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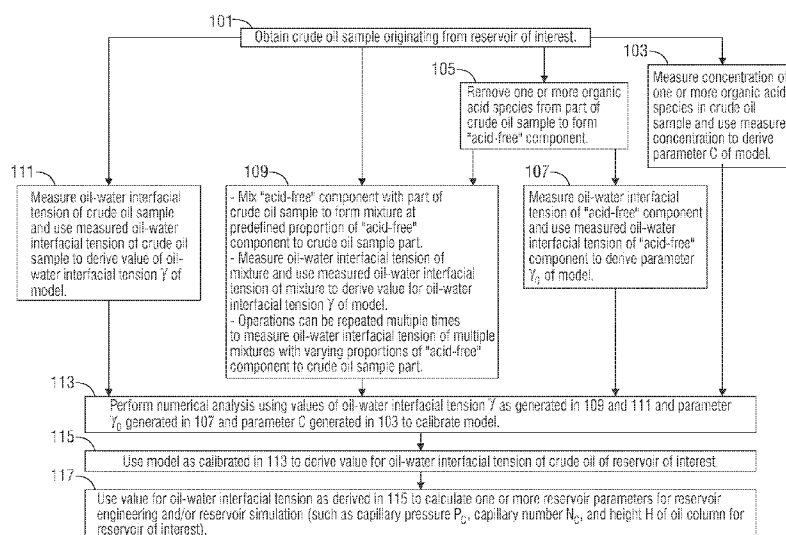


FIG. 1

(57) **Abstract:** A method of reservoir analysis for a reservoir of interest, which includes obtaining a crude oil sample originating from the reservoir of interest. Oil-water interfacial tension of the crude oil sample is measured. An empirical model that relates oil-water interfacial tension of the crude oil sample to concentration of at least one organic acid species in the crude oil sample is calibrated based on the measured oil-water interfacial tension of the crude oil sample. The concentration of the at least one organic acid species in the crude oil sample may be absolute or relative. At least one reservoir parameter characteristic of the reservoir of interest can be calculated based on the calibrated empirical model.



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METHOD AND APPARATUS FOR ANALYSIS OF RESERVOIR FLUIDS

BACKGROUND

Field

[0001] The present application relates to analysis of properties of reservoir fluids and associated reservoir modeling and simulation.

Related Art

[0002] Interfacial or surface tension exists when two phases are present. Interfacial tension is the force that holds the surface of a particular phase together and is normally measured in dynes/cm. In hydrocarbon systems, these phases can be hydrocarbon gas (gaseous phase) and oil (liquid phase), oil (liquid phase) and aqueous (liquid phase), or hydrocarbon gas (gaseous phase) and aqueous (liquid phase). The interfacial tension between an oil phase and an aqueous phase, typically referred to as oil-water interfacial tension, is commonly in the range of 20 to 40 dynes/cm at atmospheric conditions.

[0003] In reservoir modeling, it is commonplace to calculate oil-water interfacial tension (γ_{ow}) in dynes/cm as:

$$\gamma_{ow} = \left[\frac{1.58(\rho_w - \rho_o) + 1.76}{T_r^{0.3125}} \right]^4 \quad (1)$$

where ρ_w is the density of the aqueous phase in g/cm³;

ρ_o is the density of the oil phase in g/cm³; and

T_r is reduced temperature.

This equation does not account for variations in the concentration of naturally-occurring organic acid species in the oil phase that act as a surfactant that lowers the oil-water interfacial tension.

[0004] Several other correlations exist, such as a number of Parachor-based methods, but these other correlations also do not account for variations in the concentration of

naturally-occurring organic acid species that act as a surfactant that lowers the oil-water interfacial tension.

[0005] Oil-water interfacial tension is routinely measured by methods such as pendant drop, drop volume, and other methods at both high and low pressure.

SUMMARY

[0006] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0007] Illustrative embodiments of the present disclosure are directed to a method of reservoir analysis for a reservoir of interest. A crude oil sample originating from the reservoir of interest is obtained. Oil-water interfacial tension of the crude oil sample is measured. An empirical model that relates oil-water interfacial tension of the crude oil sample to concentration of at least one organic acid species in the crude oil sample is calibrated based on the measured oil-water interfacial tension of the crude oil sample.

[0008] In one embodiment, at least one reservoir parameter characteristic of the reservoir of interest can be calculated based on the calibrated empirical model.

[0009] In another embodiment, the empirical model can include a first parameter that represents bulk concentration of the at least one organic acid species in the crude oil sample. The method can further include measuring the concentration of the at least one organic acid species in the crude oil sample and using the measured concentration to derive the first parameter of the empirical model.

[0010] In yet another embodiment, the empirical model can include a second parameter that represents oil-water interfacial tension of the crude oil sample with the at least one organic acid species removed from the crude oil sample. The method can further include processing a part of the crude oil sample to produce a sample component with the at least one organic acid species removed from the crude oil sample part,

measuring oil-water interfacial tension of the sample component, and using the measured oil-water interfacial tension of the sample component to derive the second parameter of the empirical model. The processing of the crude oil sample part that produces the sample component can be carried out at an elevated pressure above ambient pressure, for example, by an ion exchange resin column. Both the measuring of the oil-water interfacial tension of the crude oil sample and the measuring of the oil-water interfacial tension of the sample component can be carried out at elevated pressures above ambient pressure, for example, within an optical cell. Alternatively, the processing of the crude oil sample part that produces the sample component as well as the measuring of both the oil-water interfacial tension of the crude oil sample and the oil-water interfacial tension of the sample component can be carried out at ambient pressure. The processing of the crude oil sample part that produces the sample component as well as the measuring of the oil-water interfacial tension of the sample component can be carried out in a continuous process or a batch mode process.

