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(57) Abrégé(suite)/Abstract(continued):
a closed vessel containing the heated hydrocarbon and water mixture in the presence of gas or by injecting with gas; releasing the pressure of the heated hydrocarbon and water mixture in the vessel so as to create microbubbles from the dissolved gas in the water mixture; and collecting the hydrocarbon from the water. Optionally, the process is substantially devoid of adding caustic agents to the hydrocarbon and water mixture.
Title: CYCLIC GASEOUS COMPRESSION/EXPANSION FOR HEIGHTENED OIL SANDS EXTRACTION

Abstract: A method for extracting hydrocarbons from sands can include: providing sands containing a hydrocarbon; mixing the hydrocarbon sands with water; heating the water before, during, or after being mixed with the hydrocarbon sands; increasing the pressure within a closed vessel containing the heated hydrocarbon and water mixture in the presence of gas or by injecting with gas; releasing the pressure of the heated hydrocarbon and water mixture in the vessel so as to create microbubbles from the dissolved gas in the water mixture; and collecting the hydrocarbon from the water. Optionally, the process is substantially devoid of adding caustic agents to the hydrocarbon and water mixture.
CYCLIC GASEOUS COMPRESSION/EXPANSION FOR HEIGHTENED OIL SANDS EXTRACTION

CROSS-REFERENCE TO RELATED APPLICATIONS


BACKGROUND

[0002] Population centers in the U.S. and around the world are facing increasing challenges to provide sufficient energy, and will continue to demand new technologies for preparing usable energy resources for public consumption. Accordingly, attention is being turned from conventional oil deposits to oil sand deposits. However, the technologies available for obtaining bitumen from conventional oil deposits are not suitable for obtaining bitumen from oil sands.

[0003] Oil sand deposits in northern Canada contain about 142 billion cubic meters (or 890 billion barrels) of bitumen, thus constituting the largest oil sands deposit in the world. In the Athabasca region of Alberta, the oil sands deposit is typically composed of (by weight) about 12% bitumen, 82% to 85% mineral matter (solids), and 3% to 6% water. Of the solids fraction, the solids smaller than 45 microns in size (e.g., silt and clay) are referred to as fines. The clay fraction of the fines can be a significant factor in processes for both extraction of bitumen and disposal of oil sand tailings (e.g., residue from primary oil sand processing).

[0004] The bitumen of the Athabasca deposits has been commercially extracted by various oil sand-water slurry-based extraction processes and thermal in-situ processes. The liberated bitumen can be upgraded to synthetic crude oil at a production capacity of over one million barrels per day. In the major bitumen recovery operations in the Athabasca region, bitumen is produced from surface-mineable oil sands using water-slurry-based extraction processes, in which the oil sands "ore" (e.g., the raw oil sand material, as excavated from the oil sand deposits) is mixed with hot water to form an ore-water slurry. Asphal tic acids present in bitumen, which contain partly aromatic oxygen functional groups such as phenolic,
carboxylic and sulphonic types, become water-soluble, especially when the pH of the ore-water slurry is slightly over 7, and act as surfactants reducing surface and interfacial tensions. Reduction of the surface and interfacial tensions of the ore-water slurry system results in the disintegration of the ore structure and liberation of bitumen from the ore. Accordingly, the water-liberated or water-extracted fraction of bitumen asphaltenes plays an important role in the recovery of bitumen from the surface-mineable oil sands.

[0005] However, oil sands in different regions are chemically different and extraction processes that are successful for the oils sands of one region may not be sufficient for a different region. The selection of recovery and treatment processes of different oil sand deposits are influenced by the properties and composition of the oil sands and the bitumen. Since Canadian oil sands contains more moisture than Utah oil sands, optimal extraction methods for Utah oil sands are likely to be different from those in Canada. Thus, there remains a need for developing different oil sands extraction methods that can be applied to the various different oil sands or to particular oil sands, such as the Utah oil sands.

SUMMARY

[0006] In one embodiment, a method for extracting hydrocarbons from sands can include: providing sands containing a hydrocarbon; mixing the hydrocarbon sands with water; heating the water before, during, or after being mixed with the hydrocarbon sands; increasing the pressure within a closed vessel containing the heated hydrocarbon and water mixture in the presence of gas or by injecting with gas; releasing the pressure of the heated hydrocarbon and water mixture in the vessel so as to create microbubbles from the dissolved gas in the water mixture; and collecting the hydrocarbon from the water. Optionally, the process is substantially devoid of adding caustic agents to the hydrocarbon and water mixture.

[0007] The hydrocarbon can be any hydrocarbon, such as bitumen, tar, and molecules that can be processed into fuel. The gas is selected from the group consisting of air, N₂ (nitrogen), O₂ (oxygen), CO₂ (carbon dioxide), Ar (argon), BF₃ (boron trifluoride), CH₄ (methane), C₂H₂ (acetylene), C₂H₄ (ethylene), H₂S (hydrogen sulphide), C₂H₆ (ethane), C₃H₆ (propylene), C₃H₈ (propane), 1-butene, 1,3-butadiene, vinyl chloride, 1,1,1,2-tetrafluoroethane, isobutane, n-butane, isobutene, or any mixtures thereof.
[0008] The sands and water can be conditioned in batch tumblers or conditioning drums or are mixed during transport through a pipeline.

[0009] The process can be performed with at least one of the following: increasing the pressure to a range of about 10 to about 210 psi followed by reducing the pressure by at least 10 psi; maintaining the temperature between about 20 degrees C to about 120 degrees C; cycling the pressure for about 2 to about 30 pressure cycles; solid water volume ratio is from 0.1:1 to 2:1; increasing the pressure at a rate of compression that is about 5 to about 300 seconds to reach maximum pressure; or decreasing the pressure at a rate of decompression that is about 0.01 to about 300 seconds to vent to reach ambient pressure or any other lowered pressure.

[0010] The process can further include introducing the hydrocarbon and water into primary separation vessel (PSV).--Also, the process can further include settling the mixture into stratified layers in the PSV: impure bitumen froth on the top; a combination of bitumen, sand, clay and water in the middle (middlings); and sand precipitated to the bottom. The process can further include pumping the precipitated sand into a settling basin with water to form tailings. The process can further include separating the hydrocarbon from the tailings. The process can further include separating and cleaning the middlings by gas injection and steam de-aeration. The process can further include recovering the hydrocarbon from the middlings. The process can further include recovering the hydrocarbon from the froth.

[0011] In one embodiment, a method for extracting hydrocarbons from a particle can include: providing a particle containing a hydrocarbon; mixing the hydrocarbon-containing particle sands with water; heating the water before, during, or after being mixed with the hydrocarbon-containing particle; increasing the pressure of the heated mixture within a closed vessel; releasing the pressure in the vessel so as to create microbubbles in the mixture that liberate the hydrocarbon from the particle; and collecting the hydrocarbon from the water and particle. The pressure can be increased by any of the following; by decreasing the volume of the vessel; by increasing the number of molecules in the vessel; or by increasing the temperature in the vessel; by injecting a gas into the vessel. The gas can be selected from the group consisting of air, N₂, O₂, CO₂, Ar, BF₃, CH₄, C₂H₆, C₂H₄, H₂S, C₂H₆, C₃H₆, C₃H₈, 1-butene, 1,3-butadiene, vinyl chloride, 1,1,1,2-tetrafluoroethane, isobutane, n-butane, isobutene, or any mixtures thereof. The method can further include introducing additional hot water to separate the bitumen froth layer and solids.
In one embodiment, a method for extracting hydrocarbons from oil sands can include: introducing water into a low-pressure vessel at about 20 to about 40% of vessel capacity; heating the water to over 50 degrees C and less than 120 degrees C; introducing oil sands into the vessel at a solid/water volume ratio of about 0.1 to about 3 volume to form a water/oil sands mixture; closing and pressuring the vessel with a gas to a pressure of about 25 to about 210 psi; maintaining the temperature of the water/oil sands mixture between about 20 degrees C to about 120 degrees C; decompressing the pressure in the vessel so as to generate gaseous microbubbles that release the hydrocarbon from the oil sands; and recovering the hydrocarbon from the water and sands. Also, the process can be performed with at least one of the following: increasing the pressure to a range of about 10 to about 150 psi followed by reducing the pressure by at least 10 psi; maintaining the temperature between about 50 degrees C to about 110 degrees C; cycling the pressure for about 2 to about 30 pressure cycles; a solid/water volume ratio that is from 0.1:1 to 2:1; increasing the pressure at a rate of compression that is about 5 to about 300 seconds to reach maximum pressure; or decreasing the pressure at a rate of decompression that is about 0.01 to about 300 seconds to vent to reach ambient pressure or any other lowered pressure.

