corrosion in the overhead system is caused by hydrogen chloride combining with liquid water. The corrosion occurs in the overhead components of the flash drum which include the top tower trays, the piping that comes off the top of the drum and the reflux lines, the heat exchangers, the condensers and rundown lines, and the distillate drums where the condensed overhead stream is separated into liquid naphtha product and reflux. Materials commonly used in overhead trays and components include carbon steel, Monel 400 and 410 stainless steel. Corrosion damage can be very severe, including metal loss severe enough to cause leakage to the external environment and internal heat exchanger leaks, plugging of trays and other internals which interfere with tower operation and control and impair energy efficiency. In addition, corrosion in the overhead system can cause operating problems in downstream units. Because of the severity of the corrosion, even one day of uncontrolled corrosion can have serious consequences.

Temperature decreases moving up the tower and into the overhead system. At some point, temperature falls below the dewpoint temperature of the process gas and water condenses on the equipment surfaces in a thin film. This point is called the initial condensation point. Water continues to condense as the process gas moves downstream and is further cooled. The overhead gas is totally condensed in the overhead condensers, is accumulated in a condensate

- 11 -

drum, and is removed from the bottom boot of the condensate drum. Operators usually maintain the temperature at the top of the tower at least 30° F. to 40° F above the water dewpoint to avoid corrosion in the top trays. The trend, however, is to reduce tower top temperature to improve recovery of naphtha, and this drives the dewpoint down into the tower.

5 In one embodiment of this invention, hydrogen chloride neutralizers are added to the crude prior to flashing to inhibit hydrogen chloride corrosion. The most common neutralizer is ammonia. It can be added as ammonia gas or as an aqueous solution to the crude either before or after pre-heating. In this case ammonium chloride is flashed from the crude. A disadvantage is that ammonium chloride solids may precipitate from the gas. Sodium hydroxide, or other
10 hydroxides, are also useful hydrogen chloride neutralizers. However, these hydrogen chloride neutralizers increase the sodium chloride (or similar salt) content of the crude. Therefore, the amount of neutralizers is typically insufficient to completely neutralize the hydrochloric acid that is eventually formed.

15 In the process of this invention, it is preferred that the water in the overhead trays contain an excess of ammonia. The water is therefore advantageously recirculated to increase contacting. A small purge stream is extracted from the water to reduce the build up of impurities in the water.

20 In addition to being subject to severe corrosion at the condensation point, the overhead trays are also vulnerable to severe corrosion where ammonium chloride precipitates as a solid out of the gas phase onto internal surfaces. If the partial pressure of ammonium chloride above the internal surface exceeds the vapor/equilibrium pressure, then ammonium chloride will precipitate on the surface and accumulate.

25 Ammonium chloride is formed in the system by the reaction between ammonia and hydrochloric acid. The ammonium chloride, which is vaporized during elevated temperature processing, is sublimed onto the internal surfaces of the overhead equipment. Sublimation, as herein defined, is intended to mean that the ammonium chloride passes directly from the vapor state to its solid crystalline form, bypassing its liquid phase. Crystalline ammonium chloride builds up on these surfaces resulting in the operational problems. Ammonium chloride deposits are hygroscopic and, when exposed to wet process gas streams flowing by, absorb moisture,
30 forming a wet paste with a highly corrosive pH. A method for the inhibition and removal of ammonium chloride deposits on the internal surfaces of the equipment in a refinery which

- 12 -

processes consists of adding to the crude a non-filming polyamine. These amines are particularly effective in systems where acid concentrations are high and where a water wash is absent. Systems without a water wash exhibit a lower dew point than systems which employ a water wash. The combination of high levels of acidic species and the absence of a water wash increase the likelihood of the amine salt depositing on overhead equipment before the initial dewpoint is reached.

It is also possible to inhibit corrosion in condensing systems comprising wet hydrocarbons and chloride by feeding a mixture of amines to the condensing system to elevate the pH profile of condensed water above the range in which severe corrosion of system internals can occur. The amine blend is formulated to preclude deposition and accumulation of the hydrochloride salts of the amines above the water dewpoint and is optimized to the condensing system to minimize amine treat rate.