[0011] In another embodiment, the method can further include mixing the sample component with a part of the crude oil sample to form at least one mixture at a predefined proportion of the sample component to the crude oil sample and measuring oil-water interfacial tension of the at least one mixture. The mixing of the sample component with a part of the crude oil sample as well as the measuring of the oil-water interfacial tension of the at least one mixture can be carried out at an elevated pressure above ambient pressure, for example, with a high pressure mixer and an optical cell, respectively using techniques such as pendant drop, drop volume or weight, maximum drop pressure, or any other suitable method. Alternatively, the mixing of the sample component with a part of the crude oil sample as well as the measuring of the oil-water interfacial tension of the at least one mixture is carried out at ambient pressure.

[0012] In still another embodiment, the empirical model can include at least one additional parameter characteristic of the at least one organic acid species of the crude oil sample. The method can further include adjusting the at least one additional parameter based on numerical analysis employing the measured oil-water interfacial tension of the crude oil sample, the measured oil-water interfacial tension of the sample component, and

the measured oil-water interfacial tension of the at least one mixture. In one example, the at least one additional parameter is selected from the group including a parameter representing the monolayer surface excess concentration of the at least one organic acid species (or a collection of acids) and an adsorption constant for the at least one or several organic acid species.

[0013] A variety of reservoir parameters can be calculated, including, but not limited to, capillary pressure, capillary number, and oil column height for the reservoir of interest.

[0014] The crude oil sample can be a stabilized oil, a live oil, or other suitable form of oil.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 is a schematic diagram of the test workflow of the present disclosure.

[0016] FIG. 2 is a graph illustrating measurements of oil-water interfacial tension for a number of crude oil sample mixtures with varying fractions of naturally occurring organic acid species along with an empirical model calibrated from such oil-water interfacial tension measurements as performed in an embodiment of the test workflow of FIG. 1.

[0017] FIG. 3 is a schematic diagram of a test apparatus that can be utilized to perform certain operations of the test workflow of FIG. 1 as part of a continuous process.

[0018] A more complete understanding will become apparent to those skilled in the art upon reference to the detailed description taken in conjunction with the provided figures.

DETAILED DESCRIPTION

[0019] Illustrative embodiments of the present disclosure are described below. In the interest of clarity, not all features of an actual implementation are described in this specification. It will be appreciated that in the development of any such actual

embodiment, numerous implementation-specific decisions can be made to achieve the developer's specific goals, such as compliance with system-related and business-related constraints, which will vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time-consuming but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure. Further, like reference numbers and designations in the various drawings indicate like elements.

[0020] For the purposes of this disclosure, the term "crude oil sample" means a sample of crude oil that includes one or more hydrocarbon components as well as naturally-occurring organic acid species or a similar natural surface active component.

[0021] The term "reservoir parameter" means a parameter used in reservoir engineering and/or reservoir modeling that is characteristic of a reservoir of interest.

[0022] The embodiments of the present disclosure allow for estimation of oil-water interfacial tension of a crude oil sample obtained from a reservoir of interest in a manner that accounts for the contribution of naturally-occurring organic acid species to the oil-water interfacial tension of the crude oil sample. The naturally-occurring organic acid species act as a surfactant that lowers the oil-water interfacial tension.

[0023] The embodiments of the present disclosure rely on an empirical model that relates oil-water interfacial tension of a crude oil sample to the bulk concentration of one or more naturally-occurring organic acid species in the crude oil sample. In one embodiment, the Gibbs-Langmuir empirical model of oil-water interfacial tension is used, which has the form:

$$\gamma - \gamma_0 = -RT\Gamma_m \ln(1 + K_L C) \quad (2)$$

where γ is the oil-water interfacial tension of a crude oil sample (including one or more naturally-occurring organic acid species);

γ_0 is the oil-water interfacial tension of the crude oil sample without the one or more naturally-occurring organic acid species;

R is the gas constant;

T is the temperature of the crude oil sample;

Γ_m is the monolayer surface excess concentration of the one or more naturally-occurring organic acid species in the crude oil sample;

K_L is the Langmuir adsorption constant; and

C is the bulk concentration of the one or more naturally-occurring organic acid species in the crude oil sample.

Note that Γ_m and K_L are empirical parameters that can vary over different crude oil samples. K_L represents the strength at which the surface active compounds bind to the interface and therefore is an indicator of the surface activity different from the surface or interfacial tension. Several different adsorption isotherms can be applied depending on the data available and the theory applied to the adsorption phenomenon. Some examples are indicated in Table I. Here both surface tension and surface adsorption models are given applicable both to air-liquid and liquid-liquid interfaces.

TABLE I

Types of Adsorption and Surface Tension Isotherms

Kralchevsky, P.A., Danov, K.D., and Denkov, N.D., in *Handbook of Surface and Colloid Chemistry*, (Ed. K.S. Birdi, CRC Press 2003), p. 143.

