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**INHIBITOR ENHANCED THERMAL UPGRADING
OF HEAVY OILS VIA MESOPHASE SUPPRESSION
USING OIL SOLUBLE POLYNUCLEAR AROMATICS**

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 inhibitor is selected from oil soluble polynuclear aromatic compounds that are capable of suppressing mesophases formed by hydrocarbon compounds present in 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

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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 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-

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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 which is comprised of one or more oil soluble polynuclear aromatic compounds 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] In a preferred embodiment the polynuclear aromatic compound is comprised of 2 to 8 aromatic rings.

[0006] In another embodiment the polynuclear aromatic compound contains 2 to 5 aromatic rings.

[0007] In still another preferred embodiment the polynuclear compound is selected from the group consisting of 1-methyl naphthalene, 2-methyl naphthalene, 2-ethyl naphthalene, isoquinoline, triphenylene, and perylene.

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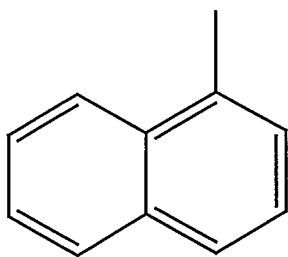
[0008] In still another preferred embodiment the inhibitor additive suppresses the mesophase formed by hydrocarbon compounds present in the heavy oil.

DETAILED DESCRIPTION OF THE INVENTION

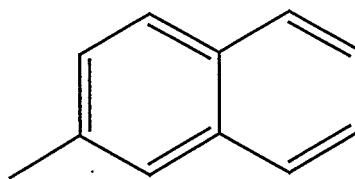
[0009] According to one embodiment of the invention, there is provided a method for upgrading heavy oils, such as heavy oils and crude oil residuum. At least one polynuclear aromatic inhibitor additive is added to the crude or crude oil residuum followed by thermal treatment at temperatures in the range of 250°C to 500°C for 30 second to 6 hours. The polynuclear aromatic compound contains 2 to 15 aromatic rings, preferably 2 to 6 aromatic rings, and more preferably from 2 to 4 aromatic rings. 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.

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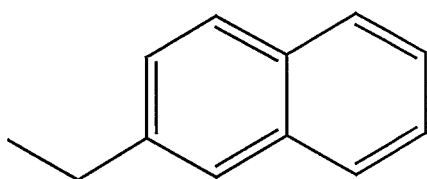
[0010] Non-limiting examples of PNAs suitable for use in the present invention include:



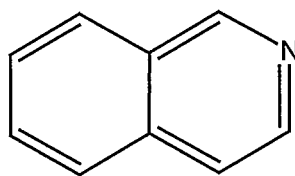
1-methyl naphthalene



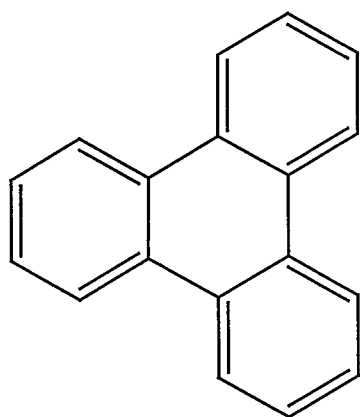
2-methyl naphthalene



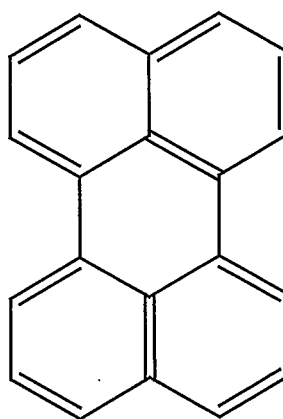
2-ethyl naphthalene



isoquinoline



triphenylene



perylene

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[0011] 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.

[0012] 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-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.

[0013] 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

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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.

[0014] 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 upgraded heavy oil, the added inhibitor additive and products, if any, formed from the added inhibitor additive during the thermal upgrading process.

[0015] 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

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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.

EXAMPLE

[0016] The following examples are included herein for illustrative purposes and are not meant to be limiting.

