DECREASING FOULING IN HYDROCARBON-BASED FLUIDS

Applicant: BAKER HUGHES INCORPORATED, Houston, TX (US)

Inventors: Thomas J. Falkler, Missouri City, TX (US); Roger D. Metzler, Sugar Land, TX (US)

Assignee: BAKER HUGHES INCORPORATED, Houston, TX (US)

Appl. No.: 15/090,912

Filed: Apr. 5, 2016

Related U.S. Application Data

Provisional application No. 62/144,649, filed on Apr. 8, 2015.

Publication Classification

Int. Cl. C10G 75/04 (2006.01)

U.S. Cl. CPC C10G 75/04 (2013.01)

ABSTRACT

An effective amount of at least one first component and an effective amount of at least one second component may contact a hydrocarbon-based fluid or be introduced into a hydrocarbon-based fluid having at least one foulant for decreasing the fouling by the foulant(s) as compared to an otherwise identical hydrocarbon-based fluid absent the first component(s) and second component(s). The first component(s) may be considered a dispersant, and the second component(s) may be considered free radical inhibitors in a non-limiting embodiment.
DECREASING FOULING IN HYDROCARBON-BASED FLUIDS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Patent Application Ser. No. 62/144,649 filed Apr. 8, 2015, incorporated herein by reference in its entirety.

TECHNICAL FIELD

The present invention relates to methods and compositions for decreasing or preventing fouling of a hydrocarbon-based fluid, and more specifically relates to methods and compositions for decreasing foulants within hydrocarbon-based fluids in a refinery.

BACKGROUND

As the price or shortage of high quality crude oil increases, there will be an ever-increasing demand to find ways to better exploit lower quality feedstocks and extract fuel values therefrom. Lower quality feedstocks may have relatively high quantities of foulants, such as asphaltenes, coke, and coke precursors, acid gases, carbon dioxide (CO₂), hydrogen sulfide (H₂S), mercaptans (R—SH), which are difficult to process and commonly cause fouling of conventional catalysts and hydrosprocessing equipment. As more economical ways to process lower quality feedstocks become available, such feedstocks may possibly catch, or even surpass, higher quality crude oils, in the not-too-distant future, as the primary source of refined fossil fuels used to operate automobiles, trucks, farm equipment, aircraft, and other vehicles that rely on internal combustion.

Hydrocracking is used in the petroleum industry to process crude oil and/or other petroleum products for commercial use by preventing or inhibiting the fouling by the foulants. Hydrocracking is a catalytic cracking process using an elevated partial pressure of hydrogen gas to purify the hydrocarbon stream. Ebullated-bed hydrocracking is one type of hydrocracking that may be used for resid conversion, and the ebullated-bed hydrocrackers may have a continuous addition and/or removal of catalysts. However, hydrocracking is subject to asphaltene precipitation as the saturates and aromatics contained in the hydrocarbon-based fluid that hold the asphaltenes in solution are removed or converted, which is driven by asphaltene-solubility chemistry. Fouling may occur downstream from the ebullated bed hydrocracker reactor, such as in bottom stream areas, atmospheric column bottoms, vacuum-column bottoms, vacuum-column furnaces, high- and mid-pressure separators, and the like. Extensive fouling may result in unplanned shutdowns, downtime and lost production and consequently increased operating costs.

Conversion reaction rates (thermal cracking), leading to fouling by asphaltenes decomposition, increase more rapidly with rising temperatures compared to the hydrogen-saturation reactions that inhibit sediment formation. Accordingly, temperatures and conversions above pre-determined limits may lead to uncontrolled sediments and coke generation. However, operating below the pre-determined limits only results in lost conversion with no major advantages in terms of sediment deposition control and run lengths.

Asphaltenes are most commonly defined as that portion of petroleum, which is soluble in xylene and toluene, but insoluble in heptane or pentane. Asphaltenes exist in crude oil as both soluble species and in the form of colloidal dispersions stabilized by other components in the crude oil. Asphaltenes have higher molecular weights and are the more polar fractions of crude oil, and can precipitate upon pressure, temperature, and compositional changes in crude oil resulting from blending or other mechanical or physico-chemical processing. Asphaltene precipitation and deposition can cause problems in subterranean reservoirs, upstream production facilities, mid-stream transportation facilities, refineries, and fuel blending operations. In petroleum production facilities, asphaltene precipitation and deposition can occur in near wellbore reservoir regions, wells, flowlines, separators, and other equipment. Once deposited, asphaltenes present numerous problems for crude oil producers. For example, asphaltene deposits can plug downhole tubulars, wellbores, choke off pipes and interfere with the functioning of safety shut-off valves, and separator equipment. Asphaltene have caused problems in refinery processes such as desalters, crude oil distillation preheat units, and cokers.