Surfactant Adsorption Isotherms (for nonionic surfactants: $a_{1s} = c_1$)

Henry	$K a_{1s} = \frac{\Gamma_1}{\Gamma_\infty}$	(3)
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$$\text{Freundlich} \quad K a_{1s} = \left(\frac{\Gamma_1}{\Gamma_\infty} \right)^{1/m} \quad (4)$$

$$\text{Langmuir} \quad K a_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \quad (5)$$

$$\text{Volmer} \quad K a_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp \left(\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \right) \quad (6)$$

$$\text{Frumkin} \quad K a_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp \left(-\frac{2\beta\Gamma_1}{kT} \right) \quad (7)$$

$$\text{van der Waals} \quad K a_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp \left(\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} - \frac{2\beta\Gamma_1}{kT} \right) \quad (8)$$

Surface Tension Isotherm $\gamma = \gamma_0 - kTJ + \gamma_d$ (for nonionic surfactants $\gamma_d \equiv 0$)

$$\text{Henry} \quad J = \Gamma_1 \quad (9)$$

$$\text{Freundlich} \quad J = \frac{\Gamma_1}{m} \quad (10)$$

$$\text{Langmuir} \quad J = -\Gamma_\infty \ln \left(1 - \frac{\Gamma_1}{\Gamma_\infty} \right) \quad (11)$$

$$\text{Volmer} \quad J = \frac{\Gamma_\infty \Gamma_1}{\Gamma_\infty - \Gamma_1} \quad (12)$$

$$\text{Frumkin} \quad J = -\Gamma_\infty \ln \left(1 - \frac{\Gamma_1}{\Gamma_\infty} \right) - \frac{\beta\Gamma_1^2}{kT} \quad (13)$$

$$\text{van der Waals} \quad J = \frac{\Gamma_\infty \Gamma_1}{\Gamma_\infty - \Gamma_1} - \frac{\beta\Gamma_1^2}{kT} \quad (14)$$

K = Adsorption parameter; the greater the K value the higher the surface activity.

Γ_1 = Surface Concentration (Adsorption). 1 denotes the surfactant.

Γ_∞ = Maximum possible value for adsorption (in Freundlich adsorption isotherm it is a parameter scaling the adsorption rather than saturation adsorption).

β = Boltzmann constant (Interaction parameter).

T = Absolute temperature.

a_{1s} = Concentration of surfactant.

J = Surface concentration function.

The adsorption of the surface active components at liquid–liquid interfaces and solid–liquid interfaces has been very well studied. Eqs. 3 - 8 correspond to surfactant adsorption at the interface and Eqs. 9 – 14 correspond to surface tension as a result of surfactant adsorption. Equations 9 – 13 were deduced from respective adsorption isotherms. However, none of these equations can differentiate the interfacial tension change as a result of the adsorption of surface active components without experimental calibration or measurements. This is significant in determining the interfacial tension between complex fluids such as crude oil and an aqueous system. The present method, a combination of experimental and modeling parts, facilitates the determination of the interaction between such fluids more accurately and precisely.

The concentration of the surfactant used to determine the isotherm constants can be absolute or relative. If the surface tension is determined from the original oil (relative surface active concentration of 1) and the natural surfactant-free or acid-free oil (relative concentration 0) as well as blends of these (concentration between 0 and 1) the isotherm can be fitted based on this and any volume change caused by hydrocarbon composition change, pressure, or temperature can now be used to calculate a relative change in concentration and therefore a change in interfacial tension due to the change in composition, pressure, or temperature.

[0024] The embodiments of the present application employ a testing methodology that calibrates (or tunes) the parameters of the empirical model that relates oil-water interfacial tension to the bulk concentration of one or more naturally-occurring organic acid species for a particular crude oil sample. After being calibrated, the empirical model can accurately describe the oil-water interfacial tension of the particular crude oil sample as a function of the bulk concentration of the one or more naturally-occurring organic acid species within the particular crude oil sample. The calibrated empirical model can

be used to derive a value for oil-water interfacial tension of the crude oil as a function of varying concentrations of organic acid, naphthenic acid, or naturally-occurring surface active components and added surfactant, which can be used to calculate one or more reservoir parameters for reservoir engineering and/or reservoir simulation, such as capillary pressure, capillary number, and oil column height within a reservoir of interest.

[0025] FIG. 1 is a flow chart that illustrates an embodiment of a workflow and test methodology of the present disclosure. The interfacial tension measurements of the workflow can be carried out in a temperature-controlled environment at a set temperature with the respective sample equilibrated to this set temperature before performing the interfacial tension measurements. In this case, the temperature of the temperature-controlled environment can be equated to the temperature T of the Gibbs-Langmuir empirical model of Eq. (2) as described above. The set temperature of the temperature-controlled environment can correspond to the high temperature reservoir conditions of the reservoir of interest from which the crude oil sample originated, if desired, for example from 273⁰K to 473⁰K. Moreover, the interfacial tension measurements of the methodology can be carried out in an ambient pressure environment or possibly in a pressure-controlled environment at an elevated pressure above ambient pressure. The elevated pressure can correspond to the high pressure reservoir conditions of the reservoir of interest from which the crude oil sample originated, if desired, for example from 1 to 2000 bar. The workflow begins at 101 where a crude oil sample originating from a reservoir of interest is obtained. The crude oil sample can be obtained as stabilized oil (after degasification which removes gaseous hydrocarbons and light liquid fractions from the crude oil) or other suitable oil. The crude oil sample can be collected from the reservoir of interest by downhole fluid sampling from the formation at reservoir conditions, collecting crude oil from a wide range of locations (such as a wellbore, a wellhead, a separator, a pipeline, and a tank), extracting crude oil from a core sample, or other suitable reservoir fluid collection methods.

[0026] In 103, the bulk concentration of one or more naturally-occurring organic acid species (such as the naphthenic acid species and/or carboxylic acid species) in the crude oil sample is measured, and the measured concentration is equated to the parameter C of

the Gibbs-Langmuir empirical model of Eq. (2) as described above. The bulk concentration of the one or more naturally-occurring organic acid species in the crude oil sample can be measured by a variety of techniques, such as Fourier-transform infrared (FTIR) spectroscopy, gas chromatography (GC) – mass spectrometry (MS), titration, and other suitable methods. Combinations of these techniques can also be employed with acid extraction and specific chemical reactions to enhance detection by indirect measurements. If the actual concentration is not determined, a relative concentration may be used based on the original oil or the natural surfactant-free (e.g. acid-free) oil, and mixtures of these can be used to estimate relative changes.

