

INHIBITOR ENHANCED THERMAL UPGRADING OF HEAVY OILS

FIELD OF THE INVENTION

[0001] The present invention relates to a method for upgrading heavy oils by contacting the heavy oil with an inhibitor additive and then thermally treating the inhibitor additized heavy oil. The invention also relates to the upgraded product from the inhibitor enhanced thermal treatment process.

BACKGROUND OF THE INVENTION

[0002] Heavy oils are generally referred to those hydrocarbon comprising oils with high viscosity or API gravity less than 20. Crude oils and crude oil residuum obtained after atmospheric or vacuum distillation of crude oils that exhibit an API gravity less than 20 are examples of heavy oils. Upgrading of heavy oils is important in production, transportation and refining operations. An upgraded heavy oil typically will have a higher API gravity and lower viscosity compared to the heavy oil that is not subjected to upgrading. Lower viscosity will enable easier transportation of the oil. A commonly practiced method for heavy oil upgrading is thermal treatment of heavy oil. Thermal treatment includes processes such as visbreaking and hydro-visbreaking (visbreaking with hydrogen addition). The prior art in the area of thermal treatment or additive enhanced visbreaking of hydrocarbons teach methods for improving the quality, or reducing the viscosity, of crude oils, crude oil distillates or residuum by several different methods. For example, the use of additives such as the use of free radical initiators is taught in US Patent No. 4,298,455; the use of thiol compounds and aromatic hydrogen donors is taught in EP 175511; the use of free radical

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acceptors is taught in US Patent No. 3,707,459; and the use of a hydrogen donor solvent is taught in US Patent No. 4,592,830. Other art teaches the use of specific catalysts, such as low acidity zeolite catalysts (US 4,411,770) and molybdenum catalysts, ammonium sulfide and water (US 4,659,543). Other references teach upgrading of petroleum resids and heavy oils (Murray R. Gray, Marcel Dekker, 1994, pp.239-243) and thermal decomposition of naphthenic acids (US 5,820,750).

[0003] Generally, the process of thermal treatment of heavy oil can result in an upgraded oil with higher API. In some instances, the sulfur and naphthenic acid content can also be reduced. However, the main drawback of thermal treatment of heavy oils is that with increased conversion there is the formation of toluene insoluble (TI) material. These toluene insoluble materials comprise organic and organo-metallic materials derived from certain components of the heavy oil during the thermal process. Generally, the TI materials tend to increase exponentially after a threshold conversion. Thus, the formation of TI materials limits the effectiveness of thermal upgrading of heavy oils. Presence of TI material in upgrading oils is undesirable because such TI materials can cause fouling of storage, transportation and processing equipment. In addition, the TI materials can also induce incompatibility when blended with other crude oils. Increasing conversion without generating toluene insoluble material is a long-standing need in the area of thermal upgrading of heavy oils. The instant invention addresses this need. As used herein, crude oil residuum or resid refers to residual crude oil obtained from atmospheric or vacuum distillation of a crude oil.

SUMMARY OF THE INVENTION

[0004] In one embodiment, there is provided a method for upgrading a heavy oil comprising the steps of:

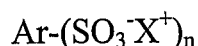
- contacting the heavy oil with an effective amount of an inhibitor additive to provide an inhibitor additized heavy oil, and then
- thermally treating said inhibitor additized heavy oil at a temperature in the range of 250°C to 500°C for 0.5 to 6 hours to upgrade the heavy oil.

[0005] Another embodiment is an upgraded heavy oil prepared by:

- contacting the heavy oil with an effective amount of an inhibitor additive to provide an inhibitor additized heavy oil, and then
- thermally treating said inhibitor additized heavy oil at a temperature in the range of 250°C to 500°C for 0.5 to 6 hours.

[0006] In still another embodiment, there is provided a method for upgrading heavy oils which method comprises:

- a) contacting the heavy oil with an effective amount of a water-soluble inhibitor additive to provide an inhibitor additized heavy oil, which water-soluble inhibitor additive is represented by the chemical structure:



where Ar is a homonuclear aromatic group of at least 2 rings, n is an integer from 1 to 5, X is selected from Group I (alkali) and Group II (alkaline-earth) elements of the periodic table of elements and n is an integer from 1 to 5 when an alkali metal is used and from 2-10 when an alkaline earth metal is used;

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- b) thermally treating said inhibitor additized heavy oil at a temperature in the range of 250°C to 500°C for a time between 0.1 to 10 hours;
- c) contacting said thermally treated additized heavy oil with water wherein the water-soluble inhibitor additive migrates to the water phase;
- d) separating the thermally treated heavy oil from the water phase containing said water-soluble inhibitor additive;
- e) separating the inhibitor additive from the water; and
- f) recycling said separated inhibitor additive to contacting a heavy oil in step a) above.

[0007] Yet another embodiment is a method for upgrading a heavy oil comprising the steps of:

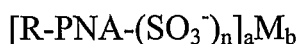
- contacting the heavy oil with an effective amount of a bifunctional inhibitor additive to provide a bifunctional inhibitor additized heavy oil, and then
- thermally treating said inhibitor additized heavy oil at a temperature in the range of 250°C to 500°C in the presence of hydrogen at hydrogen partial pressure of between 500 to 2500 psig (3447.38 to 17236.89 kPa) for a time between 0.1 to 10 hours to upgrade the heavy oil.

[0008] Another embodiment is an upgraded heavy oil prepared by:

- contacting the crude oil with an effective amount of a bifunctional additive to provide a bifunctional additized heavy oil, and then
- thermally treating said additized heavy oil at a temperature in the range of 250°C to 500°C in the presence of hydrogen at hydrogen partial pressure of between 500 to 2500 psig (3447.38 to 17236.89 kPa) for a time between 0.1 and 10 hours.