In one embodiment, a method for extracting hydrocarbons from sands can include: providing sands containing a hydrocarbon; mixing the sand containing the hydrocarbon with water; cycling the pressure of the mixture in a vessel by increasing the pressure and then decreasing the pressure so as to change gas solubility in the water and form gaseous microbubbles in the mixture; and collecting the hydrocarbon from the water and sands. The method can further include introducing a gas into the vessel, wherein the gas is selected from the group consisting of include ammonia, ozone, chlorine, air, nitrogen, oxygen, carbon monoxide, carbon dioxide, argon, helium, water vapor, BF₃, CH₄, C₂H₂, C₂H₄, H₂S, C₂H₆, C₃H₆, propane, 1-butene, 1,3-butadiene, vinyl chloride, 1,1,1,2-tetrafluoroethane, isobutane, n-butane, and sobutene and combinations thereof.

These and other embodiments and features of the sensor device will become more fully apparent from the following description and appended claims, or may be learned by the practice of the sensor device as set forth hereinafter.

The foregoing summary is illustrative only and is not intended to be in any way limiting. In addition to the illustrative aspects, embodiments, and features
described above, further aspects, embodiments, and features will become apparent by reference to the drawings and the following detailed description.

FIGURES

[0016] To further clarify the above and other advantages and features of the sensor device and compositions, an illustrative description of the sensor device will be rendered by reference to the appended drawings. It is appreciated that these drawings depict only illustrated embodiments of the sensor device and are therefore not to be considered limiting of its scope.

[0017] Figure 1 is a schematic diagram of an extraction system.

[0018] Figure 2 is a graph showing the bitumen recovery efficiency (wt%) vs. cycle number, wherein the solid to water ratios are volume ratios, and the separation vessel is pressurized to 100 psi by air.

[0019] Figure 3 is a graph showing bitumen recovery efficiency (wt%) vs. cycle number, wherein the solid to water volume ratio is 0.5:1, and the separation vessel is pressurized to 150 psi by air.

[0020] Figure 4 is a graph showing bitumen recovery efficiency (wt%) vs. cycle number, wherein the solid to water volume ratio is 0.5:1, and the separation vessel is pressurized to 100 psi by air.

[0021] Figure 5 is a graph showing bitumen recovery efficiency (wt%) vs. cycle number, wherein the solid to water volume ratio is 0.5:1, and the separation vessel is pressurized to 50 psi by air.

[0022] Figure 6 is a graph showing the CO₂ pressurized hot water extraction of bitumen from oil sands when CO₂ is at 100 psi compared to when CO₂ is at 50 psi.

[0023] Figure 7 is a graph showing the recovered bitumen at different pH conditions under overheated condition when the solid/water volume ratio is 1:1.

[0024] Figures 8A-8B are graphs showing bitumen recovery efficiency (wt%) from Canadian high grade oil sands vs. cycle number when the solid to water volume ratio is 0.5:1.

[0025] Figure 9 is a graph showing bitumen recovery efficiency (wt%) from Canadian low grade oil sands vs. cycle number when the solid to water volume ratio is 0.5:1.
[0026] Figure 10 is a graph showing the sand concentration (wt %) in the extracted bitumen at different temperature using different gases, wherein the solid to water volume ratio is 0.5:1 and the extraction pressure is 100 psi.

**DETAILED DESCRIPTION**

[0027] In the following detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be utilized, and other changes may be made, without departing from the spirit or scope of the subject matter presented here.

[0028] The present invention is drawn to systems and methods of removing hydrocarbons from solid samples. More specifically, the invention relates to processes and methods using a cyclic pressurizing-depressurizing gaseous treatment for extraction of hydrocarbons from soil, sand, rock, and other solid samples.

[0029] A pressure cycling process can improve removal of hydrocarbons from samples, particularly fluidized sand samples. The pressure cycling process can include the steps of pressurizing a fluid in a chamber with the sample and depressurizing the fluid and sample for one or more pressure cycles. The fluidized samples can be prepared by combining a hydrocarbon-containing sand (e.g., tar sand or oil sand) and a suitable fluid, such as water. The fluidized sand sample and fluid are pressurized together and then depressurized in a cyclic manner so that the fluid causes the formation of microbubbles in the proximity of hydrocarbons in the sand. In one aspect, the injection of a fluid into a chamber with the sample can be performed simultaneously, and may result in the pressurization, although sequential pressure cycling can also be suitable. After pressurizing, the sample is depressurized such that the fluid forms microbubbles in the sample proximal with the hydrocarbon. The microbubbles disrupt any solids within the sample in a manner sufficient to increase hydrocarbon separation efficiency from the solids, such as sand and fines.

[0030] The pressurizing and depressurizing cycle can be repeated at least once or any number of times that liberates a desired amount or percentage of hydrocarbon. The pressurizing can be obtained by increasing the amount of fluid in the chamber, by reducing the volume of the chamber, or by increasing the
temperature in the chamber. The pressure cycle can be performed at a substantially a constant temperature or within a temperature range, or the temperature can be varied along with the pressure.

[0031] The pressure cycling process can use liquids or gasses to improve the removal of the hydrocarbons from oil sands or tar sands. The pressure cycling can include the steps of injecting the sand a liquid and/or a gas, and then cyclically pressurizing and depressurizing the composition so as to create microbubbles. The liquid and/or gas as well as the sand sample can be substantially devoid of a caustic compound that is typically used in hydrocarbon extraction from sands. For example, the pressure cycling process can be performed substantially without or devoid of caustic compounds being selected from oxidizing agents, phase transfer agents, and extraction agents. In another example, after the pressurizing, the sample can be depressurized to a second pressure which is at least 10 psi lower than the first pressure. The pressure cycling, even without a caustic agent, can cause the sand particles to fracture and expose the hydrocarbon contained inside. The injecting, pressurizing, and depressurizing steps can be then repeated from 2 to 100 times or more, depending on the particular system.

A. Definitions

[0032] As used herein, the term “slurry” or “slurry sample” refers to a liquid sample containing a solids content which is more than incidental solids debris. Although the percent solids can vary considerably, a slurry sample can have from 2% to 95% by weight of solids. High solids (e.g. 20% to 70%) and low solids (e.g. 2% to 15%) slurries can be of particular interest in the present invention. Sand slurries can also include those substantially free of solids, e.g. non-slurry samples.

[0033] As used herein, the term “fines” is meant to refer to the small particulate nature of powders or silt in a sand particle or liberated from sand that is less than 45 microns in size or less than 80 mesh. As such, the fines, such as sand fines or mineral fines, or other fines are small, finely divided, and light weight particulates that are easily airborne when handled or exposed to minimal air currents. Such fines are also susceptible to attachment to air bubbles, such as microbubbles.