In addition to carbon and hydrogen in the composition, asphaltenes may contain nitrogen, oxygen and sulfur species, and may also contain metal species such as nickel, vanadium, and iron. Typical asphaltenes are known to have different solubilities in the formation fluid itself or in certain solvents like carbon disulfide or aromatic solvents, such as benzene, toluene, xylene, and the like. However, the asphaltenes are insoluble in solvents like paraffinic compounds, including but not limited to pentane, heptane, octane, etc. Asphaltene stability can even be disturbed by mixing hydrocarbon-based fluids i.e. such as mixing two types of crude oils together, two types of shale oils together, condensates, and others, of different origins at certain ratios as the chemistry of the hydrocarbon-based fluids from different sources may be incompatible and induce destabilization of the asphaltenes therein. In non-limiting examples, such as during refining or fuel blending, two or more hydrocarbon-based fluids may be mixed together. Sometimes, changes in physical conditions are sufficient to induce destabilization, or even the mixture of different hydrocarbon-based fluids that have incompatible chemistries. Said differently, even if neither hydrocarbon-based fluid, alone, has destabilized foulants or the hydrocarbon-based fluid would not act as a destabilizing additive by itself, the mixing or the mixture of two or more hydrocarbon-based fluids may destabilize the foulants present in either hydrocarbon-based fluid.

Coke is an insoluble organic portion of crude oil, distillation residua, or residua from thermal/catalytic conversion processes, such as including, but not limited to, visbreaker tar or L.C. tar/HC oil residuum. Coke may have polyaromatic hydrocarbons (PAHs) dispersed therein with a ring structure of about 4 to about 5 or more condensed aromatic rings.

Coke precursors are the fragments that make up the coke. They are often formed by thermal cracking, dealkylation and/or dehydrogenation processes commonly used for the breaking down of complex organic molecules. They are barely soluble in the crude oil and/or residual, but they tend to precipitate. Once they precipitate, the coke precursors tend to polymerize or conglomerate and form coke.

Accordingly, there are large incentives to mitigate fouling during refining. There are large costs associated with
shutting down production units because of the foulants within, as well as the cost to clean the units. The foulants may create an insulating effect within the production unit, reduce the efficiency and/or reactivity, and the like. In either case, reducing the amount of fouling would reduce the cost to produce hydrocarbon-based fluids and the products derived therefrom.

[0011] Conventional individual antifoulants have not been working well to improve fouling control in refinery processes running shale, tight oils and/or blends with tight oils. The fouling mechanisms of shale oils are not as well defined or understood. It is suspected that some of the foulant precursors or initiators may be below detection limits, or that they are more intermittent in nature, which makes the discovery and definition of the mechanism more difficult.

[0012] There is an ongoing need to prevent or inhibit the fouling by the foulants in a hydrocarbon-based fluid.

SUMMARY

[0013] There is provided, in one form, a method for decreasing fouling during the refining of a hydrocarbon-based fluid comprising at least one foulant. The method may include contacting the hydrocarbon-based fluid with an effective amount of at least one first component and an effective amount of at least one second component to decrease fouling by the at least one foulant as compared to an otherwise identical hydrocarbon-based fluid absent the first component(s) and the second component(s). The contacting of the hydrocarbon-based fluid with the first component(s) and the second component(s) may occur at the same time or at a different time. The first component(s) may be or include an acrylate vinyl pyridolmine copolymer; a succinimide, an alpha olefin and maleic anhydride reaction product, a reaction product from nonyl phenol reaction with ethylene diamine, a C₉₋₁₄ olefin and maleic anhydride copolymer, a Mannich reaction product, a dodecyl/tert-octyl phenol resin, a sulfonic acid, an inorganic overbase, and combinations thereof. The second component(s) may be or include N,N'-di-sec-butyl-p-phenylenediamine; 2,6-di-tert-butyl-4-methylphenol; 4-sec-butyl-2,6-di-tert-butyl-phenol; mixed tertiary butyl phenols; mixed hindered phenols; butylated hydroxytoluenes; blend of substituted p-phenylenediamines; quinones; amino-para-creosols; and combinations thereof.