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[0009] Still another embodiment is a bifunctional inhibitor-hydrotreating additive having the chemical structure:



wherein PNA is a polynuclear aromatic hydrocarbon containing 2 to 15 aromatic rings; n is an integer from 1 to 15 representing the number of sulfonic SO_3^- functionality on the PNA hydrocarbon; R is an alkyl group containing from 0 to 40 carbon atoms; M is an element selected from the group consisting of Group IV-B, V-B, VI-B, VII-B and VIII of the Long Form of The Periodic Table of Elements; and a and b are integers each ranging from 1 to 4.

BRIEF DESCRIPTION OF THE FIGURES

[0010] Figure 1 hereof shows illustrative examples of $\text{R-PNA}-(\text{X})_n$ inhibitor additives of the instant invention wherein $\text{R}=\text{O}$, $\text{X}=\text{SO}_3^-$ and the additives are sodium salts of the PNA-sulfonic acids.

[0011] Figure 2 hereof is a schematic of Run 1 and Run 2 of Example 2 shown as scheme-1 and scheme-2 respectively.

[0012] Figure 3 hereof is a bar graph of toluene insolubles (TI) for thermally treated Athabasca bitumen with no additive labeled none and with two additives 1,3,6-NTSS and 2,6-NDSS

[0013] Figure 4 hereof is a is a bar graph of toluene insolubles (TI) for thermally treated Athabasca bitumen with no additive labeled none and with the additive 1,3,6-NTSS worked up according to scheme-1 and scheme-2.

DETAILED DESCRIPTION OF THE INVENTION

[0014] According to one embodiment of the invention, there is provided a method for upgrading heavy oils, such as heavy oils and crude oil residuum. Resid feedstocks include but are not limited to residues from the atmospheric and vacuum distillation of petroleum crudes or the atmospheric or vacuum distillation of heavy oils, visbroken resids, tars from deasphalting units or combinations of these materials. Atmospheric and vacuum topped heavy bitumens can also be employed. Typically, such feedstocks are high-boiling hydrocarbonaceous materials having a nominal initial boiling point of 538°C or higher, an API gravity of 20° or less, and a Conradson Carbon Residue content of 0 to 40 weight percent.

[0015] An inhibitor additive is added to the crude or crude oil residuum followed by thermal treatment at temperatures in the range of 250°C to 500°C for 30 second to 6 hours.

[0016] The inhibitor additive is a polynuclear aromatic acid of the structures:



wherein PNA is a polynuclear aromatic hydrocarbon containing 2 to 15 aromatic rings and X is an acid functionality selected from the group consisting of SO₃H, COOH, and PO₃H and n is an integer from 1 to 15 representing the number of acid functionality (X) on the PNA structure. The aromatic rings can be fused or isolated aromatic rings. Further, the aromatic ring can be homo-nuclear or hetero-nuclear aromatic rings. By homo-nuclear aromatic ring is meant aromatic rings containing only carbon and hydrogen. By hetero-nuclear aromatic ring is meant aromatic rings that contain nitrogen, oxygen or sulfur in addition to carbon and hydrogen. R is an alkyl group containing from 0 to 40 carbon atoms. R can be a

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linear or branched alkyl group. Mixtures of R-PNA-(X)_n can be used. R-PNA-sulfonic acids are preferred. Salts of the R-PNA-(X)_n additives are more preferred. Group I or Group II elements of the Long Form of The Periodic Table of Elements such as sodium, potassium or calcium are the most preferred. Some illustrative non-limiting examples of preferred R-PNA-(X)_n inhibitor additives are given in Figure 1 hereof.

[0017] As previously mentioned, the preferred inhibitor additive of the present invention is an aromatic polysulfonic acid salt of the chemical structure:



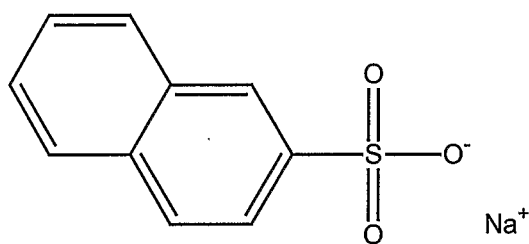
where Ar is a homonuclear aromatic group of at least 2 rings, n is an integer from 1 to 5, and X is selected from Group I (alkali) and Group II (alkaline-earth) elements of the periodic table of elements and n is an integer from 1 to 5 when an alkali metal is used and from 2-10 when an alkaline earth metal is used.

Preferably X is selected from the alkali metals, preferably sodium or potassium and mixtures thereof. Group I and Group II refer to the groups of the Periodic Table of Elements. Preferably X is selected from the alkali metals, more preferably sodium. It is also preferred that Ar have from 2 to 15 rings, more preferably from 2 to 4 rings, and most preferably from 2 to 3 rings. It is within the scope of this invention that the aromatic polysulfonic acid salts of the present invention be prepared from the polysulfonation of a light catalytic cycle oil. Light catalytic cycle oil is a complex combination of hydrocarbons produced by the distillation of products from the fluidized catalytic cracking (FCC) process with carbon numbers in the range of C₉ to C₂₅, boiling in the range of 340°F (171°C) to 700°F (371°C). Light catalytic cycle oil is also referred to herein as light cat cycle oil or LCCO. LCCO is generally rich in 2-ring aromatic molecules. LCCO from a US refinery typically comprises 80% aromatics. The aromatics are typically

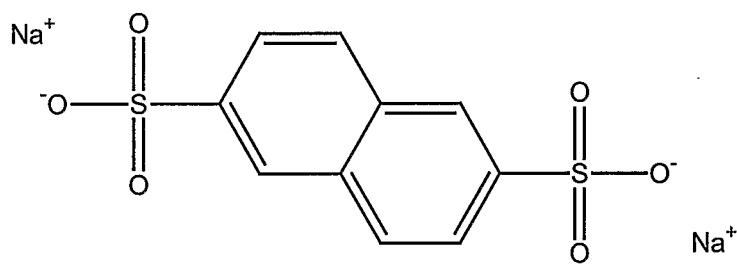
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33% 1-ring aromatics and 66% 2-ring aromatics. Further, the 1- and 2-ring aromatics can be methyl, ethyl and propyl substituted. The methyl group is the major substituent. Nitrogen and sulfur containing heterocycles, such as indoles, quinolines and benzothiophenes are also present in minor quantities.