I. Introduction

[0034] Hydrocarbon-containing sands (e.g., oil sands, tar sands, or bituminous sands) are a combination of clay, sand, water, and bitumen. The bitumen extracted from hydrocarbon sands has a similar chemical structure with conventional crude
oil, but has higher density (e.g., a lower API gravity) and higher viscosity. On average, bitumen from hydrocarbon sands contains 83.2% carbon, 10.4% hydrogen, 0.94% oxygen, 0.36% nitrogen, and 4.8% sulfur. Oil sands are found in over 70 countries throughout the world, and represent about 66% of the world's total reserves of bituminous hydrocarbons. About 75% of the hydrocarbon sand deposits are in Venezuela (e.g., 1.8 trillion barrels) and Canada (1.7 trillion barrels). In the United States, hydrocarbon sands (e.g., oil sands and tar sands) are primarily concentrated in Eastern Utah and the surrounding basin area, where the in-place bitumen content in hydrocarbon sand is estimated at about 12 to 20 billion barrels. Presently, the United States has very little experience with producing oil from tar sands.

[0035] Previously, the bitumen in hydrocarbon sands has been attempted to be extracted both by mining and in situ extraction, including hot water extraction process (HWEP), cold flow, cold heavy oil production with sand (CHOPS), cyclic steam stimulation (CSS), steam assisted gravity drainage (SAGD), vapor extraction process (VAPEX), toe-to-heel air injection (THAI), and closed-loop solvent extraction. Currently, the only commercially operated hydrocarbon liberation and recovery technologies in Canada are HWEP and CHOPS for open-pit mines. Since all in situ extraction methods have to overcome two obstacles, 1) viscosity reduction of the bitumen and 2) recovery of the bitumen, most in situ thermal methods, such as CSS and SAGD, are very energy intensive. VAPEX has better energy efficiency since is similar to SAGD except that an organic solvent is injected into the reservoir instead of steam. THAI is also an in situ combustion method with much higher recovery efficiency, but it requires favorable deposit conditions and it will totally destroy the sands layer. Recent enhancements, such as tailings oil recovery (TOR) can recover oil from the tailings, diluent recovery units (DRU) can recover hydrocarbons from the froth, and inclined plate settlers (IPS) and the use of disc centrifuges, can recover over 90% of the bitumen in the sand.

[0036] The hot water extraction process (HWEP) has been commercially employed in order to recover bitumen from surface mined oil sands ore in hot water. This technology utilizes the effects of ablation, mixing, mass and heat transfer, and chemical reactions to separate and recover bitumen from the sand and mineral particles. The hot water process contains two steps: 1) liberation of bitumen from sand; and 2) recovery of the liberated bitumen. The efficiency of separation by
HWEP is greatly affected by the addition of caustic reagents and other additives. Also the fines content of oil sands affects recovery efficiency. One problem with HWEP is the high costs of liberation and recovery of bitumen. As such, a reduction in the slurry temperature could be cost effective. However, the lower temperatures result in longer conditioning times and require more additives, and have complicated this process.

[0037] In HWEP, a composition of hydrocarbon sand and hot water is conditioned for liberation of bitumen in batch tumblers or conditioning drums. Also, the hydrocarbon sand can be conditioned during transportation from the quarry by combining the sand and water into a slurry mixture for transportation in a pipeline to the extraction plant. The blended slurry is settled into three layers in a primary separation vessel (PSV) after gas floatation: impure bitumen froth on the top; a combination of bitumen, sand, clay and water in the middle (middlings); and sand to the bottom. The sand precipitate can be pumped into settling basins with water, which is called tailings. The middlings are further separated and cleaned by air injection and steam de-aeration, respectively. The HWEP requires two to four barrels of water for each barrel of oil. On average, less than 75% bitumen can be recovered from oil sands by HWEP. It has been shown that ORS (e.g., organic rich solids – toluene insoluble organics directly absorbed onto particle surface) fraction in hydrocarbon sands is an impediment to for bitumen separation and recovery. Also, the clay fines and polar organics can cause poor bitumen separation and recovery.

[0038] The selection of recovery and treatment processes of different oil sands deposits are influenced by the properties and composition of the oil sands and the bitumen. Since Canadian Alberta oil sands contains more moisture than Utah oil sands, optimal extraction methods for Utah oil sands are likely to be different from those in Alberta. Since Utah oil sands are different from Canadian oil sand, HWEP is inefficient for Utah oil sands. Attempts to increase the efficiency of liberation and recovery for Utah oil sands have modified the HWEP process to provide more intense shearing forces and more caustic wetting agents, such as sodium hydroxide, due to much higher viscosity of bitumen in the Utah oil sands. In response to the problems with HWEP and the nature of Utah oil sands, the pressure cycle process of the present invention can be used in order to enhance recovery of bitumen from oil sands, especially for Utah oil sands.
Accordingly, the present invention includes an improvement in bitumen liberation and recovery by introducing pressure cycling to the liberation and recovery process. For example, any of the above-references liberation and recovery processes, such as HWEP, can be modified to include a pressure cycling process that increases the pressure of a fluidized oil sand sample, and then releases the pressure so as to obtain a decompression pressure drop that forms microbubbles and introduces shear forces to the bitumen and sand interface. The pressure cycling can be adapted to various processes by preparing a fluidized oil sand sample, and then performing the pressure cycling process.

II. Pressure Cycle Bitumen Extraction

The pressure cycle process is an improvement over conventional heated or hot water extraction of oil sands by modulating the pressure of the sample by increasing and decreasing the pressure of the sample through pressure cycles (e.g., 10 to 100 psi cycles). The pressure cycles result in dissolution of gas into water during the compression stage and subsequent degassing via microbubble formation during the decompression stage. The pressure cycle process improves the conventional hot water extraction of bitumen so as to be faster with a higher-yield, and is more economical. Additionally, the pressure cycle allows for bitumen extraction at lower temperatures than previously obtained and with the use of many different gases. The pressure cycle process is an important tool for developing oil sands for which energy consumption and water availability are critical concerns, such as the Utah oil sands.

The creation or presence of gaseous microbubbles and even nanobubbles in the processing of oil sands can enhance the liberation and recovery of the entrapped hydrocarbons. In part, the presence, generation, or amplification of gaseous microbubbles enhances the extraction of hydrocarbons from sands because: a) microbubbles provide abundant interfacial surface areas that acts as a detergent film to collect bitumen, resulting in their efficient collection; b) the formation of gas bubbles in the space containing bitumen pries open bitumen-coated sand grains, helping to release the bitumen; and c) gaseous microbubbles serve to lift the separated bitumen, thus performing the separation and floatation collection in a single step. The use of different types of gases can modulate the rate, efficiency, and total amount of hydrocarbon recovery.
An improved bitumen liberation and recovery process employs cyclic compression and decompression of oil sands in the presence of a fluid that can generate gas bubbles. For example, sands can be prepared into a liquid slurry in a separation vessel, gas can be injected into the separation vessel to increase the pressure, and then the pressure can be reduced. The gas can be air, carbon dioxide, or other suitable gas. The pressure cycle process can accelerate the displacement and disengagement rates of bitumen from oil sands. The pressure cycles can provide an action on the bitumen in the sands similar to the use of mechanical agitation and/or caustic reagents, without the requirement of using mechanical agitation or caustic reagents. A pressure cycle process performed with a water temperature that is higher than the boiling point at atmospheric pressure (e.g., 100 °C, 1 atm) during air compression procedure can provide even more liberation and recovery efficiency. The pressure cycle process can be performed with or without intense agitation, caustic reagents, and other additives. The pressure cycle process can provide for more than about 95% bitumen liberation and recovery in a short time period.

The pressure cycle process takes advantage of the high heat and mass transfer rates, quicker chemical reaction rates such as hydration of quartz, mixing, lower viscosity, and ablation during decompression. The energy density per unit volume to treat oil sands obtained by decompression can be much higher than the energy density of mechanical agitation because the potential heat is released in a short time, and optionally under a overheated condition (e.g., over 100 °C). When CO₂ is injected into water instead of air, recovery efficiency of bitumen still can be as high or higher than about 85%, but at much lower temperature. Also, because the pressure cycle process combines the separation procedure and recovery procedure together, the total processing time is much shorter than processing time of convention HWEP.