Illustrative compounds coming which are used to reduce NH_4Cl precipitation include such primary amines as n-dodecyl amine, n-tetradecyl amine, n-hexadecylamine, lauryl amine, myristyl amine, palmityl amine, stearyl amine, and oleyl amine. Other examples of such products are dimethylaminopropylamine, diethylenetriamine, ethylenediamine, tris-(2-aminoethyl) amine, trimethylamine and triethylamine. The amount of non-filming polyamine added to the system is based upon the amount of ammonium chloride present in the system and is preferably in the range of about 1 to 10 moles per mole of ammonium chloride.

U.S. Pat. No. 4,703,865 describes a method where low melting point/oxygenated liquid amines are injected in hydrocarbon processing units to remove and/or to prevent the formation of ammonium salt deposits. Furthermore, oxygen containing hydrocarbon compounds are injected in hydrocarbon processing units to remove metal compound deposits. The oxygenated amines and/or the oxygen containing compounds may be injected alone or in combination. In addition, these amines and/or the oxygen containing compounds are used in combination with filming agents which causes corrosion in such units.

Conventional neutralizing compounds include ammonia, morpholine, and ethylenediamine. U.S. Pat. No. 4,062,764 discloses that alkoxyated amines are useful in neutralizing the initial condensate. U.S. Pat. No. 3,472,666 suggests that alkoxy substituted aromatic amines in which the alkoxy group contains from 1 to 10 carbon atoms are effective corrosion inhibitors in petroleum refining operations. Representative examples of these materials

- 13 -

are aniline, anisidine and phenetidines. Alkoxylated amines, such as methoxypropylamine, are disclosed in U.S. Pat. No. 4,806,229. They may be used either alone or with the film forming amines of previously noted U.S. Pat. No. 4,062,764.

The gaseous overhead stream containing the hydrochloric acid and NH_4Cl is condensed, adding to the water phase and forming a hydrocarbon phase, leaving non-condensables. More aqueous base, i.e. ammonia is added to ensure that any hydrochloric acid that might be carried over is neutralized. The condensed hydrocarbons mixed into partially refined hydrocarbon stream downstream so that they become product. The non-condensables such as light hydrocarbons and hydrogen sulfide are routed to the gasifier, also called the thermal gasifier, or other appropriate unit operation.

In a preferred embodiment, an excess of ammonia-laden water is circulated, effectively washing and neutralizing acid from the walls and trays of the flash drum. The ammonia water is collected in a chimney tray. Trayed vessels, especially chimney trays, are preferred so that the neutralizing water and base do not contact the oil. This excess water washing prevents the accumulation of ammonium chloride crystals. A sidestream is removed to prevent salt accumulation.

Petroleum crudes are subjected to various processes in order to form lower boiling components such as gasoline. First, the lower boiling components are removed via distillation. The lower boiling fractions, and particularly gasoline, are recovered as an overhead fraction from the distilling zones. The intermediate components are recovered as side cuts from the distillation zone. The fractions are cooled, condensed, and sent to collecting equipment.

Other fractions are separated from this processed crude and are converted to lighter hydrocarbons by, for example, hydrocracking. The product that is obtained from such conversion is distilled to produce a gasoline fraction, a fuel oil fraction, lubricating oil fraction, etc. Calcium oxide and magnesium oxide, by-products of the current invention, are essentially inert and do not poison most catalysts used in these conversion processes. As a practical matter, however, these solids are removed prior to conversion processes.

Asphaltenes in crude makes further processing such as hydrocracking of the crude difficult. To maximize the value of heavy petroleum oils, separation of the asphalt components in the oil has been practiced for years. The asphaltenes in the crude are typically separated from the crude after the light hydrocarbons have been removed by distillation. In the process of this

- 14 -

invention, an asphaltene-rich fraction is separated from the processes crude, and then this asphaltene-rich fraction is gasified in the thermal oxidizer.

Deasphalting the heavy crude is accomplished by, for example, solvent deasphalting. The extraction of asphaltenes from an asphaltene-containing hydrocarbon material with a low-boiling solvent, typically a low-boiling alkane, is known. See, for example, U.S. Patent Number 4,391,701 and U.S. Patent Number 3,617,481, the disclosures of which are incorporated herein by reference. The deasphalting step involves contacting the solvent with the asphaltene-containing hydrocarbon material in an asphaltene extractor. It is advantageous to maintain the temperature and pressure such that the asphaltene-containing hydrocarbon material and the low-boiling solvent are fluid or fluid like.