[0018] Non-limiting examples of preferred polysulfonic aromatic acid salts of the present invention are shown below.

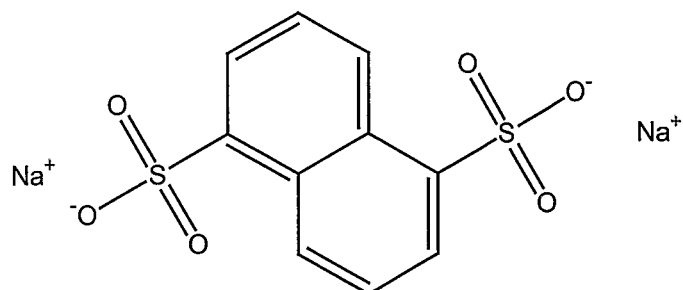


naphthalene-2-sulfonic acid sodium salt

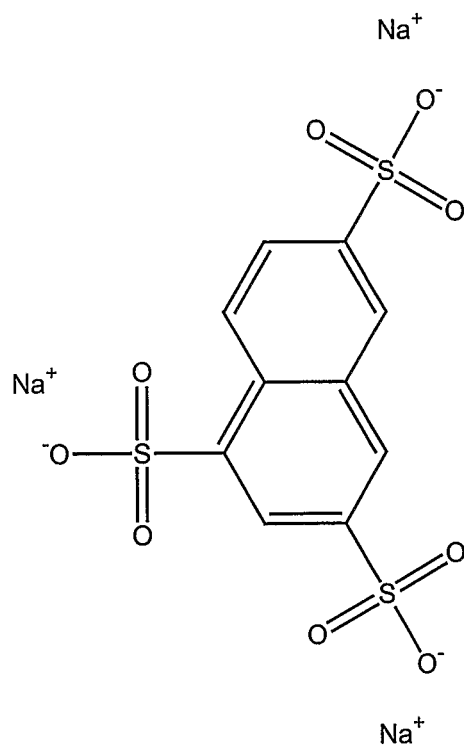


naphthalene-2,6-disulfonic acid sodium salt

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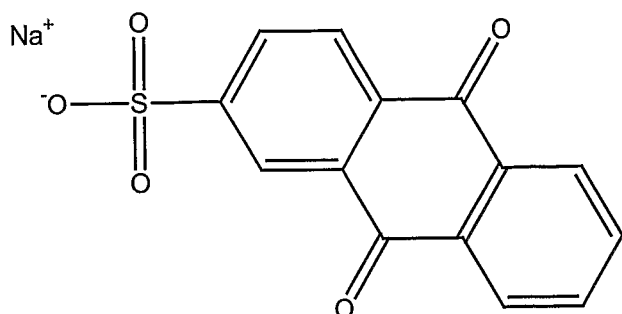


naphthalene-1,5-disulfonic acid sodium salt

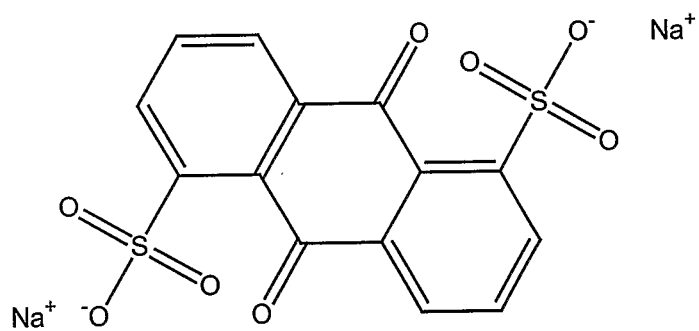


naphthalene-1,3,6-trisulfonic acid sodium salt

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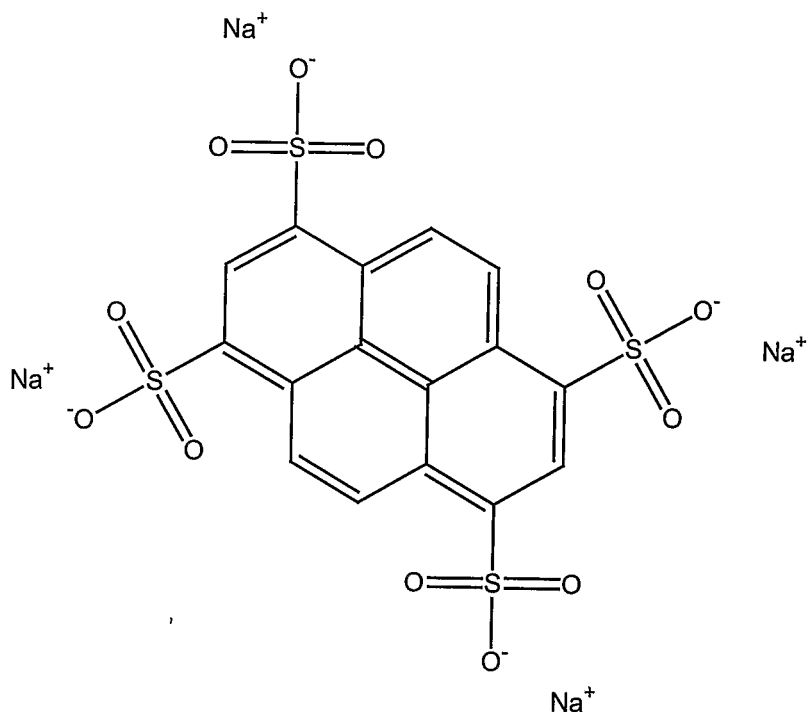
anthraquinone-2-sulfonic acid sodium salt



anthraquinone-1,5-disulfonic acid sodium salt

and

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pyrene-1,3,6,8-tetra sulfonic acid sodium salt