Most of the hot water used in the pressure cycle process can be quickly recycled due to the fast separation of solids from hot water. Since the pressure cycle process is conducted in a batch reactor, it is more flexible and practical, especially for small deposits and/or Utah oil sands deposits. Additionally, the equipment requirements, such as those shown in Figure 1, are less than conventional HWEP requirements because the separation vessel and recovery vessel are combined together. Moreover, the relatively low elevated pressure does not need special, expensive equipment.
[0045] The pressure cycle process can be applied on different kinds and grades of oil sands, such as Canadian and Utah oil sands. In part, this is because the separation efficiency is more reliable than other hot water processes, and can allow for the oil sands to have different fines concentrations and different viscosities of the liberated bitumen. This process can lower the cost and has much lower contaminant concentrations in the discharged water and solids (e.g., tailings). Thus, most environmental problems associated with tailing are avoided.

[0046] Preliminary studies have shown that the pressure cycle process can greatly simplify the operating procedure of bitumen recovery from oil sands by combining the separation step and flotation step together and being performed without using any chemical additives. The compression/decompression process leads to displacement and disengagement of bitumen from sands without requiring intensive agitation, which is especially desirable for Utah oil sands and can be employed with any oil sands.

[0047] Additionally, the pressure cycle process can be a more environmentally friendly in the liberation and recovery of bitumen. In part, this is because the pressure cycle process can avoid the subsequent environmental problems caused by caustic additives and the presence of hydrocarbons in water that are difficult to separate. The pressure cycle process is efficient even when no caustic reagents or other chemical additives are added. The pressure cycle process does not emulsify bitumen in aqueous phase, and thereby the recovery efficiency is increased.

[0048] In addition, the pressure cycle process has a much higher separation rate compared to conventional HWEI because the liberation step and recovery step are combined into a single step. For example, if a gas, such as carbon dioxide, is injected in a separation vessel with a slurried oil sand, even at much lower temperature (e.g., < 55 °C), the pressure cycle process can still recover more than about 90% bitumen. High recovery efficiency can be achieved due to high solubility of carbon dioxide in water and in hydrocarbons at relative low temperatures, which solubility can be increased with increased pressure. Also, the pressure cycle can disrupt the physical structure of the sand and expose more bitumen for liberation. Since conventional gases, such as carbon dioxide, can be recycled, the energy cost of the pressure cycle process can be much lower than the cost of a conventional hot water process, such as WHEP.
[0049] Bitumen can be obtained from hydrocarbon sand by using pressure cycles to obtain the following: good liberation of bitumen from sand grains; good attachment of bitumen to an air bubble; and flotation of the aerated bitumen (e.g., bitumen on air bubble). In addition to or in conjunction with pressure cycle process described herein, bitumen liberation from sands can be enhanced by increasing: mechanical shear; water addition ratios; mechanical energy input levels; chemical addition levels; temperatures; residence times; the base (NaOH) addition amount; surface surfactant to affect the interfacial properties of the bitumen and the sand grains; and aeration of the hydrocarbon-sand slurry.

[0050] High content of clay fines in the bitumen extraction process is not favored because the surface of bitumen and air bubbles can be covered by the fines, and the probability of adequate bitumen-air bubble attachment is reduced. The presence of divalent ions further aggravates this situation, and reduces recovery of hydrocarbons. After the bitumen is liberated from the sand, a good flotation environment can increase bitumen recovery. A good chemical additive can improve bitumen recovery and at the same time to act as a good flocculent for the fines, such as an optimal concentration, hydrolyzed polyacrylamide (HPAM) can improve both bitumen recovery from oil sands and fines settling. Other means of increasing the settling and precipitation of fines can also be used to reduce fines content.

[0051] When the temperature of water is heated above its boiling point at atmospheric pressure (e.g., above 100 °C, 1 atm), the operation condition is defined as an overheated condition. Although the water does not boil at elevated pressure (e.g., 50 – 150 psi), the water is overheated and will spontaneously boil when the pressure is released. It is believed that the expanding and shearing forces caused by microbubbles and other effects due to decompression of overheated water can accelerate displacement of bitumen from the surface of oil sands. Also, the coagulation and rising of microbubbles can coagulate and bring bitumen droplets to the surface to generate bitumen froth.

[0052] The recovery of bitumen can be influenced by the overheated temperature and decompression rate. Higher temperatures can release more potential heat, but more energy is required to heat the vessel. Fast decompression can separate bitumen more quickly, but the recovered bitumen may contain more solid and moisture.
[0053] In one embodiment, the present invention can provide a method of removing hydrocarbons from fluid samples, particularly slurry samples of oil sands. The method can include pressure cycling a slurry of oil sand and a fluid that is capable of generating bubbles during decompression. As such, the method can include the steps of pressurizing the sample, injecting the sample with a gas, and depressurizing the sample. The sample can be pressurized by directly injecting the gas into the sample. Accordingly, a slurry sample can be compressed and then decompressed to liberate and recover hydrocarbons from oil sands. As such, separate pressurization and injection are not necessary, and can be conducted in one single step. For example, a fluid sample of hydrocarbon sand can be prepared prior to pressurizing with air only or other gas. After pressurizing, the sample can be depressurized such that the gas forms microbubbles in the sample. The microbubbles disrupt the hydrocarbon from the solids within the sample in a manner sufficient to increase hydrocarbon separation efficiency. The pressurizing and depressurizing steps can be repeated at least once. Optionally, the pressure can be increased by reduction of volume or increasing temperature when a gas is present with the slurry sample.

[0054] The duration of each of the pressurizing and depressurizing steps can be varied based on a number of factors including, but not limited to, the nature or quantity of the sample, the magnitude of hydrocarbon of the sample, the type of gas being used, the change in pressure during each of the pressurization or depressurization steps, and the like.

[0055] The pressurizing and depressurizing steps can have a time duration varying from seconds to minutes for the individual steps depending on the particular system of sand, hydrocarbons, and gases. The rate of compression can be between about 5 seconds and about 300 seconds or longer, more preferably between about 10 seconds and about 200 seconds, and most preferably between about 15 seconds and about 100 seconds. The rate of decompression can be between about 0.01 seconds and about 300 seconds, more preferably from about 0.1 seconds to about 200 seconds, and most preferably between about 1 second to about 100 seconds. An optimal cycle can include compression and decompression steps that are performed as fast as possible.

[0056] The number of repetitions of the pressurization, injection, and depressurization steps (e.g., pressure cycle) can also be varied from 1 to 30 cycles, 1
to 100 cycles, or more. In one embodiment the number of repetition of the pressurization and depressurization steps can be at least 3 cycles, such as from 3 to 15 cycles. As a guideline, optimal time duration and number of decontamination cycles can be readily determined for each sample based on monitoring and/or testing.

[0057] The pressure cycle process can be performed at a variety of temperatures ranging from room temperature to overheated water temperatures. Also, the pressure cycle process can operate with a reduced temperature compared to HWEP. The processing temperature can be between about 20 °C to about 120 °C, more preferably from about 30 °C to about 105 °C, and most preferably from about 55 °C to about 80 °C. Gases such as carbon dioxide with high water solubility can be functional at lower temperatures (e.g., 20 °C to about 50 °C, more preferably from about 30 °C to about 40 °C, and most preferably from about 35 °C to about 80 °C. Gases such as air, oxygen, or nitrogen as well as gases such as carbon dioxide and other highly soluble gases can be functional at higher temperatures (e.g., 50 °C to about 120 °C, more preferably from about 75 °C to about 115 °C, and most preferably from about 95 °C to about 110 °C. The optimal extraction temperature can be identified by a determination of other conditions such as compression/decompression pressure, stirring intensity, and gas composition and quality of oils sands. The temperature can also be lowered when more pressure cycles are employed. Higher pressure and temperature can use few pressure cycles, especially for water heated higher than its boiling point under ambient pressure. The pressurized cycles can greatly accelerate separation of bitumen from sands due to lower bitumen viscosity and higher density of micro bubbles generated during decompression procedure.