When the predominately light alkane solvent is admixed with the crude, the viscosity of the crude is reduced. At this point solids, including sodium chloride, calcium oxide, magnesium oxide, iron and rust may be advantageously removed by, for example, filtering or gravity separation. Alternatively, these solids can be precipitated with the asphaltenes. These solids will then be fed to the gasifier with the asphaltenes. These solids may form a slag in the gasifier, and both solids and slag will then be trapped in the gasifier quench system.

The non-asphaltene components are recovered, processed as necessary, and sold as valuable products. The asphaltene-rich component that has very little value. Asphaltenes are a hydrocarbonaceous material suitable for gasification. See, for example, U.S. patent Number 4,391,701, the disclosure of which is incorporated herein by reference. Gasification of heavy oils and hydrocarbonaceous solids, i.e., an asphaltene-rich composition, involves mixing the hydrocarbonaceous materials with an oxygen-containing gas in a gasification zone, wherein conditions are such that the oxygen and hydrocarbonaceous material react to form synthesis gas. Gasification thereby converts the heavy oil and solids into synthesis gas which is a valuable product.

Such a gasification process results in considerable waste heat which is advantageously used in the remaining process operations, such as the hydrogen chloride removal process of this invention. Typically, both high and low pressure steam is generated as a byproduct of the gasification process. This steam is advantageously used to heat the crude and to remove the hydrogen chloride from the crude. Additionally, gasification generates low level heat, which

- 15 -

may be used directly via heat exchangers to heat the crude mixture entering either a preliminary desalting process or the thermal degradation of calcium/magnesium salts process.

Advantageous use can be made of the water used to capture and neutralize the corrosive gases. The overhead gases are condensed, and vaporized hydrocarbons will also condense.

5 These may form an emulsion with the circulating ammonia-laden water, which may be broken by conventional methods.

To prevent buildup of salts, a side stream of this ammonia-laden water is removed, advantageously stripped to remove ammonia which can be recycled. The NH_4Cl rich water is stripped with low-pressure steam to liberate any free ammonia so that it can be recycled to the process. A portion of this water is then routed to the gasifier. The remaining water is routed to the gray water tank in the gasification section where it is utilized in the process. The water typically contains residual hydrocarbons, such as water in oil-water emulsions that are not effectively broken. These hydrocarbons are advantageously turned into valuable synthesis gas in the gasifier. The water helps moderate the gasifier temperatures. Entrained solids are gasified if carbon containing or vitrified if metallic.

Water not injected into the gasifier can be used in other portions of the gasification process, particularly in the quench process. Wastewater can be admixed with wastewater from the gasification process for efficient treatment and disposal.

Particular benefits are realized by integration the process of stripping corrosive materials from the crude with the subsequent processes of deasphalting and of gasifying at least a portion of the crude. The gasification process provides the steam and, optionally, the lower grade heat necessary to heat the crude and to strip the corrosive acids. This steam is also beneficially used in the deasphalting process. The subsequent deasphalting and gasification processes provides a means of disposing the wastewater used in collecting the corrosive gases, wherein the waste stream provides benefits such as moderating the gasifier temperature. The subsequent deasphalting and gasification processes also provides a means of removing the remaining solids from the processed crude by separating the solids during the deasphalting process and, optionally, by vitrifying these solids in the gasifier.

IN THE CLAIMS:

1. A process of treating a heavy oil comprising:
providing the heavy oil, wherein the heavy oil is a reaction mass comprising,
water and salts;
generating steam or heat as byproducts of a gasification process;
heating the reaction mass to maintain the temperature between about 350° F to about
600° F using the steam or the heat:
exposing the reaction mass to between about 0.2 to about 20 atmospheres of pressure;
and
separating vapor from the reaction mass, wherein the vapor comprises steam and
hydrochloric acid.
2. The process of claim 1 further comprising adding water to the heavy oil to
provide a reaction mass comprising between about 0.1 and about 20 percent by weight water.
3. The process of claim 1 further comprising neutralizing the vapors.
4. The process of claim 1 wherein the temperature of the reaction mass is
maintained from about 400° F to about 500° F.
5. The process of claim 1 wherein the temperature of the reaction mass is
maintained at from about 450° F to about 500° F.

-17-

6. The process of claim 2 wherein the added water comprises steam.

7. The process of claim 1 further comprising neutralizing the hydrochloric acid vapor by contacting the vapor with an aqueous base.