[0019] The polysulfonic acid compositions can be produced from LCCO by a process that generally includes the polysulfonation of the LCCO with a stoichiometric excess of sulfuric acid at effective conditions. Conventional sulfonation of petroleum feedstocks typically use an excess of the petroleum feedstock - not an excess of sulfuric acid. It has unexpectedly been found by the inventors hereof that when a stoichiometric excess of sulfuric acid is used to sulfonate an LCCO the resulting polysulfonated product has novel properties and uses. The aromatic polysulfonic acid is converted to the aromatic polysulfonic acid salt by treatment with an amount of caustic to neutralize the acid functionality. The LCCO polysulfonic acid composition can best be described as a mixture of 1- and 2-ring aromatic cores with one or more sulfonic acid groups per aromatic core. The aromatic cores are methyl, ethyl, and propyl substituted, with the methyl group being the more preferred substituent.

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[0020] Typically, the amount of inhibitor additive added can be 10 to 50,000 wppm, preferably 20 to 3000 wppm, and more preferably 20 to 1000 wppm based on the amount of crude oil or crude oil residuum. The inhibitor additive can be added as is or in a suitable carrier solvent. Preferred carrier solvents are aromatic hydrocarbon solvents such as toluene, xylene, crude oil derived aromatic distillates such as Aromatic 150 sold by ExxonMobil Chemical Company, water, alcohols and mixtures thereof. When the inhibitor additive is a salt of the PNA-acid it is preferred to use water or water-alcohol mixtures as the carrier solvent. Preferred alcohols are methanol, ethanol, propanol and mixtures thereof. When mixtures of PNA-acid and PNA-acid salts are used, it is preferred to use an emulsion of water and hydrocarbon solvents as the carrier medium. The emulsion can be a water-in-oil emulsion or an oil-in-water emulsion. The carrier solvent is preferably 10 to 80 weight percent of the mixture of additive and carrier solvent.

[0021] Contacting the inhibitor additive with the heavy oil can be achieved at any time prior to the thermal treatment. Contacting can occur at the point where the heavy oil is produced at the reservoir, during transportation or at a refinery location. In the case of crude oil resids, the inhibitor additive is contacted at any time prior to thermal treatment. After contacting, it is preferred to mix the heavy oil and additive. Any suitable mixing means conventionally known in the art can be used. Non-limiting examples of such suitable mixers include in-line static mixers and paddle mixers. The contacting of the heavy oil and additive can be conducted at any temperature in the range of 10°C to 90°C. After contacting and mixing the heavy oil and additive, the mixture can be cooled from contacting temperature to ambient temperature, i.e., 15°C to 30°C. Further, the additized-

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cooled mixture can be stored or transported from one location to another location prior to thermal treatment. Alternately, the additized and cooled mixture can be thermally treated at the location of contacting if so desired.

[0022] Thermal treatment of the additized heavy oil comprises heating the oil at temperatures in the range of 250°C to 500°C for 30 seconds to 6 hours. Process equipment such as visbreakers can be advantageously employed to conduct the thermal treatment. It is preferred to mix the additized heavy oil during thermal treatment using mixing means known to those having ordinary skill in the art. It is also preferred to conduct the thermal treatment process in an inert environment. Using inert gases such as nitrogen or argon gas in the reactor vessel can provide such an inert environment.

[0023] The inhibitor enhanced thermal upgrading process provides a thermally upgraded product that is higher in API gravity compared to the starting feed and lower in toluene insoluble material compared to a thermally upgraded product that is produced in the absence of the inhibitor additive of the instant invention. The inhibitor additive of the instant invention inhibits the formation of toluene insoluble material while facilitating thermal conversion, such as thermal cracking, to occur in a facile manner. The thermally upgraded product of the process of the instant invention has at least 20% less toluene insoluble material compared to the product from a thermally upgraded process conducted at the same temperature for the same period of time, but in the absence of the inhibitor additive. The thermally upgraded product of the process of the instant invention has at least 15 API units higher compared to the product from a thermally upgraded process conducted at the same temperature for the same period of time, but in the absence of the inhibitor additive. The upgraded oil of the instant invention comprises the

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upgraded heavy oil, the added inhibitor additive and products, if any, formed from the added inhibitor additive during the thermal upgrading process.

[0024] When the upgrading is conducted in a pre-refinery location, it is customary to mix the upgraded oil with other produced but not thermally treated crude oils prior to transportation and sale. The other produced but not thermally treated crude oils, can be the same heavy oil from which the upgraded oil is obtained or different crude oils. The other produced but not thermally treated crude oils can be dewatered and or desalted crude oils. By “non-thermally treated” is generally meant not thermally treated at temperatures in the range of 250°C to 500°C for 30 seconds to 6 hours. A particular advantage of the upgraded oil of the instant invention is that the presence of a relatively low amount of toluene insoluble (TI) material enables blending of the upgraded oil and other oils in a compatible manner. The mixture of upgraded oil of the instant invention with other compatible oils is a novel and valuable product of commerce. Another feature of the upgraded oil product of the instant invention is that the product can also be mixed with distillates or resids of other crude oils in a compatible manner. The low TI levels in the product enables this mixing or blending.

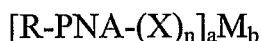
Thermal Upgrading With Hydrogen and Bifunctional Additive

[0025] According to another embodiment of the invention, there is provided a thermal treatment method for upgrading heavy crude oils and crude oil residuum including hydrogen. A bifunctional additive that provides the dual functionality of TI inhibition and catalysis of hydrogenation reactions is added to the crude or crude oil residuum followed by thermal treatment. The thermal treatment comprises treating the bifunctional additized oil at a temperature in the range of

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250°C to 500°C in the presence of hydrogen at hydrogen partial pressures of between 500 to 2500 psig (3447.38 to 17236.89 kPa) for a time between 0.1 to 10 hours to result in an upgraded oil.