[0015] The first component(s) and the second component(s) appear to decrease the amount of fouling by the foulant(s) as compared to an otherwise identical hydrocarbon-based fluid absent both the first component(s) and the second component(s).

BRIEF DESCRIPTION OF THE DRAWING

[0016] FIG. 1 is a graph depicting the stability of four different samples in the presence or absence of various components.

DETAILED DESCRIPTION

[0017] It has been discovered that an effective amount of at least one first component and at least one second component may decrease and/or inhibit at least one foulant within a hydrocarbon-based fluid by contacting the hydrocarbon-based fluid with the first and second component(s) or introducing the component(s) into the hydrocarbon-based fluid. The foulant(s) may be or include, but are not limited to, asphaltene, coke precursors, coke, polyolefins, and combinations thereof. Inorganic materials such as carbon dioxide, hydrogen sulfide, mercaptans, carbonyl derivatives, and combinations thereof, if present can contribute to the total foulant content, but are generally thought to be caught in the organic matrix. The method thus reduces the potential of the inorganic materials to deposit and cause fouling. The formation of the organic matrix and the potential of the inorganic materials to deposit is reduced.

[0018] The first component(s) and second component(s) may decrease, prevent, and/or inhibit the fouling by the foulant(s) therein as compared to an otherwise identical hydrocarbon-based fluid absent both the first component(s) and second component(s). In one non-limiting embodiment, the first component(s) can increase the dispersion of the foulant(s) within the hydrocarbon-based fluid. Use of the first component(s) can be done into the hydrocracking fluid and decrease the aggregation and/or precipitation of the foulant(s) in a non-limiting embodiment. The second component(s) can inhibit the free radicals produced from the foulant(s).

[0019] “Inhibit” is defined herein to mean that the antifoulant(s) may suppress or reduce the amount of total fouling by the foulant(s) within the hydrocarbon-based fluid, assuming there are foulant(s) present within the fluid. That is, it is not necessary for fouling to be entirely prevented for the methods and compositions disclosed herein to be considered effective, although complete prevention is a desirable goal. Moreover, the fouling by the foulant(s) may be prevented or inhibited by decreasing the ability of the foulant(s) from polymerizing or otherwise agglomerating, reducing the ability of the foulant(s) to form deposits or precipitates, and the like.

[0020] The methods described are considered successful if the first component(s) and the second component(s) together decrease an amount of fouling than would otherwise occur in the absence of the first and second components. Alternatively, success is obtained if a majority of the fouling is decreased or inhibited or inactivated, i.e. at least 51 wt %, alternatively from about 70 wt % independently to about
99.9 wt %, or from about 90 wt % independently to about 96 wt % in another non-limiting embodiment.

[0021] The foulants may or may not already exist in the hydrocarbon-based fluid prior to refining (e.g. hydrocracking) of the hydrocarbon-based fluid. In one non-limiting example, asphaltenes may crack and/or polymerize during the reaction process of hydrocracking. Thus, regardless of whether the foulant(s) are present in the hydrocarbon-based fluid before or after hydrocracking, the foulant(s) may precipitate, or the asphaltenes may form coke precursors and possibly coke, in a non-limiting embodiment.

[0022] The first component(s) may be or include, but is not necessarily limited to, an acrylate vinyl pyridinodine copolymer, a succinimide, an alpha olefin and maleic anhydride reaction product, a reaction product from nonyl phenol reaction with ethylene diamine (EDA), a C₃₋₁₅ oлеfin and maleic anhydride copolymer, a Mannich reaction product, a dodecyl/tet-octyl phenol resin, a sulfonic acid, an inorganic overbase, and combinations thereof. Non-limiting examples of the Mannich reaction product may be or include, but are not necessarily limited to tetraethylenepentamime (TEPA), aromatic amine derivatives, poly allyl amine, and combinations thereof. Non-limiting examples of the sulfonic acid may be or include dodecylbenzensulfonic acid (DBBSA), polyalkylsulfonic acid, polyaromaticsulfonic acid, and combinations thereof.

[0023] Non-limiting examples of the inorganic overbase may be or include, but are not necessarily limited to, magnesium sulfonates, magnesium oxides, magnesium carboxylates, calcium sulfonates, calcium oxides, calcium carboxylates, and combinations thereof. “Overbase” as used herein refers to where the amount of base is more than the amount of metal within the first component. The inorganic overbase refers to inorganic compounds with a great capacity of neutralizing acids. For example, when a magnesium oxide overbase is used as a first component, the amount of oxide is lower than the amount of magnesium to form the inorganic overbase. The inorganic overbase may be prepared in any manner known to those of ordinary skill in the art.

