The invention is a low viscosity oil composition derived from crude oils and crude oil residuum comprising dispersed asphaltene salts in a hydrocarbon continuous phase.
LOW VISCOSITY HYDROCARBON OILS BY SONIC TREATMENT


FIELD OF THE INVENTION

[0002] The present invention relates to low viscosity and low viscoelastic heavy oil compositions.

BACKGROUND OF THE INVENTION

[0003] Heavy oils are generally referred to those oils with high viscosity or API gravity less than about 23. Crude oils and crude oil residuum derived from atmospheric or vacuum distillation of crude oil are examples of heavy oils. The origin of high viscosity in these oils has been attributed to high asphaltene content of the oils. Viscosity reduction of heavy oils is important in production, transportation and refining operations of crude oil. Transporters and refiners of heavy crude oil have developed different techniques to reduce the viscosity of heavy crude oils to improve its pumpability.

[0004] Commonly practiced methods include diluting the heavy oil with gas condensate and emulsification with caustic and water. Thermally treating heavy oil to reduce its viscosity is also well known in the art. Thermal techniques for visbreaking and hydro-visbreaking (visbreaking with hydrogen addition) are practiced commercially to chemically alter the heavy oil to produce the viscosity reduction. The prior art in the area of thermal treatment or additive enhanced visbreaking of hydrocarbons teaches methods for improving the quality, or reducing the viscosity, of crude oils, crude oil distillates or residua by several different methods. For example, several references teach the use of additives such as the use of free radical initiators (U.S. Pat. No. 4,298,455), thiol compounds and aromatic hydrogen donors (EP 17511), free radical acceptors (U.S. Pat. No. 3,707,459), and hydrogen donor solvent (U.S. Pat. No. 4,592,830). Other art teaches the use of specific catalysts such as low acidity zeolitic catalysts (U.S. Pat. No. 4,411,770) and molybdenum catalysts, ammonium sulfide and water (U.S. Pat. No. 4,659,453). Other references teach upgrading of petroleum resids and heavy oils (Murray R. Gray, Marcel Dekker, 1994, pp.230-243) and thermal decomposition of naphthenic acids (U.S. Pat. No. 5,820,750). Each of these methods produces reduced viscosity heavy oils, the chemical composition of which is determined by the nature of the treatment used. For example, thermal treatment such as visbreaking produces products that are a result of thermal cracking known to one of ordinary skill in the art. Hydro-visbreaking produces hydrotreated or hydrogenated products known to one of ordinary skill in the art of hydrotreating. Thermal treatment involving thermal decomposition of naphthenic acids result in decarboxylated naphthenic products. Dilution methods involve changes in composition of the final product that is dependent on the diluent used. For example, if a gas condensate such as butane or propane is used, then the product is a mixture of the starting heavy oil and the diluent butane or propane.

[0005] Sonic treatment for viscosity reduction has also been practiced. Sonication or sonic treatment, generally is a process of treatment of a fluid with sound waves and is termed sonication or sonic treatment. When used alone, the main drawback of sonic treatment for viscosity reduction of heavy oils is that the effect is reversible. The viscosity of the sonic treated oil recovers back to the original viscosity of the oil and in some crude oils viscosity of the product after sonication is higher than the starting oil. There is, therefore, a continuing need to produce heavy oil (i.e. crude oil and crude oil residuum) products that have decreased viscosity. There is also a need for hydrocarbon oil products produced from heavy oils that have decreased viscosity and wherein the products are not thermally cracked or hydrogenated. The instant invention addresses this need.

SUMMARY OF THE INVENTION

[0006] Provided are sonicated, acid treated low viscosity crude oils and crude oil residuum compositions. The compositions are made by sonicating heavy oils in the presence of acids.

[0007] One embodiment of the invention is directed to decreased viscosity hydrocarbon oil compositions comprising a dispersed phase of asphaltene salts of acids in a hydrocarbon continuous phase.

[0008] The acids are selected from the group of mineral acids, organic acid and mixtures thereof. The treatment is carried out without hydrotreating the heavy oil.