[0026] Examples of bifunctional additives suitable for thermal treatment method, including hydrogen for upgrading of heavy oils, are polynuclear aromatic sulfonic acid and alkyl polynuclear aromatic sulfonic acid salts of the metals of Group IV-B, V-B, VI-B, VII-B and VIII of the Periodic Table of Elements. The bifunctional additive is represented by the chemical structure:



wherein PNA is a polynuclear aromatic hydrocarbon containing 2 to 15 aromatic rings; X is a sulfonic acid functionality, n is an integer from 1 to 15 representing the number of sulfonic acid functionality on the PNA hydrocarbon; R is an alkyl group containing from 0 to 40 carbon atoms; M is an element selected from the group consisting of Group IV-B, V-B, VI-B, VII-B and VIII of the Long Form of The Periodic Table of Elements; and a and b are integers each ranging from 1 to 4. The R group can be a linear or branched alkyl group. The aromatic rings can be fused or isolated aromatic rings. Further, the aromatic rings can be homo-nuclear or hetero-nuclear aromatic rings. By homo-nuclear aromatic rings is meant aromatic rings containing only carbon and hydrogen. By hetero-nuclear aromatic ring is meant aromatic rings that contain nitrogen, oxygen and sulfur in addition to carbon and hydrogen.

[0027] When the metal component of the bifunctional additive is a Group IV-B metal it may be titanium (Ti), zirconium (Zr), or hafnium (Hf). When the metal is a Group V-B metal it may be vanadium (V), niobium (Nb), or tantalum (Ta). When the metal is a Group VI-B metal it may be chromium (Cr), molybdenum

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(Mo), or tungsten (W). When the metal is a Group VII-B metal it can be manganese (Mn) or rhenium (Re). When the metal is a Group VIII metal it may be a non-noble metal such as iron (Fe), cobalt (Co), or nickel (Ni) or a noble metal such as ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), or platinum (Pt). Preferably, the metal is a Group VI-B metal, most preferably molybdenum.

[0028] An effective amount of the bifunctional additive may be oil-miscible or oil-dispersible. It is preferred that the bifunctional additives of the instant invention, by virtue of their molecular structure, exhibit favorable compatibility with asphaltene-rich heavy oils. The bifunctional additives may also be activated under the conditions of the hydroconversion process.

[0029] The impact of the bifunctional additive may be augmented by use of mixtures of bifunctional additives of more than one metal. For example, if molybdenum is used, it is desirable to add an additional quantity of cobalt. This is anticipated to yield a positive synergistic effect on catalytic hydrogenation process. Typically, cobalt may be added in an amount from 0.2 to 2 mols, preferably 0.4 mols per mol of molybdenum.

[0030] The bifunctional additive can be present in an amount ranging from 1 to 300 wppm metal. More preferably in the range of 1 to 60 wppm of metal based on hydrocarbon oil to be hydroconverted. It is preferred to mix the heavy oil and additive during the thermal treatment upgrading process. Mixing means and process equipment known to one having ordinary skill in the art can be used. Process equipment operable at high pressure, such as high pressure visbreakers,

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can be advantageously used to conduct the thermal treatment process in the presence of hydrogen.

[0031] The bifunctional additive can be contacted with the heavy oil as is or with use of a carrier solvent. Preferred carrier solvents include aromatic hydrocarbon solvents such as toluene, xylene, crude oil derived aromatic distillates such as Aromatic 150 sold by ExxonMobil Chemical Company, water, alcohols and mixtures thereof. Preferred alcohols are methanol, ethanol, propanol and mixtures thereof. The carrier solvent can range from 10 to 80 weight percent of bifunctional additive and carrier solvent.

[0032] Contacting the heavy oil with the bifunctional additive can be achieved at any time prior to thermal treatment. Contacting can occur at the point where the heavy oil is produced at the reservoir, during transportation, or at a refinery location. In the case of crude oil resids, the bifunctional additive is contacted at any time prior to the thermal treatment. After contacting, it is preferred to mix the heavy oil and additive. Any suitable mixing means conventionally known in the art can be used. Non-limiting examples of such suitable mixers include in-line static mixers and paddle mixers. The contacting of the heavy oil and additive can be conducted at any temperature in the range of 10°C to 90°C for an effective amount of time. After contacting and mixing the mixture of heavy oil and additive the mixture can be cooled from contacting temperature to ambient temperature, i.e., 15°C to 30°C. Further, the additized-cooled mixture can be stored or transported from one location to another location prior to thermal treatment. Alternately, the additized and cooled mixture can be thermally treated at the location of contacting if so desired. Thermal treatment of the bifunctional additized heavy oil comprises heating said additized heavy oil at a temperature in

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the range of 250°C to 500°C in the presence of hydrogen at hydrogen partial pressure of between 500 to 2500 psig (3447.38 to 17236.89 kPa), for a time between 0.1 to 10 hours to result in an upgraded oil product.

[0033] The bifunctional additive enhanced hydrotreating upgrading process of the present invention provides an upgraded product that is higher in API gravity compared to the starting feed and lower in toluene insoluble material compared to a hydrotreated upgraded product that is produced in the absence of the bifunctional additive of the instant invention. By virtue of the inhibitor function of the bifunctional additive, the formation of toluene insoluble material is inhibited while facilitating hydroconversion to occur in a facile manner. The upgraded product of the thermal treatment process in the presence of hydrogen has at least 20% less toluene insoluble material compared to the product from a thermal treatment process conducted at the same temperature for the same period of time but in the absence of the bifunctional inhibitor-hydrotreating additive. The upgraded oil of the instant invention comprises the upgraded heavy oil, the added bifunctional additive and products formed from the added bifunctional additive during the thermal upgrading process.

[0034] The following examples are included herein for illustrative purposes and are not meant to be limiting.