[0024] The second component(s) may be or include, but is non-limiting embodiment not limited to, N,N'-di-sec-butyl-p-phenylenediamine; N,N'-di-sec-butyl-4-methylphenol, 4-sec-butyl-2,6-di-tert-butylphenol (a g. ISONOX® 132); mixed tertiary butyl phenols (e.g. ISONOX® 133); mixed hindered phenols; butylated hydroxytoluene (BHT); blend of substituted p-phenylenediamines (e.g. NAUGARD® R); quinones; amino-para-creosol; and combinations thereof. Non-limiting examples of the mixed hindered phenols include polyalkyl substituted phenol, hydroquinone derivatives, and combinations thereof. Non-limiting examples of the quinones may be or include substituted alkyl quinone, benzoquinone derivatives, substituted quinone methide, and combinations thereof. A non-limiting example of the amino-para-creosol may be or include nitroso phenol derivatives.

[0025] The first component(s) and the second component(s) may contact or be introduced into the hydrocarbon-based fluid as an additive mixture (i.e. at the same time), or at different times. The terms “first component” and “second component” are not used herein to denote an order that the components must be added; “first” and “second” are simply used to distinguish the two groups of chemicals from each other. Said differently, the “second component” may be added before the “first component”. 

[0026] The effective amount of the first component(s) and the second component(s) is difficult to predict in advance because it would depend on the particular hydrocarbon-based fluid, the type of targeted foulant, the operating conditions (e.g. temperature), and the like. However, in one non-limiting embodiment, the effective amount of the first component(s) may range from about 1 ppm independently to about 10,000 ppm based on the total hydrocarbon-based fluid. Alternatively, the amount of the first component(s) may range from about 10 ppm independently to about 1,000 ppm, or from about 50 ppm independently to about 300 ppm, in another non-limiting embodiment. As used herein with respect to a range, “independently” means that any lower threshold may be used together with any upper threshold to give a suitable alternative range.

[0027] In one non-limiting embodiment, the effective amount of the second component(s) may range from about 1 ppm independently to about 10,000 ppm based on the total hydrocarbon-based fluid. Alternatively, the amount of the second component(s) may range from about 10 ppm independently to about 1,000 ppm, or from about 50 ppm independently to about 300 ppm, in another non-limiting embodiment.

[0028] In a non-limiting embodiment, the volume ratio of the formulated product of the first component to the second component may range from about 1:1 independently to about 1:20, alternatively from about 2:1 independently to about 20:1.

[0029] The first component(s) and second component(s) may be introduced into the hydrocarbon stream at one or more of a variety of locations, such as but not limited to, upstream from or into an ebullated bed hydrocracking unit (e.g. an LC finer or H-oil reactor), into an intermediate separator, into a crude oil vacuum distillation unit, into an atmospheric crude oil distillation units, and combinations thereof. The first component(s) and second component(s) may be added into the hydrocarbon-based fluid by adding them into a distillate flow to blend with a distillate residue feed, adding them into the hydrocracking unit feed by a connected feed line, and combinations thereof. The first component(s) and second component(s) may be added into the hydrocarbon-based fluid at a pre-determined rate, which may be a continuous rate, an intervallic rate, an intermittent rate, and combinations thereof. “Distillate flow” is used herein to refer to an atmospheric or vacuum distillation cut or distillate from a conversion process, such as but not limited to gasoline, kerosene, gas oil, vacuum gas oil, visbreaker gas oil, FCC light cycle oil, FCC slurry oil, and the like.