[0027] In 105, the one or more organic acid species (such as the naphthenic acid species and/or carboxylic acid species) are removed from a part of the crude oil sample to form an “acid-free” component. The removal of the one or more organic acid species can be carried out by solvent-based extraction procedures and/or solid extraction procedures (such as solid ion exchange resins or similar adsorbent-based separation). For testing of the crude oil sample at high pressures and/or high temperatures corresponding to reservoir conditions, the removal of the one or more organic acid species can be carried out by a high pressure ion exchange resin column possibly at controlled temperatures corresponding to the reservoir conditions.

[0028] In 107, the oil-water interfacial tension of the “acid-free” component is measured and equated to the parameter γ_0 of the Gibbs-Langmuir empirical model of Eq. (2) as described above. The oil-water interfacial tension of the “acid-free” component can be measured by the pendant drop method, a Wilhelmy plate, a du Nouy ring, the drop volume or drop weight method, the spinning drop method, or any other suitable technique. For measuring the oil-water interfacial tension of the “acid-free” component at reservoir pressure and/or temperature conditions, an optical cell capable of withstanding the high pressures and temperatures corresponding to the reservoir conditions can be used.

[0029] In 109, the “acid-free” component is mixed with a part of the crude oil sample to form a mixture at a predefined proportion of the “acid-free” component to the crude oil

sample part. The oil-water interfacial tension of the mixture is measured and equated to a value for the oil-water interfacial tension γ of the Gibbs-Langmuir empirical model of Eq. (2) as described above. These operations can be repeated multiple times to measure the oil-water interfacial tension of multiple mixtures with varying proportions of the “acid-free” component. The oil-water interfacial tension of the “acid-free” component can be measured by the pendant drop method, a Wilhelmy plate, a du Nouy ring, the drop volume or drop weight method, the spinning drop method, or any other suitable technique. For measuring the oil-water interfacial tension of the mixture(s) at reservoir pressure and/or temperature conditions, the mixing of the crude oil sample part and the “acid-free” component can be carried out under high pressure corresponding to the reservoir conditions using a high pressure micromixer or small pycnometers with and without stirring device. An optical cell capable of withstanding the high pressures and high temperatures corresponding to the reservoir conditions can also be used.

[0030] In 111, the oil-water interfacial tension of the crude oil sample is measured and equated to a value of the oil-water interfacial tension γ of the Gibbs-Langmuir empirical model of Eq. (2) as described above. The oil-water interfacial tension of the crude oil sample can be measured by the pendant drop method, a Wilhelmy plate, a du Nouy ring, the drop volume and drop weight method, the spinning drop method, and any other suitable technique. For measuring the oil-water interfacial tension of the crude oil sample at reservoir pressure and/or temperature conditions, an optical cell capable of withstanding the high pressures and temperatures corresponding to the reservoir conditions can be used.

[0031] In 113, numerical analysis is performed that uses the values of the oil-water interfacial tension γ as generated in 109 as a function of C and 111 and the parameter γ_0 generated in 107 and the parameter C generated in 103 in order to calibrate the Gibbs-Langmuir empirical model of Eq. (2) as described above. Γ_m and K_L are calibrated by using at least two levels of acid concentrations (C_i) which may include one mixture of acid-free and original oil and one sample of the original oil. More concentrations can be made by mixing the original oil and the acid-free oil in different proportions. The more sample concentrations examined the better the quality of the data and enhancement of the

ability to extrapolate beyond the acid concentration of the original oil. This is especially applicable if acid concentration is expected to vary across the reservoir due, for example, to gravity segregation or the like. A similar numerical analysis approach is performed to determine model parameters if a different type of interfacial tension model other than the Gibbs-Langmuir model is used.

[0032] FIG. 2 is a graph showing the measurements of oil-water interfacial tension of a heavy oil with varying amounts of naturally-occurring organic acid content as generated in 109 and 111 of the methodology of FIG. 1, which are labeled as square data points in the graph. The y-axis represents the oil-water interfacial tension in units of mNewton/meter. The x-axis represents the log of the weight fraction of the naturally-occurring organic acid content relative to the “acid-free” oil component in the oil. The calibrated empirical model that results from 113 is shown in the line labeled “Gibbs-Langmuir Model”.

[0033] In 115, the empirical model as calibrated in 113 can be used to derive a value for the oil-water interfacial tension of the crude oil of the reservoir of interest. The calibrated model can now be used to calculate the interfacial tension at reservoir conditions for any given variation in carboxylic or naphthenic acid content simply by a measurement of this concentration from samples or from known measured acid concentration gradients in the reservoirs. The measurement can be either by extraction or direct measurement on samples by a spectroscopic technique such as infrared spectroscopy or mass spectrometry combined with chromatographic techniques as known to those skilled in the art. The concentration effects caused by pressurization and or gas dissolution may be taken into account by calculation of the changes in fluid volume such as the formation volume factor.

[0034] In 117, the value for oil-water interfacial tension of the crude oil as derived in 115 can be used to calculate one or more parameters for reservoir engineering and/or reservoir simulation, such as capillary pressure P_C , capillary number N_C , and the height H of the oil column within the reservoir of interest.

[0035] Note that the oil-water interfacial tension of the crude oil sample is important

in the evaluation of the reservoir of interest and in planning production from the reservoir of interest. Specifically, the oil-water interfacial tension is important in developing oil field exploration and production strategies, enhanced oil recovery, and oil-water separation. Thus, oil-water interfacial tension is an important parameter used in reservoir engineering and reservoir simulators.