[0058] The depressurizing step in the pressure cycle process can result in any pressure reductions sufficient to create microbubbles. Typically, the pressure cycle range can be a change in pressure from about 10 psi to about 1000 psi, and more preferably from about 10 psi to about 500 psi, and most preferably between 10 psi and 200 psi, although pressure drops outside this range can also be suitable. In another embodiment, the pressure reduction during the depressurization step leaves the sample at ambient pressure.
In one embodiment, the pressure can range between about 10 psi to about 210 psi, more preferably 25 psi to about 175 psi, and most preferably about 40 psi to about 150 psi.

The solid concentration in the extraction medium can have a solid/water volume ratio of about 0.01 to about 3, more preferably about 0.1 to about 2, and most preferably about 0.1 to about 1. For example, the solid water volume ratio can be from 0.1:1 to 2:1, especially from 0.2:1 to 1:1.

The extraction pH can be controlled from about 2 to about 12, more preferably from about 3 to about 11, and most preferably from about 5 to about 10. The pH can be controlled by adding acids, such as HCl (hydrogen chloride) and acetic acid, or caustic reagents, such as NaOH (sodium hydroxide) and Na₂CO₃ (sodium carbonate), into the water oil sands mixture, or be allowed to change without control. Also, the pH of water can be affected by the gas compositions such as when CO₂ is pressurized into the water and oil sands mixture during compression decompression cycles.

In one embodiment, the process for the removal of hydrocarbons from a hydrocarbon-containing sample can be further aided by some form of agitation during at least one of the steps of pressurizing or depressurizing. Examples of agitation means include, but are not limited to stirring, shaking, ultrasound, and the like. It is noted multiple means of agitation can be combined during any given step of hydrocarbon extraction. Agitation can also be sufficiently achieved solely via degassing and movement of microbubbles during the depressurizing step with significant energy savings.

The stirring intensity of the water and oil sands mixture is another important parameter that can be regulated. The optimal stirring intensity is decided by the extraction vessel size, configuration of the agitator, solid loading, bitumen viscosity, extraction temperature and other parameters. Good mixing of oil sands and water can increase extraction rate and enhance bitumen quality. In this implementation, the stirring rate or equivalent agitation by bubble formation can be between about 0 rpm and about 1000 rpm, more preferably between about 10 rpm to about 600 rpm, and most preferably between about 30 rpm and about 120 rpm. Agitation provided by liquid motion brought by compression and decompression cycles, with or without additional means, is possible.
The pressure cycle process can be performed with various gases that are pressurized with the oil sands and hot water bath by compression. General examples of gases include air, O₂, N₂, CO₂, methane, ozone, noble gases, combinations thereof, and the like. The gas can be introduced into the fluid sample at different times, although in each scenario the gas must be in contact and preferably dissolved at least partially in the fluid sample before decompression is to proceed. It may be important in some instances for the gas and the fluid sample to contact and reach some degree of dissolution prior to decompression.

In one embodiment of the present invention, the gas can be added to the fluid sample before the pressurizing step. In another embodiment, the fluid sample can be injected with the gas during or after the pressurizing step. In another embodiment, the repetition of the pressurizing step and the depressurizing step can be performed without repetition of injecting additional gas. Additionally, when repeated, the pressurizing step can result in a different pressure increase when compared to the initial or first pressurizing step. Similarly, when repeated, the depressurizing step can result in a different pressure reduction as compared to the initial depressurization step. Thus, the cycling of pressure can have varying high and low pressures or can have substantially the same high and low pressures. In one aspect of the invention, the fluid sample having the hydrocarbon can be heated sufficiently so that the sample can be super saturated with the gas.

The nucleation and growth of microbubbles, which occurs at the energetically favorable (e.g., non-wetting) surface of particulate matter, can accelerate the extraction of the hydrocarbon. During depressurization, microbubbles appear at the particulate surfaces in the liquid phase. The various sizes of microbubbles can vary continually from their initial formation in a sub-nanometer (< 1 nm) range through a visible range (e.g., < 1 mm) in their final coalescing into large bubbles (e.g., < 1 cm) that rise rapidly to the water surface. The concentration of bubbles as well as the duration of their appearance depends on the degree of saturation with the gas, which in turn depends on the pressure employed, and the volumes of liquid and available headspace. A large amount of dissolved gas at high pressure will support more extensive bubble formation during depressurization, and the rate of growth of the bubbles along with the duration of the bubbles are controlled by the rate of depressurization. In addition, the rate, duration, and pressure employed during pressurization will determine the level of saturation. Thus,
the pressure, pressurization rate, and depressurization rate can be fine tuned to support the concentration and duration of microbubbles, thus the abundance of reactive interfacial zone, for optimal hydrocarbon extraction.

[0067] A variety of gases can be used in the methods of the present invention. Non-limiting examples of suitable gases can include ozone, chlorine, air, nitrogen, oxygen, carbon monoxide, carbon dioxide, argon, helium, water vapor, and the like. Mixtures of gases can also be used in the invention. The elevated pressure applied during the pressurizing step can enable the dissolved gas to effectively penetrate the pores of particulate matter in a slurry sand sample or can cause liquefaction. Particulates and agglomerations of debris often shield hydrocarbons in tar sands. When the gases have penetrated the particles and expand during the depressurizing step, they can cause the solid particle to explode, partially disintegrate, or at the very least cause the pores of the particulate matter to expand thus enhancing the exposure of hydrocarbons.

[0068] In one embodiment, the gas for use in the compression/decompression cycles is comprised of carbon dioxide (CO₂). The use of a CO₂ assisted pressure cycle extraction process can decrease energy costs associated with the use of hot water in the separation process. The CO₂ assisted pressure cycle extraction process can be used at a greater rage of temperatures. Also, CO₂ solubility decreases dramatically when approaching the water boiling point, and higher pressures and/or more cycles may be used for desirable extraction. If the water temperature is higher than its boiling point under normal pressure, the CO₂ assisted pressurized extraction process can function similarly to the overheated hot water extraction process that uses air. It has been found that carbon dioxide is exceptionally efficient for use in separating bitumen (e.g., hydrocarbons) from tar sands. Also, the use of carbon dioxide allows for lower temperatures and pressures with increased efficiency. For example, the temperature for use with carbon dioxide can be as low as 55 degrees and a low pressure of 50 psi. The separation and extraction of hydrocarbon from tar sands is very good. Instead of using 85 °C or above, the separation can now be performed at a very low temperature, and instead of using 150 psi or 100 psi the hydrocarbon can be separated using a pressure as low as 50 psi, and in some instances as low as 40 psi, and in other instances as low as 30 psi.

[0069] Additionally, with carbon dioxide as the gas, the temperature can be reduced to below 50 °C to about 40 °C, more preferably to about 30 °C, and most
preferably to about 35 °C or room temperature. The reduction in temperature changes the viscosity of the bitumen. Bitumen changes from being fluidic at very hot temperature to being more solid at cold, low temperatures. The low temperature changes the viscosity of bitumen and hydrocarbons in general. It is thought that the cold temperature processing can be efficient when used in multiple cycles.

[0070] In one embodiment, the gas can be substantially pure carbon dioxide. Also, the gas can be a mixture of carbon dioxide and another gas, such as air, nitrogen, oxygen, noble gas, ozone, carbon monoxide and the like. The percentage of carbon dioxide can range from about 10% to about 100% (volume percentage), from about 20% to about 90%, from about 30% to about 80%, from about 40% to about 70%, and from about 50% to about 60%.