BRIEF DESCRIPTION OF THE FIGURES

[0009] FIG. 1 is a plot of viscosity versus shear rate plots for the untreated and sonic treated crude oil-K at 25°C. The X axis is shear rate (sec⁻¹) and the Y axis is viscosity (cp). The line with diamonds is the untreated crude oil. The line with squares is crude oil treated with acid and sonicated.

[0010] FIG. 2 is a plot of the elastic modulus (G) along the Y-axis as a function of sweep frequency in radians/second along the X-axis for a fixed sinusoidal oscillation at 25°C. The line with triangles is the untreated crude oil. The line with squares is crude oil-K treated with sulfuric acid and sonicated.

[0011] FIG. 3 is a plot of the viscous modulus (G' ) as a function of sweep frequency in radians/second along the X-axis for a fixed sinusoidal oscillation at 25°C. The line with triangles is the untreated crude oil-K. The line with squares is crude oil-K treated with sulfuric acid and sonicated.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] According to one embodiment there is provided decreased viscosity hydrocarbon compositions derived from crude oils and crude oil residuum. The compositions contain asphaltene salts of acids dispersed in a hydrocarbon continuous phase. The continuous hydrocarbon phase of a decreased viscosity crude oil compositions are known to those skilled in the art, and are characteristic of the heavy oil from which they are derived. The continuous phase of a decreased viscosity (atmospheric or vacuum) residua are also known to those skilled in the art and are characteristic of those oils. In both cases, typically the oils contain mixtures of aromatic compounds with alkanes, alkenes, and cycloalkanes. Crude oil distillation methods to produce
atmospheric and vacuum residuum are known to one of ordinary skill in the art of crude oil refining.

[0013] The dispersed phase component of the heavy oil compositions contain asphaltene salts of acids. Asphaltenes are well known to those skilled in the art and typically are alkyl poly-aromatic compounds typically present in crude oils and crude oil residuum. Further, the asphaltenes typically contain nitrogen, sulfur, oxygen hetero-atoms in their chemical structure. The nitrogen, sulfur and oxygen atoms are typically present in a variety of functional groups. Some non-limiting examples of such functional groups are sulfides for sulfur secondary and tertiary amines for nitrogen and ethers for oxygen. These asphaltene compounds are present in aggregated form in a crude oil or crude oil residuum. Typically, at least four asphaltene molecules can be present in an asphaltene aggregate. The occurrence of asphaltene aggregates is believed to be the primary cause for the observed high viscosity of heavy oil i.e., crude oils and crude oil residuum with an API less than about 25.

[0014] Applicant has found that when a heavy oil is treated with specified acid in the absence of hydrotreating conditions and subjected to sound waves, the asphaltenes deaggregate or break up, and the deaggregated asphaltites react with the acid and form deaggregated asphaltite salts of the added acids. The asphaltite salts are dispersed in the hydrocarbon continuous phase during sonic treatment and do not re-aggregate upon removal of the sonic treatment i.e., the sound wave energy source. The resulting heavy oil compositions desirably have decreased viscosity in comparison to treated heavy oils with acid alone or sonicated in absence of acids. It is preferred to sonicate the heavy oil in the presence of acid and under conditions sufficient to deaggregate the asphaltites and neutralize at least one of its basic nitrogen with the added acid. Preferably, the acid is added to the heavy oil as an aqueous solution. That is, the acid can be diluted with water and the mixture of acid and water be added to the heavy oil prior to or during the sonication. The ratio of acid:water can range from 99:1 to 50:50. Preferably, the ratio is 80:20 of acid:water.

[0015] The types of acids used to produce the acid salt of asphaltites of the low viscosity composition of the instant invention include mineral acids such as sulfuric acid, hydrochloric acid and perchloric acid. Organic acids like acetic, para-toluene sulfonic, alkyl toluene sulfonic acids, mono di- and trialkyl phosphoric acids, organic mono or di carboxylic acids, C₂ to C₁₅ organic carboxylic acids, succinic acid, and low molecular weight petroleum naphthenic acid are also effective in this invention. Crude oil high in naphthenic acid content (TAN) can be used as the source of petroleum naphthenic acids. Mixtures of mineral acids, mixtures of organic acids or combinations of mineral and organic acids may be used to produce the same effect. The preferred mineral acid is sulfuric or hydrochloric acid. The preferred organic acid is acetic acid. Nitric acid should be avoided since it could potentially form an explosive mixture. Formic acid is excluded from the group of preferred acids since formic acid upon sonication can form hydrogen as disclosed by Paul and Davis (U.S. Pat. No. 5,824,214).