[0036] For example, the oil-water interfacial tension can be used to derive capillary pressure of the reservoir of interest. More specifically, the capillary pressure P_c of the reservoir of interest can be calculated as:

$$P_c = 2\gamma \cos\theta / r \quad (15)$$

where γ is the oil-water interfacial tension of the crude oil sample originated from the reservoir of interest;

θ is the wetting angle characteristic of the reservoir of interest; and

r is the pore throat radius characteristic of the reservoir of interest.

[0037] In another example, the oil-water interfacial tension can be used to derive the capillary number of the reservoir of interest. More specifically, the capillary number N_c of the reservoir of interest can be calculated as:

$$N_c = \frac{\mu_w V_w}{\phi \gamma_{wo}} \quad (16)$$

where μ_w is the viscosity of the aqueous or displacing phase;

V_w is the flow rate of the displacing phase;

ϕ is the effective porosity of the reservoir of interest; and

γ_{wo} is the oil-water interfacial tension of the crude oil sample originating from the reservoir of interest.

Note that capillary pressure and capillary number can be used to determine the residual oil saturation and displacement efficiency, and therefore greatly influence oil recovery.

[0038] The oil-water interfacial tension is also an important parameter in oil reserve calculation. For example, the height H of trapped oil column can be calculated by equating the capillary pressure with buoyancy pressure, which result in

$$H = \frac{2\gamma \cos\theta}{rg(\rho_w - \rho_h)} \quad (17)$$

where γ is the oil-water interfacial tension of the crude oil sample originated from the reservoir of interest;

θ is the wetting angle characteristic of the reservoir of interest;

r is the pore radius characteristic of the reservoir of interest;

g is the gravity constant, and

ρ_w and ρ_h are the densities of water and oil, respectively.

Note that recovery rate estimates and water coning calculations are also affected by incorrect estimates of the oil-water interfacial tension.

[0039] In all of these examples, the oil-water interfacial tension of the crude oil sample represents the liquid-liquid interfacial tension between the oil phase and aqueous phase of the reservoir fluid samples.

[0040] Note that calculation of the oil-water interfacial tension of the crude oil sample as described herein can be extrapolated to other temperatures by experiments at varying conditions and/or compositions, or possibly by semi-empirical correlations between oil-water interfacial tension and temperature. One may also use pressure-volume-temperature (PVT) data to correct concentration for any uptake of gas during pressurization below saturation pressure, and/or volume changes due to compression and expansion due to pressure and temperature. A determination of oil-water interfacial tension in the saturated region above the bubble point pressure of the crude oil sample will enhance the accuracy of the model especially if the model is calibrated with stabilized oils. The observations can then be used to evaluate the pressure and

temperature effects on the model parameters Γ_m and K_L .

[0041] Note that one or more of the fluid testing operations of 103 to 111 of FIG. 1 can be carried out in a batch-type process. The batch-type process can be performed at ambient pressure conditions or at elevated pressure conditions above ambient pressure (such as at reservoir pressure). For testing the oil samples at ambient pressure, the oil sample can be passed through an ion exchange resin suitable for removing naturally-occurring organic acid species (such as, but not restricted to, the naphthenic acid species and/or carboxylic acid species) in order to produce the “acid-free” component.

[0042] Alternatively, one or more of the fluid testing operations of 103 to 111 of FIG. 1 can be carried out in a continuous process. The continuous process can be performed at ambient pressure conditions or at elevated pressure (such as at reservoir pressure). An exemplary continuous process operating at elevated pressure conditions is shown in FIG. 3. In this exemplary embodiment, the oil sample at elevated pressures is passed from the high pressure reservoir 301 through a solid activated ion exchange resin cartridge 303 suitable for removing naturally-occurring organic acid species (such as the naphthenic acid species and/or carboxylic acid species) in order to produce the “acid-free” oil component under high pressure conditions. The “acid-free” oil component produced by the ion exchange resin cartridge 303 as well as the crude oil sample from the reservoir 301 can be routed to a high pressure optical cell 305 that houses a pendant drop device. The pendant drop device can be configured to measure the oil-water interfacial tension of the “acid-free” component as well as the oil-water interfacial tension of the “acid-free” component. It is also contemplated that one or more mixtures of the “acid-free” component and the crude oil sample can be formed at preset conditions (pressure and/or temperature) by mixing of original oil and “acid-free” oil using suitable micro-flow mixers with variations of flow ratios. These high pressure mixtures can also be routed to the optical cell 305 for measurement of interfacial tension by the pendant drop device, or a similar interfacial methodology suitable also for high pressure measurements.

[0043] These can then along with the low pressure fluid work be used to make a full calibration of the fluid interfacial tension description at reservoir conditions. As

described above one may use a low pressure calibration aimed at determining the surface activity as a function of concentration of natural surfactants by calculating the changes in concentration caused by compression or expansion caused by dissolution of hydrocarbon gases and/or expansion or compression of the fluid in the single phase region. An example is the application of the formation volume factor (B_o) to calculate a reduced concentration of surface active substances affecting the interfacial tension at reservoir conditions.

[0044] There have been described and illustrated herein several embodiments of a test workflow and apparatus that analyzes reservoir fluids. While particular embodiments have been described herein with reference to particular means, materials and embodiments, it is not intended to be limited to the particulars described herein; rather it extends to all functionally equivalent structures and methods, such as are within the scope of the appended claims.

CLAIMS

What is claimed is:

1. A method of reservoir analysis for a reservoir of interest comprising:
 - (i) obtaining a crude oil sample originating from the reservoir of interest;
 - (ii) measuring oil-water interfacial tension of the crude oil sample; and
 - (iii) calibrating an empirical model that relates oil-water interfacial tension of the crude oil sample to concentration of at least one organic acid species in the crude oil sample based on the oil-water interfacial tension measured in (ii).
2. A method according to claim 1, wherein the concentration of the at least one organic acid species in the crude oil sample is absolute concentration.
3. A method according to claim 1, wherein the concentration of the at least one organic acid species in the crude oil sample is relative concentration.
4. A method according to claim 1, further comprising:
 - (iv) calculating at least one reservoir parameter characteristic of the reservoir of interest based on the empirical model as calibrated in (iii).
5. A method according to claim 4, wherein the at least one reservoir parameter is selected from the group including capillary pressure, capillary number, and oil column

height.