8. The process of claim 7 wherein the aqueous base comprises aqueous ammonia.

9. The process of claim 7 wherein the aqueous base contacts the vapor in a trayed vessel.

10. The process of claim 7 wherein the aqueous base is collected on a chimney tray.

11. The process of claim 7 wherein the aqueous base is collected on a chimney tray, further comprising circulating and recycling the aqueous base.

12. The process of claim 9 further comprising adding amine to maintain a pH in the base of greater than about 5.5.

13. The process of claim 1 further comprising desalting the heavy oil prior to heating the reaction mass to between about 350 and about 600°F.

14. The process of claim 1 further comprising preheating the heavy oil to a temperature of between 400°F and about 700°F prior to heating the reaction mass.

-18-

15. The process of claim 3 further comprising cooling the neutralized vapor and collecting the condensables.
16. The process of claim 15 further comprising separating the condensables into hydrocarbon and aqueous phases.
17. A process of treating an oil comprising:
providing an oil, wherein said oil comprises between about 0.1 to about 5 percent by volume water and greater than about 400 parts per million salts;
heating the oil to from about 350° F to about 600° F;
flashing vapor comprising hydrochloric acid from the oil, thereby leaving salt solids in the oil;
neutralizing the vapors; and
gasifying a portion of the oil.

18. The process of claim 17 wherein the temperature of the reaction mass is maintained at from about 400° F to about 550° F.
19. The process of claim 17 wherein the temperature of the reaction mass is maintained at from about 450° F to about 500° F.
20. The process of claim 17 further comprising neutralizing the hydrochloric acid vapor by contacting the vapor with an aqueous amine.
21. The process of claim 20 wherein the amine comprises aqueous ammonia.
22. The process of claim 20 wherein the amine contacts the vapor in a chimney tray, and further comprising recycling the aqueous amine.
23. The process of claim 20 further comprising adding amine to maintain a pH in the amine of greater than about 5.5.
24. The process of claim 22 further comprising removing a slip stream from the recycled aqueous amine, stripping the amine from the water with steam, and then adding the amine to the recycled aqueous amine.
25. The process of claim 24 further comprising utilizing the stripped water as gray water in a gasification process, wherein said gasification process converts a portion of the crude to a gas comprising carbon monoxide and hydrogen.
26. The process of claim 17 further comprising preheating the heavy oil to a temperature of between 400° F and about 700° F prior to separating vapor comprising from the reaction mass.
27. The process of claim 17 further comprising cooling the neutralized vapor and separating the condensables into hydrocarbon and aqueous phases.

28. The process of claim 27 further comprising gasifying the non-condensables.
29. The process of claim 17 further comprising deasphalting the heavy oil after separating the vapors, thereby forming an asphaltene-rich composition and an asphaltene-depleted composition, wherein the asphaltene-rich composition is subsequently gasified.
30. The process of claim 29 wherein deasphalting comprises contacting the heavy oil with an alkane solvent to form a mixture, subjecting the mixture to conditions where asphaltenes precipitate to form an asphaltene-rich composition, and separating the asphaltene-rich composition from the asphaltene-depleted composition.
31. The process of claim 30 further comprising separating solids from the mixture prior to precipitating asphaltenes.
32. The process of claim 31 wherein the solids comprise one or more of sodium chloride, calcium oxide, and magnesium oxide.
33. The process of claim 29 further comprising generating steam in the gasification of the asphaltene-rich composition, and utilizing said steam to heat the heavy oil.
34. The process of claim 29 wherein solids in the oil are separated into the asphaltene-rich composition.
35. The process of claim 34 wherein solids comprise one or more of sodium chloride, calcium oxide, and magnesium oxide.
36. The process of claim 34 wherein the asphaltene-rich composition is gasified.
37. The process of claim 29 wherein the vapors are neutralized by contacting the vapor with an aqueous amine.

38. The process of claim 37 wherein the amine contacts the vapor in a chimney tray, and further comprising recycling the aqueous amine.

39. The process of claim 38 further comprising removing a slip stream from the recycled aqueous amine, stripping the amine from the water with steam, adding the amine to the recycled aqueous amine, and routing the water to the gasifier.

40. The process of claim 39 further comprising utilizing the stripped water as gray water in a gasification process.