[0071] The gas may also be a combination gas having CO₂ mixed with another gas. Since the overheated condition can generated more gas bubbles during decompression by vaporization of water itself, the recovery rate of bitumen with CO₂ can be faster. Also, the compression of a more water-soluble gas, such as CO₂, into a hot water and oil sands mixture can have higher separation and recovery rate. Theoretically, most gases that are more soluble in water than air can be used, such as NH₃, Cl₂, and CO₂. However, solubility of the gas should be someone limited so as to no be too high. Otherwise the gas has to be recycled from water after extraction and the process may need additional operation procedures. Also, the gas should be inert so as to avoid reacting intensively with bitumen or water. Since some gases, such as CO₂, may have some reactivity with water and carbons, the reactivity of the gas with the water and with the hydrocarbon should be as low as possible, and preferably nonreactive. In a practical application, CO₂ could be the most economic choice. In commercial oil sands extraction, water is heated by burning natural gas or other fuels, and the CO₂ that is produced during combustion of fuels can be a potential resource of CO₂. External CO₂ can be used because recycling of the released CO₂ is not complicated, and the consumption rate of CO₂ is negligible.

[0072] Based on air and CO₂, other gases with similar solubility as air or CO₂ or higher solubility than air or CO₂ in aqueous phase, or has higher solubility in bituminous phase than air or CO₂, potentially can be used for pressurized hot extraction of bitumen from oil sands. Examples of such other gases can be Ar (5.2 ml per 100 g water at 0 °C, 2.2 ml per 100 g water at 50 °C), BF₃ (106 ml per 100 g water at 0 °C), CH₄ (5.56 ml per 100 g water at 0 °C, 1.772 ml per 100 g water at 80
C₂H₂ (173 ml per 100 g water at 0°C), C₂H₆ (173 ml per 100 g water at 0°C, 1.72 ml per 100 g water at 100°C), H₂S (467 ml per 100 g water at 0°C, 81 ml per 100 g water at 100°C), O₂ (4.89 ml per 100 g water at 0°C, 1.72 ml per 100 g water at 100°C), N₂ (2.35 ml per 100 g water at 0°C, 0.95 ml per 100 g water at 100°C), C₃H₆ (propylene, 43.4 ml per 100 g water at 0°C, 23 ml per 100 g water at 20°C), C₃H₈ (propane, 3.9 ml per 100 g water at 0°C), 1-butene (8.5 ml per 100 g water at 20°C), 1,3-butadiene (45 ml per 100 g water at 21°C), vinyl chloride (131.5 ml per 100 g water at 20°C), 1,1,1,2-tetrafluoroethane (21 ml per 100 g water at 25°C), isobutane (3.25 ml per 100 g water at 20°C), n-butane (3.25 ml per 100 g water at 20°C), and isobutene (16.59 ml per 100 g water at 20°C). Mixtures of the above two gases or more than two gases, including air and carbon dioxide, also can be used for pressurized hot water process extraction. Also, internal combustion engine exhaust, turbine engine exhaust, and exhaust from furnace or boiler can be input into the separation vessel for pressure cycle bitumen extraction.

[0073] For gas mixtures such as air/CO₂ mixture and N₂/air/CO₂ mixture, the CO₂ concentration can be from 1% to 99% by volume, especially from 15% to 50% by volume. Other gases such as Ar, BF₃, CH₄, C₂H₂, C₂H₄, H₂S, C₂H₆, C₃H₆, C₃H₈, 1-butene, 1,3-butadiene, vinyl chloride, 1,1,1,2-tetrafluoroethane, isobutane, n-butane, and isobutene or any mixtures of the above gases can be used as the extraction gas.

[0074] Sand samples which can be treated by the method of the present invention generally have a solids content of from 2% to 95% by weight. In one embodiment, the slurry sample has a relatively high solids content of from 35% to 50% by weight. High solids content slurries can range from flowable slurries to thick pastes. In each case, treatment and handling can differ, although application of the present invention can be effective to remove hydrocarbons from such samples. In another embodiment, the slurry sample has a relatively low solids content of from 2% to 15% by weight. The solid components of the slurry samples can be from any environmental source, such as sand or dirt, so long as the solid components can take the form of a slurry or be suspended in a fluid.

[0075] In one embodiment, a pressure cycle process can extract hydrocarbons from a sample by at least 50%, more preferably from about 50% to about 100%, most preferably from about 75% to about 99%, and most preferably from about 85%
to about 95%. In an alternate embodiment, a process as disclosed herein extracts the hydrocarbon from the sample by at least 90%. In an alternate embodiment, a process as disclosed herein extracts the hydrocarbon from the sample by at least 95%. In an alternate embodiment, a process as disclosed herein extracts the hydrocarbon from the sample by at least 99%. In an alternate embodiment, a process as disclosed extracts the hydrocarbon from the sample by at least 99.9%.

[0076] An illustration of a pressure cycle bitumen extraction assembly of the invention is presented in Figure 1, which shows separation vessels 20, 30 for an extraction of hydrocarbon from oil sands. The use of two vessels 20, 30 allows for the simultaneous liberation and extraction of two oil sand samples in parallel. This can include one vessel 20 being in compression while the other vessel 30 is in decompression, and the gas from one being transferred to the next. Also, new gases or newly recycled gases can be used for both vessels. Of course the multiple vessels can be run on the same compression and decompression pattern. While two vessels are shown, the extraction assembly can be used with only one vessel 20. Alternatively, the extraction assembly can be used with three or more vessels. The material used to construct vessels 20, 30 is stainless steel, as it is able to withstand pressure. However, other suitable materials will be readily apparent to one of ordinary skill in the art and may be varied according to an application of a process of one embodiment of the invention, such as, but not limited to a various metals and alloys, thermoplastic polymer, rock, a geophysical formation, ceramics, composites, combinations thereof, and/or the like.

[0077] Various embodiments contemplate the use of one vessel with or without a return loop, and/or other multiple vessels, and/or return loops to increase a potential number of cycles. Likewise, further embodiments contemplate separate vessels for the same or different extraction of hydrocarbon from at least one sample in parallel or in series. In such an embodiment, two or more vessels can be used to extract hydrocarbon from the sample with one or more solvents (e.g., water) after the compression/decompression cycle.

[0078] Returning to the illustrated embodiment of Figure 1, a vessel 20 is connected to at least one valve 40, two valves in this embodiment 40, 45, 50, and 55, for vessel 20 and vessel 30.

[0079] Valves 40, 45, 40, and/or 55 may be any valve common in the art, such as a ball valve, piezo electric valve, hydraulic valve, and/or the like. In various
embodiments, valves 40, 45, 50, 55 can be used for inlet for the gas and/or fluidized sand sample. Various embodiments connect a supply of gas 60 to the extraction assembly. Further embodiments contemplate the use of multiple gases and/or multiple sources of various gases.

[0080] Further embodiments incorporate regulating valves 5, 15, which act as exhaust valves for relieving pressure from the vessel 20, 30. A mesh material 25, 35 or screen, such as an aluminum mesh can optionally be placed at the bottom end of vessel 20, 30 to support solids in the sample. Other embodiments use a shelf, net, or other supportive material can be used to support the sample.

[0081] A pressure gauge 1, 11 is mounted about an upper portion of each vessel 20, 30 to measure the pressure inside each vessel 20, 30. The range of pressure may vary and can be selected as is suitable for the particular process, taking into account such parameters as the material from which the reactor assembly is constructed, the number of cycles to be performed, the solvent used, the fluid used, the constituents of the sample, and/or the like.

[0082] In one embodiment, the method can be accomplished in a separation vessel having two (2) stainless steel pieces, which are attached to form the reactor. In various reactors, vents, inlets, outlets and the like may be arranged about the reactor as needed for the application. Further, various reactors can work as a batch or as a flow reactor with respect to the slurry, and as a flow reactor with respect to a gas mixture.

[0083] In an industrial application, the oil sands can be mixed with recycled heated or hot water, and then pumped into the extraction vessel. Also, additional oil sand can be added into the vessel. The additional oil sands can be advantageous in instances where the pump cannot transfer high solid concentration mixture into the separation vessel, such as > 1:1 volume ratio. Alternatively, additional water or gas can be introduced into the separation vessel.