EXAMPLES

EXAMPLE 1

Synthesis of Bifunctional Inhibitor-Hydrotreating Additives

[0035] As an illustration, two synthetic routes for a molybdenum containing bifunctional additive are described. The bifunctional molybdenum additive can be synthesized by the method disclosed in GB 1215120A, which is incorporated herein by reference. A reaction mixture is prepared by admixing molybdenyl bis-acetylacetonate and the PNA-sulfonic acid which, in accordance with the stoichiometry of the reaction for forming a molybdenum mono-sulfonic compound, theoretically requires the use of one mol of sulfonic acid for each mol of molybdenyl bis-acetonate present. Preferably, the mol ratio of PNA-sulfonic acid to the molybdenyl bis-acetylacetonate is from 5:1 up to 10:1, providing an excess of PNA-sulfonic acid over that required and further enhancing the formation of molybdenum PNA-sulfonate compound. Lower ratios of PNA-sulfonic acid to the molybdenyl bis-acetylacetonate can be used which may range from as low as one mol up to 5 mols of PNA-sulfonic acid per mol of molybdenum bis-acetylacetonate. It is ordinarily necessary when using such lower ratios to effect a thinning of the viscous reaction mixture with an inert organic solvent, such as a mineral oil. The reaction medium is slowly heated from room temperature to a temperature of 190°C, and thereafter held at a temperature

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of 190°C to 210°C for a period of time sufficient to effect removal of acetylacetone, followed by a cooling of the reaction mixture.

[0036] In an alternate method of synthesis, molybdenum trioxide and the corresponding PNA-sulfonic acid are mixed in the required stoichiometric ratio, in an inert high boiling solvent and heated to temperatures in the range of 150°C to 200°C to provide the molybdenum salt of the PNA-sulfonic acid salt as a colloidal suspension in the inert solvent.

EXAMPLE 2

[0037] 120 g of bitumen was rapidly heated under nitrogen [350 PSI (2413.16 kPa)] to 750°F (403.89°C) with continuous stirring at 1500 RPM. The bitumen was allowed to react under these conditions for a period of time calculated to be equivalent to a short visbreaking run at a temperature of 875°F (468.33°C) (typically 120 to 180 “equivalent seconds”). After achieving the desired visbreaking severity, the autoclave was rapidly cooled in order to stop any further thermal conversion. The gas and liquid products were analyzed and material balanced. The change in boiling point distribution and viscosity reflect the severity of the visbreaking conditions. The toluene insolubles (TI) were measured by quantitative filtration of a fresh hot toluene solution of the visbreaker product (20:1 ratio of toluene to product).

[0038] Run-1: In one run 1,3,6-naphthalene trisulfonic acid trisodium salt inhibitor additive (1,3,6-NTSS) was mixed with the bitumen prior to visbreaking. The reaction product was washed with toluene to remove toluene solubles. The resulting toluene insolubles and the inhibitor additive was contacted with water to

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recover the inhibitor additive, which can be recycled to the visbreaking reaction. A toluene insoluble fraction were left.

[0039] Run-2: In a second run 2,6-naphthalene disulfonic acid di-sodium salt (2,6-NDSS) was used as the inhibitor additive and mixed with the bitumen prior to the visbreaking reaction. The resulting visbreaking product was subjected to a water wash to remove the inhibitor additive for recycle. The remainder was contacted with toluene to remove the toluene solubles, thereby leaving a toluene insoluble fraction.

[0040] Run-1 and Run-2 are shown schematically in Figure 2 as scheme-1 and scheme-2 respectively.

[0041] The results of the two runs are shown in Figure 3 hereof (scheme-1 workup) demonstrates that use of the water-soluble additives 1,3,6-NTSS and 2,6-NDSS at a treat rate of 0.6 wt% based on the weight of oil, results in reduction in coke formation at 120 and 135 equivalent seconds severity. Figure 4 hereof (scheme-2 workup) depicts results from the water wash experiment. As can be observed, water wash of the visbroken product results in a further reduction in toluene insolubles. Thus, the inhibitors function not only to reduce toluene insolubles but because of their surfactancy property can also extract some of the toluene insolubles into an intermediate oil/water phase.

[0042] Results of the analyses of the visbroken products are shown in Tables 1 and 2 below. These visbroken product samples are ones obtained directly from the reactor. We observe a marginal difference in the 700°F+ (371.11°C) conversion between the non-additized and the additized samples. However, we observe a

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significant reduction in viscosity of the visbroken product in the additized samples relative to the non-additized sample run. These observations suggest the water-soluble inhibitors not only function to reduce the toluene insolubles but also have novel viscosity reduction attributes.

TABLE 1

Equiv. Sev, sec	120	120	120	135	135	135
Inhibitor	None	1,3,6-NTSS	2,6-NDSS	None	1,3,6-NTSS	2,6-NDSS
700°F+ (371.11°C) Conv., %	24.93	26.67	26.82	29.03	29.04	29.87

TABLE 2

Inhibitor	Product Viscosity; cp@40°C
None	225
1,3,6-NTSS	152
2,6-NDSS	145

EXAMPLE 3**Polysulfonation of LCCO**

[0043] To 25 g of LCCO was added 25g of concentrated sulfuric acid and the mixture heated to 70°C and maintained at 70°C with mixing for 2 days. After completion of reaction the product was washed with 100 ml of toluene in three aliquots and dried at 85°C to provide the LCCO polysulfonic acid product. The acid product was neutralized with caustic to provide the corresponding

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polysodium salt. It is to be noted that excess concentrated sulfuric acid was used, departing from prior art sulfonation methods, to achieve polysulfonation of the LCCO.

Product Characterization (LCCO polysulfonic acid)

[0044] FTIR and ^{13}C -NMR were used to characterize LCCO polysulfonic acid. FTIR of the product and the results showed distinct sulfonic acid stretching and bending vibration modes corresponding to hydrated sulfonic acid i.e., $\text{R-SO}_3^- \text{H}_3\text{O}^+$. The FTIR spectra resemble sulfonate salts. Sulfonate salts have bands near $\sim 1230\text{-}1120\text{ cm}^{-1}$ and $\sim 1080\text{-}1025\text{ cm}^{-1}$ (asymmetric and symmetric SO_2 stretches). H_3O^+ gives rise to features near $\sim 2800\text{-}1650\text{ cm}^{-1}$ (broad) and near $2600, 2250, \text{ and } 1680\text{ cm}^{-1}$. The "free OH" bands observed near 3520 cm^{-1} (doublet) confirm the presence of significant water of hydration - sufficient to form the hydronium ion. This indicates that the product is predominantly hydrated sulfonic acid in the hydronium sulfonate form.