6. A method according to claim 1, wherein the crude oil sample is a stabilized oil.

7. A method according to claim 1, wherein:

the empirical model includes a first parameter that represents bulk concentration of the at least one organic acid species in the crude oil sample; and

the method further includes measuring the concentration of the at least one organic acid species in the crude oil sample and using the measured concentration to derive the first parameter of the empirical model.

8. A method according to claim 1, wherein:

the empirical model includes a second parameter that represents oil-water interfacial tension of the crude oil sample with the at least one organic acid species removed from the crude oil sample; and

the method further includes processing a part of the crude oil sample to produce a sample component with the at least one organic acid species removed from the crude oil sample part, measuring oil-water interfacial tension of the sample component, and using the measured oil-water interfacial tension of the sample component to derive the second parameter of the empirical model.

9. A method according to claim 8, wherein the processing of the crude oil sample part that produces the sample component is carried out at an elevated pressure above ambient pressure.

10. A method according to claim 9, wherein the processing of the crude oil sample part that produces the sample component is carried out by an ion exchange resin column.

11. A method according to claim 9, wherein both the measuring of the oil-water interfacial tension of the crude oil sample and the measuring of the oil-water interfacial tension of the sample component are carried out at elevated pressure above ambient pressure.

12. A method according to claim 11, wherein both the measuring of the oil-water interfacial tension of the crude oil sample and the measuring of the oil-water interfacial tension of the sample component are carried out within an optical cell.

13. A method according to claim 8, wherein:

the processing of the crude oil sample part that produces the sample component is carried out at ambient pressure; and

both the measuring of the oil-water interfacial tension of the crude oil sample and the measuring of the oil-water interfacial tension of the sample component are carried out at ambient pressure.

14. A method according to claim 8, wherein the processing of the crude oil sample part that produces the sample component as well as the measuring of the oil-water interfacial tension of the sample component are carried out in a continuous process.

15. A method according to claim 8, further comprising:

mixing the sample component with a part of the crude oil sample to form at least one mixture at a predefined proportion of the sample component to the crude oil sample; and

measuring oil-water interfacial tension of the at least one mixture.

16. A method according to claim 15, wherein the mixing of the sample component with a part of the crude oil sample and the measuring of the oil-water interfacial tension of the at least one mixture are carried out at an elevated pressure above ambient pressure.

17. A method according to claim 16, wherein:

the mixing of the sample component with a part of the crude oil sample is carried out by a high pressure mixer; and

the measuring of the oil-water interfacial tension of the least one mixture is carried out within an optical cell.

18. A method according to claim 15, wherein the mixing of the sample component with a part of the crude oil sample and the measuring of the oil-water interfacial tension of the at least one mixture are carried out at ambient pressure.

19. A method according to claim 15, wherein:

the empirical model includes at least one additional parameter characteristic of the at least one organic acid species of the crude oil sample; and

the method further includes adjusting the at least one additional parameter based on numerical analysis employing the measured oil-water interfacial tension of the crude oil sample, the measured oil-water interfacial tension of the sample component, and the measured oil-water interfacial tension of the at least one mixture.

20. A method according to claim 19, wherein the at least one additional parameter is selected from the group including a parameter representing the monolayer surface excess concentration of the at least one organic acid species and an adsorption constant for the at least one organic acid species.