[0030] The term “hydrocracking” is defined herein to mean a process where the primary purpose is to decrease the boiling range of a heavy oil feedstock and where a substantial portion of the feedstock is converted into products with boiling ranges lower than that of the original feedstock. Hydrocracking generally involves fragmentation of larger hydrocarbon molecules into smaller molecular fragments having a fewer number of carbon atoms and a higher hydrogen-to-carbon ratio. Hydrocracking may involve the formation of hydrocarbon free radicals during fragmentation, which may be followed by capping the free radical ends or moieties with hydrogen. The hydrogen atoms or radicals that react with hydrocarbon free radicals during hydrocracking may be generated at or by active catalyst sites of an ebullated bed hydrocracking unit.
The operating conditions of the hydrocarbon-based fluid may require the temperature, pressure, and the like to be within a particular range. In a non-limiting example, the temperature of the hydrocarbon-based fluid may range from about 25°C, independently to about 50°C, alternatively from about 50°C, independently to about 250°C. The pressure surrounding the hydrocarbon-based fluid may range from about 0 bars (0 kPa), independently to about 250 bars (approximately 25,000 kPa); alternatively from about 10 bars (1,000 kPa) independently to about 200 bars (approximately 20,000 kPa).

The hydrocarbon-based fluid may be a still fluid, or it may be part of a hydrocarbon feed or hydrocarbon-based fluid or flowing stream; “hydrocarbon-based fluid” is defined herein to include both. In a non-limiting embodiment, the hydrocarbon fluid may be a liquid, a gas, or a combination thereof. Non-limiting examples of the hydrocarbon-based fluid may be or include a crude oil, a bitumen, a shale oil, a tight oil, a refinery fluid, and combinations thereof. In a non-limiting embodiment, the crude oil may be a combination or mixture of at least two different crude oils. “Crude oil” as used herein includes water-in-crude emulsions, a fluid that is only crude oil, and mixtures thereof.

The invention will be further described with respect to the following Example, which is not meant to limit the invention, but rather to further illustrate the various embodiments.

**EXAMPLE 1**

Now turning to FIG. 1, which is a graph depicting the stability of four different samples in the presence or absence of various components. Sample 1 included a shale oil without the addition of the first component or the second component. Sample 2 included the same shale oil in the presence of 3000 ppm of the first component, which was an alpha olefin copolymer. Sample 3 included the same shale oil in the presence of 3000 ppm of the first component and the second component, which were the alpha olefin copolymer and a blended phenolic antioxidant. Sample 4 included the same shale oil in the presence of 3000 ppm of the second component, which was a blended phenolic antioxidant.

Each sample was analyzed to obtain the inflection point value (IPV) thereof. To do this, a non-solvent was added to each sample in an intervallic fashion; the amount of non-solvent is noted on the x-axis. At each interval of non-solvent added, the transmittance was measured with a near infrared spectrometer; the transmittance is noted on the y-axis. An inflection point value was determined for each interval of non-solvent added. The non-solvent was n-heptane.

The IPV continued to rise for each sample until the point of asphaltenic flocculation, and then the IPV decreased. The near infrared transmittance data obtained from the hydrocarbon-based fluid was plotted on the graph vs. volume of non-solvent added. The maximum inflection point value is the representative value of the amount of non-solvent required to cause the foulants (e.g., asphaltenes and/or polynuclear aromatics in this instance) in the hydrocarbon-based fluid to become unstable and precipitate. The more non-solvent added correlates to a more stable hydrocarbon-based fluid.

As noted by FIG. 1, sample 3 (the shale oil, the first component, and the second component) using the composition and method described herein was the most stable.

Hydrocarbon fluids that contain little to no asphaltenes and/or polynuclear aromatics may form asphaltenes and/or polynuclear aromatics upon heating. The purpose of a thermal stress test in the case of a hydrocarbon-based fluid (e.g. a shale oil in a non-limiting example), such as by heating the fluid at sub cracking to near cracking temperatures to form asphaltenes and/or polynuclear aromatics. Heating stressing of the sample may be required if the samples do not have sufficient asphaltenes to see a flocculation point in the titration test on the crude sample as received. Shale oils are very paraffinic in nature and they inherently destabilize asphaltenes and cannot support them in solution. Thus, most of the naturally occurring asphaltenes are probably left down-hole or have dropped out during recovery and transport. Therefore, refinery processes running high percentages of shale oil in their crude blends (70-100 vol %) may contain very low levels (<0.5 wt %) of “naturally occurring” asphaltenes and this may be below the detection limit of common commercial optical devices used to detect the flocculation point by titration, or alternatively the amount of flocculated asphaltenes simply do not create a great enough optical density to be detected. The shale oils also contain relatively high levels of waxy material. The heavy waxes (C28-C72 have been identified as commonly present) and other asphaltene resinous material can chemically react at refinery process systems and form PNAS (poly-nuclear aromatics) which behave similarly to asphaltenes with respect to process fouling and in the titration test—essentially, “asphaltenes” forming in-situ at process temperatures. The heating, or thermal stressing, in the test is required to evaluate this potential effect and to evaluate the additives on that effect for crude samples that do not generate a detectable flocc point as received.