[0016] Treatment. temperatures preferably will be in the range of about 25 to about 50° C. for about 30 seconds to 1 hour can produce the compositions of the invention. The amount of acid added will be an effective amount and will be about 10 to about 10,000 ppm, preferably about 20 to 100 ppm, based on the amount of crude oil or crude oil residuum. The amount of acid to be added depends on the basic nitrogen content of the isolated asphaltites and may be ascertained by one having ordinary skill of the art. For example, the basic nitrogen content of the asphaltites can be determined by first isolating the asphaltites by n-pentane deasphalting methods known in the art of solvent deasphalting of heavy oils, and then determining the basic nitrogen content of the isolated asphaltites by analytical methods such as perchloric acid titration known in the art of basic nitrogen content determination of organic compounds. It is preferred to add an amount of acid sufficient to be at least the stoichiometric equivalent of the basic nitrogen content of the crude oil.

[0017] A typical commercial sonicator is in the shape of a tapered rod or horn. While a horn type sonicator is preferred other shapes of sonicators can also be used. The velocity of sound in liquids is typically about 1500 meters/sec. Ultrasonic spans the frequency of about 15 kHz to 10 MHz with associated wavelengths of about 10 to 0.02 cm. Frequencies of about 15 kHz to about 20 MHz can be used. The output energy at a given frequency is expressed as sonication energy in units of watts/cm². The sonication is typically accomplished at energies in the range of 200 watts/cm² to 800 watts/cm². The time of sonication can vary in the range of 0.5 minutes to 6 hours. Sonic treatment can be continuous or in pulse mode. At the time of starting the sonic treatment the crude oil can be at temperatures in the range of 15 to 70° C. and atmospheric pressure. It is preferred mix the crude oil during treatment at low shear rates. The preferred shear rates are between 50 to 200 rpm.

[0018] The sonic treatment process may be conducted in batch or flowthrough process modes. The flowthrough process mode is preferred in pipeline transportation applications. In a flowthrough mode, the crude oil is pumped through a pipe to which are attached the sonicator horn tips in a radial manner. The rate of crude oil flow is optimized for maximum desirable exposure of the crude oil to the cavitation field. If desired, a recycle loop can be introduced for repeated sonic treatment. The batch process mode is preferred. It is preferred to introduce several sonicator horn tips at various heights of the reactor vessel. A stirred reactor with low shear stirring is preferred.

EXAMPLES

[0019] The following examples are included herein for illustrative purposes and are not meant to be limiting.

[0020] In a typical experiment 10 g of heavy crude oil was placed in a 4 oz. open-mouthed glass jar. A Vibra cell model VC 600 sonicator with a sonicator horn assembly was used. The sonicator horn was immersed into the crude oil and powered for times between 30 sec to 10 minutes as desired. A 400 watt/cm² energy was introduced during sonication. During treatment, the heavy crude oil was observed to bubble with increase in temperature from ambient to about 70° C. No attempt was made to control the temperature. The open vessel configuration allowed no confining pressure to be applied to the vessel. In situations where gentle mixing was desired, a magnetic stir bar rotating at 50 to 200 rpm was used to mix the crude oil.

[0021] To 10 g of a crude oil-K having a n-pentane isolated asphaltene content of about 4 wt %, was added
dilute sulfuric acid so that the final concentration of acid was 100 ppm. The viscosity of the starting oil before sonication was recorded. The acid treated crude oil was sonicated for 2 minutes. Immediately following sonication the viscosity of the product was recorded. Results are shown in FIG. 1. About 4-fold reduction in viscosity is observed in the acid treated sonicated sample. The viscosity of the acid treated sonicated sample was recorded every hour for 6 hours and then every week for 2 months. No change in viscosity was noted in the acid treated sonicated sample. The acid treated sonicated oil was subjected to infrared analyses. Infrared analyses confirmed the presence of sulfate salts of basic nitrogen i.e., organic ammonium sulfate salts. Gas chromatography and NMR analyses indicated absence of any products due to cracking or hydrogeneration reactions.