[0084] The extraction assembly can include a device on the top of the separation vessel to collect bitumen once bitumen and oil sands have been separated. Thus, the industrial process for removal of bitumen can be included automated equipment and devices known in the petroleum industry to obtain the upper fractions of the separation depending on bitumen content.

[0085] Although steam can be used to heat the mixture, other methods, such as a heating jacket or heat coil, can also be used to increase or maintain the temperature
in the separation vessel. Methods of heating compositions are well known, and about any of such teaching methods can be used in the present invention. In previous methods, the compositions were heated to high levels. Now, with the use of carbon dioxide and similar gases the extraction of oil sands can be employed with heated water that is substantially below the boiling point.

[0086] Additionally, Utah bitumen separated form oil sands contains less sulfur in comparison with Canadian wet oil sands, and thereby this process can be useful for extraction of hydrocarbons that have less sulfur as well as those sands that have more sulfur.

[0087] The pressure cycle process of the present invention is advantageous for numerous reasons. For example, the formation of microbubbles can provide abundant interfacial regions near the gas-hydrocarbon-solid, which provide favorable partitioning zones for extracting hydrocarbons.

[0088] Another advantage is the repetition of the pressurizing and depressurizing of the sample to cause the sand particles to fracture and expose the bitumen. The repetition of these steps provides enhanced degradation of the solid particles, and thereby enhanced hydrocarbon extraction efficiency due to the increased exposure of the hydrocarbon. The elevated pressure caused by the pressurization step enables the gas to effectively penetrate the pores of particulate matter that often shields hydrocarbons in sand. The pressure cycle process provides higher product yield compared to the conventional HWEP.

[0089] The increase in pressure also causes oversaturation of the dissolved gas in water such that when the pressure is released, it results in degassing of the water and microbubble formation. The oversaturation of the slurry sample with gas and subsequent degassing can enhance the ability to remove the hydrocarbon from the sands. Also, the pressurizing/depressurizing process creates an abundance of gaseous microbubbles that can have enhanced interaction with the hydrocarbon within the sands and provides for the hydrocarbon to be liberated from the sands. Thus, cyclic gas solubility changes in the process aide in extracting the hydrocarbons from the sands.

[0090] Additionally, the pressure cycle provides easier product separation compared to convention HWEP. The decompression results in countless gaseous microbubbles that provide a huge surface area at the gas-liquid interface that attracts
and gathers hydrophobic bitumen, effectively separating and lifting the bitumen globs to the water surface for collection (i.e., the flotation effect).

[0091] The pressure cycle process can save energy compared to conventional HWEP. Due to enhanced bitumen liberation by the microbubbles, lower water temperature can be used for higher yield, which results in energy saving that more than compensates the minimal energy expended in compression with gases.

[0092] The pressure cycle process can obtain superior bitumen extraction in a shorter process time compared to HWEP. The rapid pressure cycles cut down contact time between tar sands and heated or hot water. Data has shown that greater than 90% yield of bitumen within 5 min is possible. When using CO₂ from a gas tank, each cycle can take several seconds. As such, extraction of bitumen by several cycles can take only several minutes. For a large vessel, the bitumen floatation procedure can be longer because the floatation path is longer than in a small vessel. Thus, the gas compressor capacity, vessel size, and solid loading can determine the total operation time. For example, the CO₂ pressure cycle process can yield 90% bitumen in 10 cycles in 5 minutes. In comparison to extraction without the pressure cycles, the same yield requires 3 hours of contact with hot water and under mild agitation (or under intense agitation).

[0093] The pressure cycle process is useful for a larger variety of different hydrocarbon sands compared to HWEP. HWEP was shown to be insufficient for Utah oil sands. However, the pressure cycle process can be used for extraction of Utah oil sands that are oil wet; unlike Canadian’s water wet oil sands, the oil wet property is an impediment to effective recovery by conventional hot water extraction method. Thus, this is a new tool for developing Utah’s unique, rich oil sands resources. However, the process can be used for liberating any oil from any material.

[0094] Complete extraction of bitumen is viable with the pressure cycle process at high solid concentration (e.g., up to solid/water ration of 1.5/1). This reduces the volume of process water, for which water availability is a critical issue in arid Utah where oil sands are found. A reduction in process water volume means less process water that requires treatment prior to disposal or reuse.

[0095] Additionally, a tailing pond is not necessary for the pressure cycle process. This can reduce the environmental problems that are caused by the discharge of solid and processing water because no additives are added. The COD of
water recycled from air pressurized hot water extraction process is 95±5 mg/L, while COD of water recycled from CO₂ pressurized hot water extraction process is only 47±3 mg/L (< 20 mg/L organic carbons). This is because CO₂ dissolved in water can prevent some acidic hydrocarbons from dissolving into water. Also, the processing water can be directly discharged because the hydrocarbon concentration is much lower than the discharge limitations. Thus, the pressure cycle process can solve the problems caused by hot water process currently commercialized in Canada, which requires huge amount of water and consumes lots of energy, and need large tailings pond.

**EXPERIMENTAL.**

1. **[0096]** The pressure cycle process can be conducted by dramatically increasing and then decreasing the pressure. Briefly, in a low-pressure bitumen separation vessel with mechanic agitation (e.g., 175 psi grade reactor), 1 volume of water (e.g., 20-60 % of vessel capacity) is added into the bitumen recovery vessel. After the water is heated to over 50 °C by injecting steam into the aqueous phase or by a heater, 0.1–1.5 volume oil sands are added into the vessel. After all oil sands are added into the vessel, the vessel is closed and pressurized to 50–50 psi. The gas can be air, nitrogen, CO₂, or other non-reactive gas or mixtures of them. Temperature of the water/oil sands mixture is controlled between 50 °C–105 °C. The elevated pressure in the vessel, 50 psi – 150 psi, can prevent boiling of water if the temperature is higher than water boiling point under normal pressure. The dissolved gas in aqueous phase can generate micro bubbles during decompression.

**[0097]** After the water temperature is adjusted to the set temperature, the pressure in the vessel is released through a valve installed on the bitumen extraction vessel. When the temperature is lower than water normal pressure boiling point, the pressure can be quickly released to normal pressure by totally opening the releasing valve. The oversaturated gas in aqueous phase can generate micro bubbles during decompression procedure. If before pressure releasing, the water and oil sands mixture is heated over water normal pressure boiling point, the pressure releasing rate is controlled by the openings of the releasing valve to prevent bitumen being taken out by the rush of water vapor. The bitumen floated is collected and dried to measure the weight.
[0098] Visual analysis of the products obtained from the separation shows the separation and floatation of bitumen in the vessel after decompression. In the visual analysis it was observed that 1) bitumen can be extracted from the oil sands, and 2) the process water and settled sands are significantly reduced of hydrocarbons and lack a black color while the extracted bitumen is thick like crude oil. The compression and decompression procedures can be repeated any number of times because more compression/decompression cycles can separate more bitumen from oil sands.

[0099] The recovery of bitumen from oil sands with a pressure cycle process indicates that the separation of bitumen from oil sands is significantly contributed by the decompression step. The decompression step releases the accumulated potential energy from the heat energy, and the intensive shearing force and high chemical reaction rate achieved during decomposition of overheated water accelerates separation and coagulation of bitumen. The microbubble floatation effect induced by decompression also accelerates the recovery of bitumen. The lower viscosity of bitumen under higher temperature may also be an important aspect for bitumen recovery.

2.

[00100] The number of compression/decompression cycle number can be affected by solid loading amount and extraction temperature. The volume ratio of water to oil sands can larger than 2, which can leave enough space for bitumen froth generation and floatation. In order to increase efficiency, higher oil sand loading was studied. If the water level in the vessel is not high enough for bitumen froth generation (e.g., solid/water ratio >1) after bitumen is separated from oil sands, additional hot water can be added into the reactor to further separate the bitumen froth layer and solids.