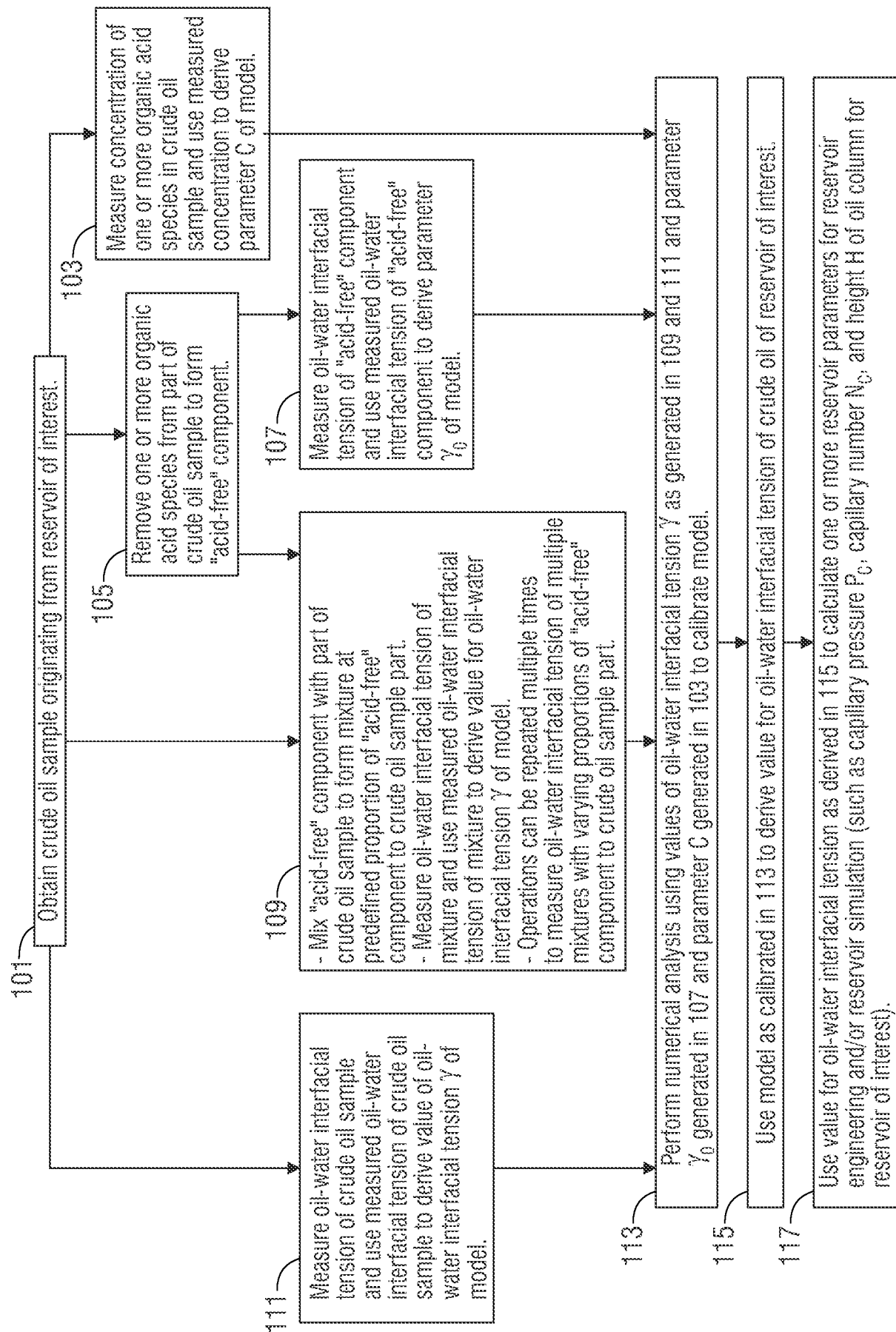


FIG. 1

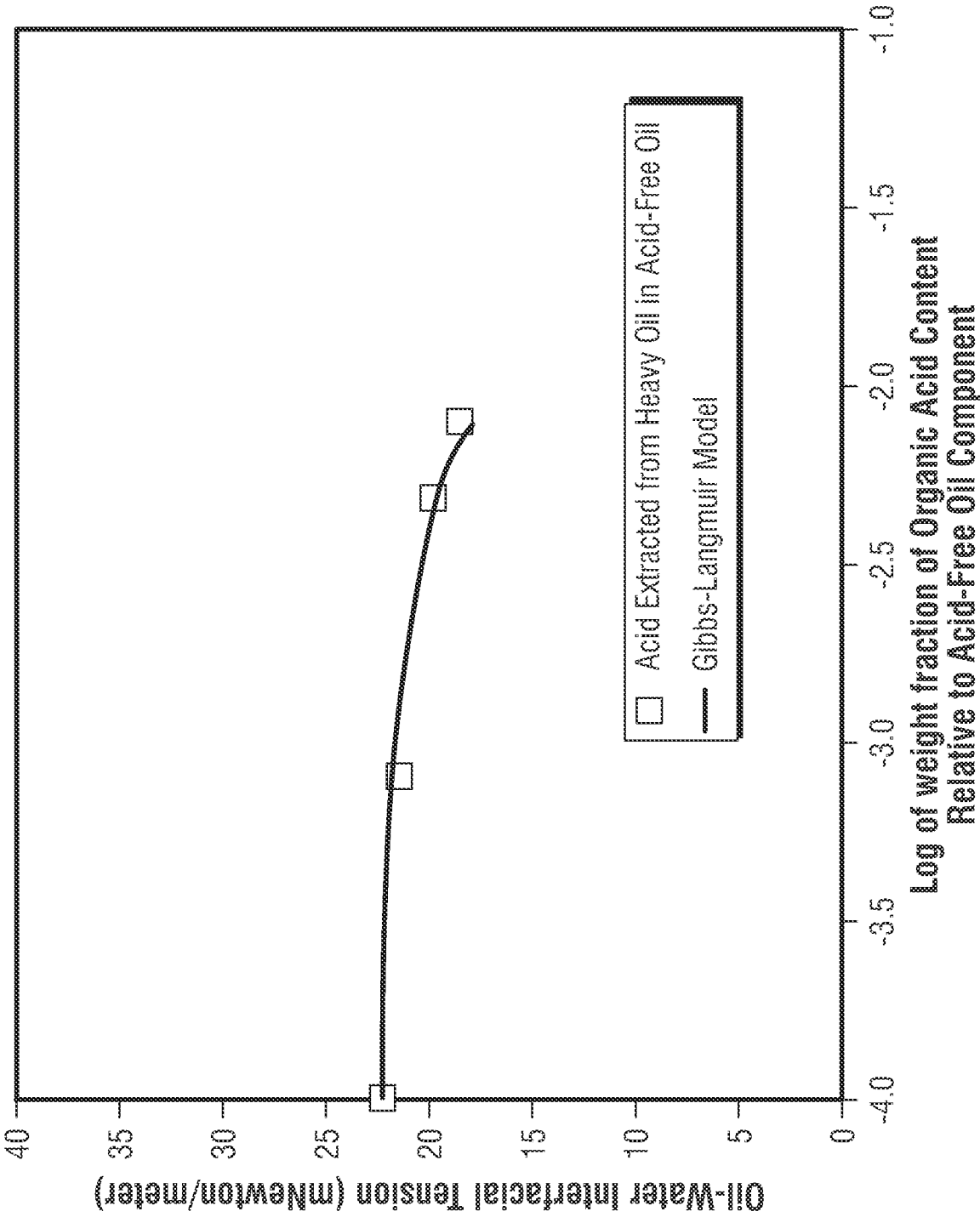


FIG. 2

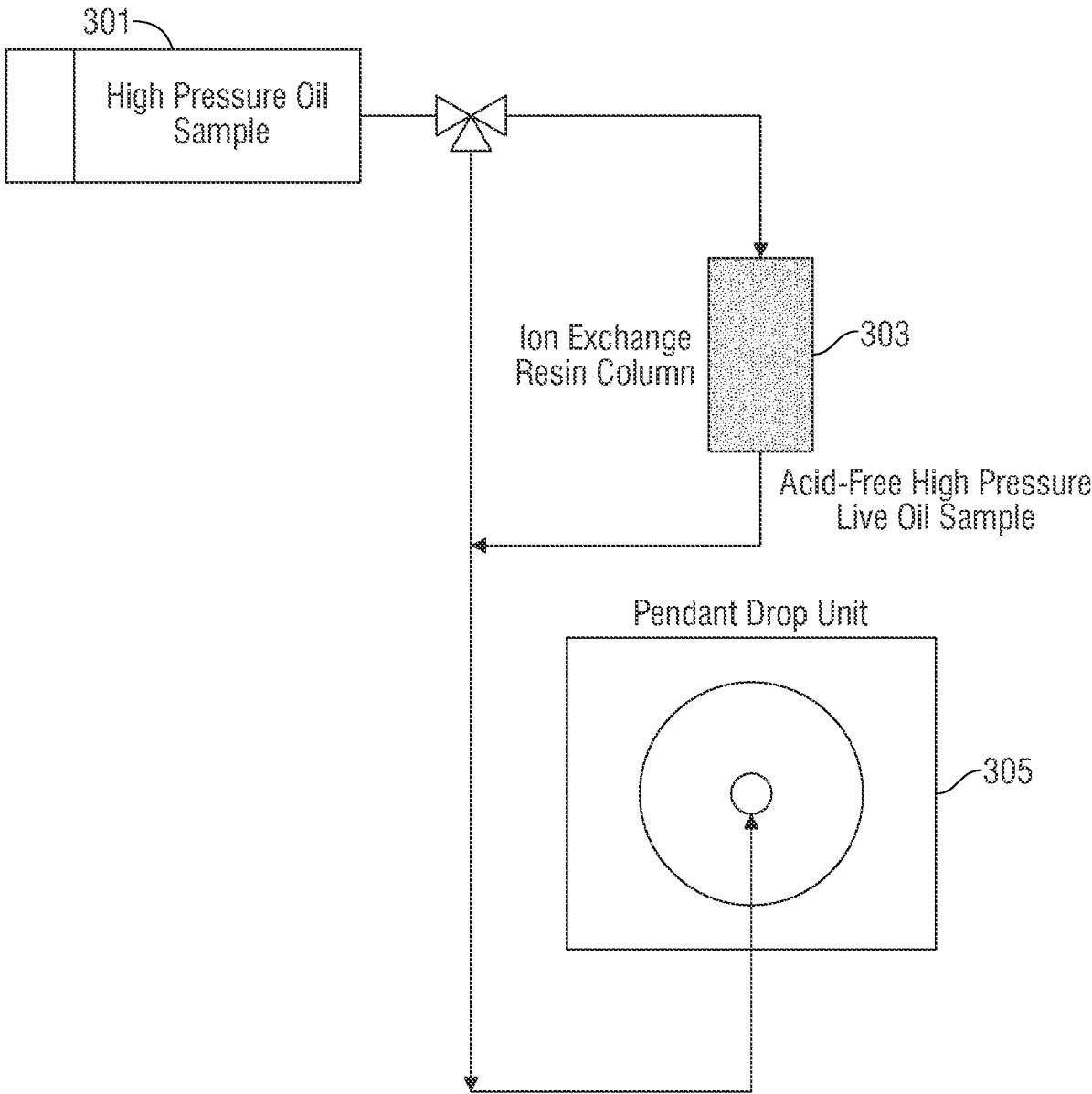


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/048478**A. CLASSIFICATION OF SUBJECT MATTER****G01N 33/28(2006.01)i, G01N 31/00(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G01N 33/28; G01N 31/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: calibrate, empirical model, oil-water interfacial tension, concentration, organic acid, crude oil, capillary, pressure, number, oil column height

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	VARADARAJ et al., Molecular origins of heavy crude oil interfacial activity part 2: Fundamental interfacial properties of model naphthenic acids and naphthenic acids separated from heavy crude oils, Energy & Fuels, 2007, Vol. 21, No. 1, pp. 199-204 See pages 199-204.	1-7
A		8-20
A	ROSEN et al., Ultralow interfacial tension for enhanced oil recovery at very low surfactant concentrations, Langmuir, 2005, Vol. 21, No. 9, pp. 3749-3756 See pages 3749-3756.	1-20
A	HEMMINGSSEN et al., Structural characterization and interfacial behavior of acidic compounds extracted from a north sea oil, Energy & Fuels, 2006, Vol. 20, No. 5, pp. 1980-1987 See pages 1980-1987.	1-20
A	HAVRE, et al., Oil/water-partitioning and interfacial behavior of naphthenic acids, Journal of Dispersion Science and Technology, 2003, Vol. 24, No. 6, pp. 789-801 See pages 789-798.	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

10 April 2015 (10.04.2015)

Date of mailing of the international search report

13 April 2015 (13.04.2015)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2014/048478

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ZHANG et al., Effect of different acidic fractions in crude oil on dynamic interfacial tensions in surfactant/alkali/model oil systems, Journal of Petroleum Science and Engineering, 2004, Vol. 41, No. 1, pp. 189-198 See pages 189-197.	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/048478Patent document
cited in search reportPublication
datePatent family
member(s)Publication
date

None