In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been described as effective in providing methods and compositions for decreasing the fouling by foulant(s) within a hydrocarbon-based fluid. However, it will be evident that various modifications and changes can be made thereto without departing from the broader spirit or scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded as illustrative rather than a restrictive sense. For example, specific first components, specific second components, hydrocarbon-based fluids, foulants, proportions, addition procedures, and locations within a refinery where the components may contact the hydrocarbon-based fluid falling within the claimed parameters, but not specifically identified or tried in a particular composition or method, are expected to be within the scope of this invention.

The present invention may suitably comprise, consist of or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed. For instance, the method for decreasing fouling during the refining of a hydrocarbon-based fluid comprising at least one foulant may consist of or consist essentially of contacting the hydrocarbon-based fluid with an effective amount of at least one of a first component and an effective amount of at least one of a second component to decrease fouling by the foulant(s) as compared to an otherwise identical hydrocarbon-based fluid absent the first component(s) and the second
component(s); the contacting of the hydrocarbon-based fluid with the first component(s) and the second component(s) may occur at the same time or a different time; the first component(s) may be or include an acrylate vinyl pyrolidinone copolymer, a succinimide, an alpha olefin and maleic anhydride reaction product, a reaction product from nonyl phenol reaction with ethylene diamine, a C_{2-5}-C_{18} olefin and maleic anhydride copolymer, a Mannich reaction product, a dodecyl/tert-octyl phenol resin, a sulfonic acid, an inorganic overbase, and combinations thereof; and the second component(s) may be or include N,N-di-sec-butyl-p-phenylene diamine; 2,6-di-ter-butyl-4-methylphenol; 4-sec-butyl-2,6-di-ter-butyl-phenol; mixed tertiary butyl phenols; mixed hindered phenols; butylated hydroxytoluene; blend of substituted p-phenylendiamines; quinones; amino-paracresols; and combinations thereof.

[0041] The treated hydrocracked hydrocarbon-based fluid composition may suitably comprise, consist of or consist essentially of a hydrocarbon-based fluid, at least one first component in an amount ranging from about 0.1 ppm to about 10,000 ppm based on the total treated fluid, at least one second component in an amount ranging from about 0.1 ppm to about 10,000 ppm based on the total treated fluid, and at least one foulant; the hydrocarbon-based fluid may be or include a crude oil, a bitumen, a shale oil, a tight oil, a refined fluid, and combinations thereof; the first component(s) may be or include an acrylate vinyl pyrolidinone copolymer, a succinimide, an alpha olefin and maleic anhydride reaction product, a reaction product from nonyl phenol reaction with ethylene diamine, a C_{2-5}-C_{18} olefin and maleic anhydride copolymer, a Mannich reaction product, a dodecyl/tert-octyl phenol resin, a sulfonic acid, an inorganic overbase, and combinations thereof; the second component(s) may be or include N,N-di-sec-butyl-4-methylphenol, 4-sec-butyl-2,6-di-ter-butylphenol; mixed tertiary butyl phenols; mixed hindered phenols; butylated hydroxytoluene; quinones; amino-paracresols; and combinations thereof.

[0042] The words “comprising” and “comprises” as used throughout the claims, are to be interpreted to mean “including but not limited to” and “includes but not limited to”, respectively. As used herein, the terms “comprising,” “including,” and “comprised by,” and grammatical equivalents thereof are inclusive or open-ended terms that do not exclude additional, unrecited elements or method acts, but also include the more restrictive terms “consisting of” and “consisting essentially of” and grammatical equivalents thereof. As used herein, the term “may” with respect to a material, structure, feature or method act indicates that such is contemplated for use in implementation of an embodiment of the disclosure and such term is used in preference to the more restrictive term “is” so as to avoid any implication that other, compatible materials, structures, features and methods usuable in combination therewith should or must be excluded.

[0043] As used herein, the singular forms “a,” “an,” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[0044] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0045] As used herein, relational terms, such as “first,” “second,” “top,” “bottom,” “upper,” “lower,” “over,” “under,” etc., are used for clarity and convenience in understanding the disclosure and accompanying drawings and do not connote or depend on any specific preference, orientation, or order, except where the context clearly indicates otherwise.