[0045] ^{13}C -NMR of the product showed distinct Aromatic Carbon- SO_3H resonances at 141.72 ppm and 181 ppm .

[0046] Aqueous LCCO-sulfonic acid product was titrated with NaOH. 5g of product were diluted with 5g of distilled water to produce a 50% active material. This 50% active material was used for the NaOH titration. From titration, for 1 gram of 50% active material, 0.143g of NaOH was required for complete neutralization. Expressed on a per gram actives basis, 1gram of the sulfonated product required 0.286g of NaOH.

Surface activity of LCCO polysulfonic acid polysodium salt

[0047] The air/water and oil/water surface tensions for the LCCO polysulfonic acid polysodium salt were determined by the Wilhelmy plate and pendant drop methods known to one of ordinary skill in the art of surface science. Table 3 and Table 4 list the observed values of air/water and oil/water surface tensions respectively for the LCCO polysulfonic acid sodium salt.(LCCO-PSS). We observe values similar to that observed for 1,3,6-naphthalene trisulfonic acid tri sodium salt. (1,3,6-NTSS) and the 1,3,6,8-pyrene tetra sulfonic acid sodium salt (1,3,6,8-PTSS). This data indicates high surface activity or surfactancy of the LCCO polysulfonic acid sodium salt. The presence of methyl, ethyl and propyl substituents on the 1- and 2-ring aromatic cores of the LCCO product do not alter the surface activity significantly.

TABLE 3

<u>Additive</u>	<u>Air/Water Surface Tension</u> (dynes/cm) {+/- 0.5}
None	72
2-NSS	43
2,6-NDSS	23
1,3,6-NTSS	21
1,3,6,8-PTSS	21
LCCO-PSS	21

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TABLE 4

<u>Additive</u>	<u>Oil/Water Interfacial Tension</u> (dynes/cm) {+/- 0.5}
None	45.5
2,6-NDSS	19.3
1,3,6-NTSS	3.2
1,3,6,8-PTSS	1.5
LCCO-PSS	1.5

[0048] The above data demonstrates that LCCO can be converted to aromatic polysulfonate salts that are water soluble and possess unexpectedly high surface activity.

CLAIMS:

1. A method for upgrading a heavy oil comprising the steps of:

a) contacting the heavy oil with an effective amount of an inhibitor additive to provide an inhibitor additized heavy oil, which inhibitor additive is represented by the chemical structure:

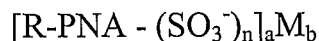


wherein R is an alkyl group containing from 0 to 40 carbon atoms; PNA is a polynuclear aromatic hydrocarbon containing 2 to 15 aromatic rings; X is an acid functionality selected from the group consisting of SO_3H , COOH , and PO_3H ; and n is an integer from 1 to 15; and

b) thermally treating said inhibitor additized heavy oil at a temperature in the range of 250°C to 500°C in the presence of hydrogen at hydrogen partial pressure of between 500 to 2500 psig (3447.38 to 17236.89 kPa) for a time between 0.1 to 10 hours.

2. A method for upgrading a heavy oil comprising the steps of:

a) contacting the heavy oil with an effective amount of an inhibitor additive to provide an inhibitor additized heavy oil, which inhibitor additive is represented by the chemical structure:



wherein PNA is a polynuclear aromatic hydrocarbon containing 2 to 15 aromatic rings; X is a sulfonic acid functionality, n is an integer from 1 to 15 representing the number of sulfonic acid functionality on the PNA hydrocarbon; R is an alkyl group containing from 0 to 40 carbon atoms; M is an element selected from the group consisting of Group IV-B, V-B, VI-B, VII-B and VIII of the Long Form of

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The Periodic Table of Elements; and a and b are integers each ranging from 1 to 4; and

b) thermally treating said inhibitor additized heavy oil at a temperature in the range of 250°C to 500°C in the presence of hydrogen at hydrogen partial pressure of between 500 to 2500 psig (3447.38 to 17236.89 kPa) for a time between 0.1 to 10 hours.

3. The method of claims 1 or 2 wherein the contacting, thermal treating, or both are conducted in an inert environment wherein the amount of inhibitor additive used is from 10 to 50,000 ppm based on the weight of the heavy oil and said contacting is conducted at a temperature from 25°C to 90°C for a time ranging from 1 minute to 24 hours.

4. The method of any one of claims 1-3 wherein the heavy oil is one or more of crude oil, vacuum resids and atmospheric resids.

5. The method of any one of claims 1-4 which further comprises the step of first providing the inhibitor additive with a carrier solvent and then contacting the heavy oil with a mixture of inhibitor additive and carrier solvent.

6. The method of any one of claims 1-5 wherein the carrier solvent is selected from water, aromatic hydrocarbon, alcohols and mixtures thereof, and is from 10 to 80 wt.% of the mixture of inhibitor additive and carrier solvent.

7. The upgraded oil of any one of claims 1-6 having at least 20 wt.% decreased toluene insolubles compared to the untreated heavy oil feedstock

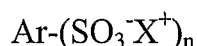
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obtained by thermal treatment under identical process conditions in the absence of inhibitor.