[0017] In order to evaluate the effectiveness of the oil soluble inhibitors of the present invention three model compounds that are known and reported to form mesophases at temperatures in the range of 100°C to 350°C were used. These model PNA mesogens and their temperature range of mesophase were: triphenylene discotic mesophase (68°C-100°C); triphenylene discotic mesophase (147°C-239°C); and perylene discotic mesophase (140°C-315°C). Differential scanning calorimetry (DSC) and optical microscopy were used to evaluate the effectiveness of the inhibitors to inhibit the mesophases of these compounds.

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[0018] The crystalline triphenylene PNA mesogen compound shows a crystalline to mesophase transition at 67°C. At 99°C the mesophase to isotropic phase change is observed. From 67°C to 99°C is the mesophase range. Each phase change is associated with a heat capacity or enthalpy. The oil soluble additives of the invention were added to the triphenylene PNA mesogen at 4 and 8 wt.% based on the weight of the PNA mesogen and DSC recorded. It was observed that a decrease in the mesophase range and a reduction in the enthalpy of the mesophase to isotropic phase transition for all the oil soluble additives. This evidences that the mesophase of the PNA mesogen is adversely affected by the oil soluble additives of the present invention.

[0019] It was observed that there was a loss in the mesophase to isotropic peak at 99°C, which indicates that the mesophase has been completely inhibited by the use of LCCO.

[0020] The DSC and microscopy for the perylene PNA mesogen was also obtained. It was observed that the crystalline compound showed a crystalline to mesophase transition at 140°C. At 315°C the mesophase to isotropic phase change was observed. The mesophase range was from 140°C to 315°C. Each phase change was associated with a heat capacity or enthalpy. Light catalytic cycle oil (LCCO), medium catalytic cycle oil (MCO), and heavy aromatic fuel oil (HAFO) was added to the perylene PNA mesogen at 4 and 8 wt.% based on the weight of the PNA mesogen and the DSC recorded. Complete inhibition of the mesophase for HAFO was observed, but not when LCCO or MCO was used. The DSC of the perylene PNA mesogen in the presence of 8 wt.% HAFO showed the

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complete loss of the mesophase to isotropic phase peak at 315°C. These results indicate the criticality of the boiling point range of the inhibitor on mesophase inhibition. LCCO and MCO are lower boiling aromatic oils and are effective on lower temperature aromatic mesophases. The higher boiling HAFO is effective on the higher temperature aromatic mesophase.

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CLAIMS:

1. A method for upgrading a heavy oil comprising the steps of:
 - contacting the heavy oil with an effective amount of an inhibitor additive which is comprised of one or more oil soluble polynuclear aromatic compounds to provide an inhibitor additized heavy oil, and then
 - thermally treating said inhibitor additized heavy oil at a temperature and for a time sufficient to upgrade the heavy oil.
2. The method of claim 1 wherein the heavy oil is selected from the group consisting of crude oil, vacuum resids and atmospheric resids; wherein the thermal treating time ranges from 0.5 to 6 hours; and wherein the thermal treating temperature ranges from 250°C to 500°C.
3. The method of any preceding claim wherein the effective amount of additive is from 10 to 50,000 wppm based on the weight of heavy oil.
4. The method of any preceding claim wherein the polynuclear aromatic compound is comprised of 2 to 15 aromatic rings.
5. The method of any preceding claim wherein the polynuclear compound is at least one of 1-methyl naphthalene, 2-methyl naphthalene, 2-ethyl naphthalene, isoquinoline, triphenylene, and perylene.
6. The method of any preceding claim wherein at least one of the (i) contacting and (ii) upgrading is conducted in an inert environment.

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7. The method of any preceding claim 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.
8. The method of any preceding claim wherein the carrier solvent is selected from water, aromatic hydrocarbon, alcohols and mixtures thereof.
9. The method of any preceding claim wherein the carrier solvent is from 10 to 80 wt.% of the mixture of inhibitor additive and carrier solvent.
10. The upgraded oil produced by the method of any preceding claim having at least 20 wt.% decreased toluene insolubles compared to the untreated heavy oil feedstock obtained by thermal treatment under identical process conditions in the absence of inhibitor.