[0046] As used herein, the term “substantially” in reference to a given parameter, property, or condition means and includes to a degree that one of ordinary skill in the art would understand that the given parameter, property, or condition is met with a degree of variance, such as within acceptable manufacturing tolerances. By way of example, depending on the particular parameter, property, or condition that is substantially met, the parameter, property, or condition may be at least 90.0% met, at least 95.0% met, at least 99.0% met, or even at least 99.9% met, regardless of the type of percentage.

[0047] As used herein, the term “about” in reference to a given parameter is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the given parameter).

What is claimed is:

1. A method for decreasing fouling during the refining of a hydrocarbon-based fluid comprising at least one foulant, wherein the method comprises:
   contacting the hydrocarbon-based fluid with an effective amount of at least one first component to decrease fouling by the at least one foulant, wherein the at least one first component is selected from the group consisting of an acrylate vinyl pyrolidinone copolymer, a succinimide, an alpha olefin and maleic anhydride reaction product, a reaction product from nonyl phenol reaction with ethylene diamine, a C_{2-5}-C_{18} olefin and maleic anhydride copolymer, a Mannich reaction product, a dodecyl/tert-octyl phenol resin, a sulfonic acid, an inorganic overbase, and combinations thereof;
   contacting the hydrocarbon-based fluid with an effective amount of at least one second component to decrease fouling by the at least one foulant, wherein the at least one second component is selected from the group consisting of 2,6-di-ter-butyl-4-methylphenol; 4-sec-butyl-2,6-di-ter-butylphenol; mixed tertiary butyl phenols; mixed hindered phenols; butylated hydroxytoluenes; quinones; amino-paracresols; and combinations thereof;
   wherein the contacting the hydrocarbon-based fluid with the at least one first component and the at least one second component occurs at the same time or a different time; and
   decreasing the fouling by the at least one foulant within the hydrocarbon-based fluid as compared to an otherwise identical hydrocarbon-based fluid absent the contacting the hydrocarbon-based fluid with the at least one first component and the at least one second component.

2. The method of claim 1, wherein the contacting the hydrocarbon-based fluid with the at least one first component occurs at a location selected from the group consisting of upstream from an ebullated bed hydrocracking unit, into an ebullated bed hydrocracking unit, into an interstage separator, into a vacuum distillation unit, into an atmospheric distillation unit, and combinations thereof.

3. The method of claim 1, wherein the contacting the hydrocarbon-based fluid with the at least one second component occurs at a location selected from the group consist-
ing of upstream from an ebullated bed hydrocracking unit, into an ebullated bed hydrocracking unit, into an interstage separator, into a vacuum distillation unit, into an atmospheric distillation unit, and combinations thereof.

4. The method of claim 1, wherein the hydrocarbon-based fluid is selected from the group consisting of a crude oil, a bitumen, a shale oil, a light oil, a refinery fluid, and combinations thereof.

5. The method of claim 4, wherein the hydrocarbon-based fluid is a crude oil blend having at least two different crude oils.

6. The method of claim 1, wherein the effective amount of the at least one first component ranges from about 0.1 ppm to about 10,000 ppm based on the total amount of the hydrocarbon-based fluid.

7. The method of claim 1, wherein the effective amount of the at least one second component ranges from about 0.1 ppm to about 10,000 ppm based on the total amount of the hydrocarbon-based fluid.

8. The method of claim 1, wherein the at least one foulant is selected from the group consisting of asphaltenes, coke precursors, coke, polyolefins, and combinations thereof.

9. A method for decreasing fouling during the refining of a hydrocarbon-based fluid comprising at least one foulant; wherein the method comprises:

   introducing an additive into the hydrocarbon-based fluid in an amount ranging from about 0.1 ppm to about 10,000 ppm based on the total amount of the hydrocarbon-based fluid to decrease fouling by the at least one foulant; wherein the additive comprises at least one first component and at least one second component; wherein the at least one first component is selected from the group consisting of an acrylate vinyl pyrolidinone copolymer, a succinimide, an alpha olefin and maleic anhydride reaction product, a reaction product from nonyl phenol reaction with ethylene diamine, a C_{24}-C_{28} olefin and maleic anhydride copolymer, a Mannich reaction product, a dodecyl/tert-octyl phenol resin, a sulfonic acid, an inorganic overbase, and combinations thereof; and decreasing the fouling by the at least one foulant within the hydrocarbon-based fluid as compared to an otherwise identical hydrocarbon-based fluid absent the introducing the additive into the hydrocarbon-based fluid; wherein the hydrocarbon-based fluid is selected from the group consisting of a crude oil, a bitumen, a shale oil, a light oil, a refinery fluid, and combinations thereof.