8. The method of claim 2 wherein M is selected from Groups VIII and VI-B.

9. A method for upgrading heavy oils which method comprises:

a) contacting the heavy oil with an effective amount of a water-soluble inhibitor additive to provide an inhibitor additized heavy oil, which water-soluble inhibitor additive is represented by the chemical structure:



where Ar is a homonuclear aromatic group of at least 2 rings, and X is selected from Group I (alkali) and Group II (alkaline-earth) elements of the Periodic Table of Elements, and n is an integer from 1 to 5 when an alkali metal is used and from 2-10 when an alkaline earth metal is used;

b) thermally treating said inhibitor additized heavy oil at a temperature in the range of 250°C to 500°C for a time between 0.1 to 10 hours, thereby resulting in an upgraded the heavy oil;

c) contacting said thermally treated additized heavy oil with water wherein the water-soluble inhibitor additive migrates to the water phase;

d) separating the thermally treated heavy oil from the water phase containing said inhibitor additive;

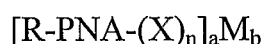
e) separating the inhibitor additive from the water; and

f) recycling said separated inhibitor additive to contacting a heavy oil in step a) above.

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10. A method for upgrading a heavy oil, which method comprises:

a) contacting the heavy oil in the presence of hydrogen with an effective amount of a water-soluble inhibitor additive to provide an inhibitor additized heavy oil, which water-soluble inhibitor additive is represented by the chemical structure:



wherein PNA is a polynuclear aromatic hydrocarbon containing 2 to 15 aromatic rings; X is a sulfonic acid functionality, n is an integer from 1 to 15 representing the number of sulfonic acid functionality on the PNA hydrocarbon; R is an alkyl group containing from 0 to 40 carbon atoms; M is an element selected from the group consisting of Group IV-B, V-B, VI-B, VII-B and VIII of the Long Form of The Periodic Table of Elements; and a and b are integers each ranging from 1 to 4;

b) thermally treating said inhibitor additized heavy oil at a temperature in the range of 250°C to 500°C for a time between 0.1 to 10 hours;

c) contacting said thermally treated additized heavy oil with water wherein the water-soluble inhibitor additive migrates to the water phase;

d) separating the thermally treated heavy oil from the water phase containing said water-soluble inhibitor additive;

e) separating the inhibitor additive from the water; and

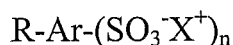
f) recycling said separated inhibitor additive to contacting a heavy oil in step a) above.

11. The method of claims 9 or 10 wherein the heavy oil is a vacuum resid.

12. The method of claims 9 or 10 wherein X is an alkali metal.

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13. The method of any one of claims 9-12 wherein the number of rings for Ar is from 2 to 3 and n is 1.
14. The method of any one of claims 9-13 wherein the polysulfonic aromatic acid salt is one or more of naphthalene-2-sulfonic acid sodium salt, naphthalene-2,6-disulfonic acid sodium salt, naphthalene-1,5-disulfonic acid sodium salt, naphthalene-1,3,6-trisulfonic acid sodium salt, anthraquinone-2-sulfonic acid sodium salt, anthraquinone-1,5-disulfonic acid sodium salt, and pyrene-1,3,6,8-tetra sulfonic acid sodium salt.
15. The method of any one of claims 9-14 wherein the effective amount of additive is from 10 to 50,000 wppm, based on the weight of the heavy oil.
16. A method for the production of aromatic polysulfonic acid compounds represented by the chemical structure:



where R is an alkyl group having from 0 to 40 carbon atoms, Ar is an aromatic ring structure comprised of from 2 to 15 aromatic rings, X is hydrogen or an alkali or alkaline-earth metal, and n is an integer from 1 to 5 when X is an alkali metal and 2 to 10 when X is an alkaline-earth meal, which method comprises:

reacting a light catalytic cycle oil with sulfuric acid in an amount from 1.2 to 2 times the stoichiometric amount at a temperature from 20°C to 100°C for an effective amount of time thereby forming a reaction product;

washing said reaction product with an organic solvent;

neutralizing the washed reaction product with a suitable base to form the corresponding polysulfonic acid salt.

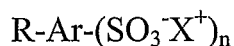
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17. The method of claim 16 wherein R is an alkyl group having from 1 to 5 carbons.
18. The method of claim 16 wherein R is O.
19. The method of any one of claims 16-18 wherein the reaction product is washed with an organic solvent or is neutralized with a caustic solution.
20. The method of any one of claims 16-19 wherein the solvent washed reaction product is neutralized with a caustic solution.
21. The method of any one of claims 16-20 wherein the caustic solution is a sodium hydroxide solution.
22. A method for the production of a light catalytic cycle oil stream rich in aromatic polysulfonic acid compounds which method comprises:
reacting a light catalytic cycle oil with sulfuric acid in an amount from 1.2 to 2 times the stoichiometric amount at a temperature from 20°C to 100°C for an effective amount of time thereby forming a reaction product, thereby resulting in a light catalytic cycle oil rich in aromatic polysulfonic acid compounds.
23. The method of claim 22 wherein an alkali metal hydroxide solution is added to convert at least a portion of the aromatic polysulfonic acid compounds to the respective salt.

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24. The method of claims 22 or 23 wherein the alkali metal hydroxide is sodium hydroxide.

25. A method for upgrading a heavy oil comprising the steps of:
adding to said heavy oil an amount of light catalytic cycle oil containing an effective amount of aromatic polysulfonic acid compounds represented by the formula:



where R is an alkyl group having from 0 to 40 carbon atoms, Ar is an aromatic ring structure comprised of from 2 to 15 aromatic rings, X is hydrogen or an alkali or alkaline-earth metal, and n is an integer from 1 to 5 when X is an alkali metal and 2 to 10 when X is an alkaline-earth meal; and

thermally treating said additized heavy oil at a temperature in the range of 250°C to 500°C for 0.5 to 6 hours to upgrade the heavy oil.

26. The method of claim 25 wherein the heavy oil is at least one of crude oil, vacuum resids and atmospheric resids.

27. The method of claims 25 or 26 wherein the effective amount of additive is from 10 to 50,000 wppm based on the weight of heavy oil and wherein the polynuclear aromatic compound is comprised of 2 to 15 aromatic rings.

28. The product produced by the method of any preceding claim.