[0022] For comparative purposes crude oil-K, which was not pretreated with sulfuric acid, was sonicated and viscosity measurements conducted as described above. The non-acid treated sonicated sample showed a 2-fold decrease in viscosity immediately following sonication. The viscosity recovered to its original value within 1 hour.

[0023] The influence of shear rate on viscosity reduction for the untreated and treated oils is evident from the results in FIG. 1. Untreated crude oil exhibits shear thickening or non-Newtonian behavior although the magnitude is small. The shear thinning non-Newtonian behavior of the untreated oil indicates that the asphaltenes in the crude oil-K are in an aggregated form. The acid treated sonicated crude oil is Newtonian and does not exhibit shear thinning, that is its viscosity is independent of shear. This Newtonian rheological property indicates the asphaltene salt of the composition of the invention is in a dispersed state.

[0024] Viscoclasticity measurements were conducted on the untreated and the acid treated sonicated composition of the instant invention. FIG. 2 is a plot of the elastic modulus (G') and FIG. 3 the viscous modulus (G'') as a function of sweep frequency for a fixed sinusoidal oscillation. The elastic modulus (G') and viscous modulus (G'') were determined using a Haake viscometer in the oscillatory mode of operation. Data for untreated crude oil-K and acid treated sonicated crude oil-K (the composition of the instant invention) are shown. It is observed that both oils are viscoelastic exhibiting an elastic and viscous modulus. A decrease in the absolute value of G' and G'' are observed in the acid treated sonicated composition compared to the untreated oil. Further, a change in the value of the intercept of the G' versus frequency and G'' versus frequency plots are also observed in the composition of the instant invention. These results reveal that the composition of the instant invention has not only low viscosity but also lower viscoelasticity. The low viscoelasticity property of the composition of the instant invention is novel. The lowering of viscoelasticity of the composition is an indicator of the dispersed nature of the asphaltene salts as opposed to the aggregated asphaltenes of the untreated crude oil.

What is claimed is:

1. A decreased viscosity heavy oil composition comprising a dispersed phase of asphaltene salts of acids wherein the acids are selected from the group consisting of mineral acids, organic acids, and mixtures thereof in a hydrocarbon continuous phase.

2. The composition of claim 1 wherein said acid is a mineral acid.

3. The composition of claim 2 wherein said acid is selected from the group consisting of sulfuric acid, hydrochloric acid, perehloric acid, acetic acid, para-toluene sulfonic acid, alkyl toluene sulfonic acids, mono dial and trialkyl phosphoric acids, organic mono and di carboxylic acids, C2 to C16 organic carboxylic acids, succinic acid, petroleum naphthenic acid and mixtures thereof.

4. The composition of claim 3 wherein said acid is sulfuric acid.

5. The process of claim 4 wherein said acid is petroleum naphthenic acid.

6. The composition of claim 4 wherein the amount of said acid of the said asphaltene salt is about 10 to about 10,000 ppm based on the amount of crude oil or crude oil residuum.

7. The composition of claim 1 wherein said hydrocarbon continuous phase comprises alkanes, alkenes, cycloalkanes and aromatic compounds present in crude oils.

8. The composition of claim 1 wherein said hydrocarbon continuous phase comprises alkanes, alkenes, cycloalkanes and aromatic compounds present in crude oil residuum.

9. The composition of claim 1 wherein said asphaltenes comprise basic nitrogen functionality.

10. The composition of claim 1 wherein said asphaltene salts are in the range of 0.5 to 30 wt % and the remainder the hydrocarbon continuous phase.

11. The composition of claim 1 wherein the heavy oil is a crude oil or residuum.

12. The decreased viscosity heavy oil composition of claim 1 produced by the process of sonication a starting heavy oil in the presence of an acid selected from the group consisting of mineral acids, organic acids and mixtures thereof in the absence of hydrotreating conditions to produce a hydrocarbon oil having a decreased viscosity.

13. The decreased viscosity heavy oil composition of claim 1 having decreased viscous modulus and elastic modulus compared to the starting heavy oil.

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