10. The method of claim 9, wherein the introducing the additive into the hydrocarbon-based fluid occurs at a location selected from the group consisting of upstream from an ebullated bed hydrocracking unit, into an ebullated bed hydrocracking unit, into an interstage separator, into a vacuum distillation unit, into an atmospheric distillation unit, and combinations thereof.

11. The method of claim 9, wherein the hydrocarbon-based fluid is a crude oil blend having at least two different crude oils.

12. The method of claim 9, wherein the at least one foulant is selected from the group consisting of asphaltenes, coke precursors, coke, polyolefins, and combinations thereof.

13. A treated hydrocracked hydrocarbon-based fluid composition comprising:

   a hydrocarbon-based fluid selected from the group consisting of a crude oil, a bitumen, a shale oil, a light oil, a refinery fluid, and combinations thereof;

   at least one first component in an amount ranging from about 0.1 ppm to about 10,000 ppm based on the total amount of the hydrocarbon-based fluid; wherein the at least first component is selected from the group consisting of an acrylate vinyl pyrolidinone copolymer, a succinimide, an alpha olefin and maleic anhydride reaction product, a reaction product from nonyl phenol reaction with ethylene diamine, a C_{24}-C_{28} olefin and maleic anhydride copolymer, a Mannich reaction product, a dodecyl/tert-octyl phenol resin, a sulfonic acid, an inorganic overbase, and combinations thereof;

   at least one second component in an amount ranging from about 0.1 ppm to about 10,000 ppm based on the total amount of the hydrocarbon-based fluid; wherein the at least second component is selected from the group consisting of 2,6-di-ter-butyl-4-methylphenol, 4-sec-butyl-2,6-di-tert-butyl phenol; mixed tertiary butyl phenols; mixed hindered phenols; butylated hydroxytoluenes; quinones; amino-para-creosols; and combinations thereof;

   at least one foulant; and wherein the treated hydrocracked hydrocarbon-based fluid composition comprises a decreased amount of the at least one foulant as compared to an otherwise identical hydrocracked hydrocarbon-based fluid composition absent the at least one first component and the at least one second component.

14. The composition of claim 13, wherein the treated hydrocracked hydrocarbon-based fluid is present at a location selected from the group consisting of upstream from an ebullated bed hydrocracking unit, into an ebullated bed hydrocracking unit, into an interstage separator, into a vacuum distillation unit, into an atmospheric distillation unit, and combinations thereof.

15. The composition of claim 13, wherein the hydrocarbon-based fluid is a crude oil having at least two different crude oils.

16. The composition of claim 13, wherein the at least one foulant is selected from the group consisting of asphaltenes, coke precursors, coke, polyolefins, and combinations thereof.

17. A treated hydrocracked hydrocarbon-based fluid composition comprising:

   a crude oil;

   at least one first component selected from the group consisting of an acrylate vinyl pyrolidinone copolymer, a succinimide, an alpha olefin and maleic anhydride reaction product, a reaction product from nonyl phenol reaction with ethylene diamine, a C_{24}-C_{28} olefin and maleic anhydride copolymer, a Mannich reaction product, a dodecyl/tert-octyl phenol resin, a sulfonic acid, an inorganic overbase, and combinations thereof;

   at least one second component selected from the group consisting of 2,6-di-ter-butyl-4-methylphenol, 4-sec-butyl-2,6-di-tert-butylphenol; mixed tertiary butyl phenols;
nols; mixed hindered phenols; butylated hydroxytolu-
enses; quinones; amino-para-cresols; and combinations thereof;
at least one foulant;
wherein the volume ratio of the at least one first compo-
nent to the at least one second component ranges from
about 1:1 to about 1:20; and
wherein the treated hydrocracked hydrocarbon-based
fluid composition comprises a decreased amount of the
at least one foulant as compared to an otherwise
identical hydrocracked hydrocarbon-based fluid com-
position absent the at least one first component and the
at least one second component.
18. The composition of claim 17, wherein the crude oil is
a crude oil blend having at least two different crude oils.
19. The composition of claim 17, wherein the at least one
foulant is selected from the group consisting of asphaltenes,
coke precursors, coke, and combinations thereof.

* * * * *