[00101] The experimental results shown in Figure 2 show that more cycles can extract more bitumen, but for energy consideration and processing capacity optimization, 4-6 cycles are the optimum number if water is overheated each cycle. The separation efficiency is also affected by solid loadings, pressure, and stirring strength.

[00102] The solid-to-water volume ratio affects bitumen recovery efficiency. To maximize energy efficiency, the solid loading should be as high as possible. When the solid-to-water ratio is lower than 0.5:1, the extraction efficiency is not
significantly affected by the volume ratio. This result indicates that the separation and floatation of bitumen in oil sands and water mixture requires liquid space. If the space is not enough for separation and bitumen floatation, bitumen could still mixed with sand grains after compression/decompression cycles. In Figure 2, oil sands are extracted under high temperature (from 102 °C to 105 °C) and the extraction efficiency decreases with higher solid loading. To keep constant volume ratio in the experiments, water is added into the extraction vessel to compensate the water evaporated during compression/decompression cycles.

3.

[00103] Processing time of each cycle can depend on the gas compressor capacity and heating capability of the device. Normally, 4 to 6 cycles take about 4 to about 8 minutes when gas is compressed into the separation vessel by a gas compressor. When nitrogen or CO₂ is injected in the extraction vessel from a gas cylinder, each compression/decompression cycle takes less than 40 seconds when the extraction temperature is lower than the normal pressure boiling point of water. In each cycle the water can be overheated because each time decompression procedure decreases water temperature. As such, it can take a little longer time to heat up water oils sands mixture over water's normal pressure boiling point for next compression cycle.

4.

[00104] The bitumen content in Utah oil sands sampled from Asphalt Ridge was measured by Soxhlet extraction method. Briefly, the oil sands are extracted with hexane and toluene for 48 hours (2x24 hour). Mass balance calculation shows that Asphalt Ridge oil sands contain about 12±1.7% bitumen. It has been reported that Utah oil sands contain less fines (e.g., 7-8 % by weight) than Canadian oil sands (> 15 % by weight), and the bitumen recovered has ultra high viscosity. Compared to 5 Pa.s of Canadian Athabasca oil sands bitumen at 50 °C, viscosity of Asphalt Ridge oil sands bitumen is about 80 Pa.s at 50 °C. The viscosity difference indicates that HWEP is not efficient for Utah oil sands. It was found that Asphalt Ridge bitumen on average contains about 48.47% C, 11.0% H, 1.06% N, 0.44 S, and 3.03% O. The inorganic solids in Utah oil sands are quartz, plagioclase, microcline, chlorite, calcite, dolomite, and mica.

5.
[00105] The recovery of bitumen from oil sands with overheated water was studied. When water is overheated and under higher pressure, such as >100 psi, the temperature has higher extraction efficiency (Figure 3, 4, and 5). Also more intensive stirring can separate a little more bitumen. Figure 3, 4 and 5 also show that pressurized hot water extraction also works when water temperature is lower than the normal pressure boiling point; however, the separation and recovery rate is lower. The bitumen recovered by overheated water separation process contains moisture and 5±2% by weight of solid (dry weight). The solid in bitumen can be separated by filtration of toluene-diluted bitumen.

6.

[00106] The pressure cycle process using air as the gas was tested under the normal pressure boiling point of water (e.g., 100 °C). In this process, all the procedures and conditions are the same as those of the overheated water process described above. The only difference is that the mixture was not heated higher than the normal pressure boiling point of water after the vessel was pressurized. Figures 3, 4, and 5 show that the recovery efficiency of bitumen is sensitive to temperature, and there is a turning point at which efficiency is decreased. When the temperature is lower than 80 °C, the separation rate of bitumen from oil sands is slower. The temperature of water in Figures 3, 4, and 5 is the average temperature.

[00107] The extraction efficiency curves in Figure 3 and Figure 4 show that when the temperature is lower than 75 °C, bitumen extraction efficiency is very low. This could be caused by high viscosity of bitumen under 75 °C. All the curves < 100 degree in Figure 3, 4, and 5 show that after the initial five cycles the bitumen separation amount is proportional to the compression/decompression cycle numbers. This indicates that bitumen could have two different dispersing situations in oil sands: loosely attached and tightly attached. The separation amount of tightly attached bitumen could be proportional to the amount of air dissolved in water. When the pressure is higher than 100 psi and temperature is higher than 75 °C, more than 80% bitumen can be extracted after 20 to 25 cycles.

[00108] If the temperature is lower than the normal pressure boiling point of water, the recovery efficiency is greatly affected by the pressure. This could be due to the low solubility of air in water at high temperature. Also, since water is a liquid at less than about 100 °C at 1 atm, the working media in the process is dissolved air in an aqueous phase instead of being a vapor generated by overheated water. The
separation capacity of each decompression step can be determined by the amount of
dissolve air in the water. Higher pressures dissolve more air into the aqueous phase.
Additionally, Figure 3, 4, and 5 show that after an initial set of cycles (e.g., 3-4
cycles), the recovery of bitumen to cycle number is almost linear. This may indicate
that after some loosely attached bitumen is separated, the remaining bitumen is
mostly liberated from the oil sands surface by microbubbles. Different from HWEP,
the recovery efficiency of bitumen under overheated condition using pressure cycles
is not greatly affected by the pressure. Accordingly, the pressure cycle process using
overheated water may have an increased agitation effect due to releasing of potential
heat. As shown, less than 5 cycles can recover 90% bitumen.

[00109] When the oil sands extraction vessel is pressurized at elevated pressure,
the water and oil sands mixture could be heated over 100 degree (°C). The above-
boiling temperature is from 102 °C to 105 °C. The volume ratio of oil sands to water
is controlled at 0.5: 1. The bulk density of oil sands is about 2.1 g/cm³. Minimal
water use is desirable. However, when the volume ratio is lower than 0.5:1, high oil
sands loading can result in lower bitumen recovery efficiency since the mixture
doesn't have enough space for bitumen floatation.

7.

[00110] The use of CO₂ in the pressure cycle process was studied. The operation
conditions of CO₂ assisted extraction of bitumen from oil sands was the same as the
process described above. The only difference is that CO₂ was injected into the hot
water instead of air or other gas. Figure 6 shows that CO₂ assisted pressurized
extraction of bitumen works at temperature that is much lower than the lowest
temperature of air pressurized hot water extraction process. The ability to perform
the extraction at a lower temperature with CO₂ may be due to the relative high
solubility of CO₂ in bitumen compared air. After CO₂ is injected into oil sand slurry,
the decompression can generate gas bubbles in the aqueous phase and also generate
gas bubbles in bitumen. This can accelerate separation and floatation of bitumen. It
has been shown that the bitumen recovered from oil sands at 85 °C contains about
12±3 % by weight of sand, but the bitumen recovered from oil sands at 55 °C
contains about 30±3 % by weight of sand. This difference shows that although
decompression can liberate and float bitumen, the higher viscosity of bitumen at the
low temperature, such as 55 °C, can cause the separation of bitumen and sand grains
to be less complete.
[00111] Since the separation rate and floatation rate of bitumen from oil sands is determined by the amount of gas dissolved in air, pressurizing higher soluble gas into the extraction mixture could have higher extraction rate. When carbon dioxide (CO₂) is pressurized into the separation vessel instead of air, higher extraction rate is observed. Results show that CO₂ extraction is more effective and faster compared to extraction by air. At higher temperature (85 °C) more than 90% by weight of bitumen can be extracted after 20 cycles. Even at low temperature where extraction by air is not effective, more than 80% bitumen is extracted. This can be due to increased compatibility of CO₂ with bitumen (or higher solubility of CO₂ in bitumen). During decompression, expansion of CO₂ bubbles in bitumen makes separation (prying bitumen from sands) and floatation of bitumen much faster.

8.

[00112] A general hot water separation process was conducted to evaluate compression/decompression effects. In a beaker filled with boiling water, oil sands were added into the aqueous phase and stirred under heat. The bitumen brought to the surface was collected while stirring. It was found that it takes at least 3 hours to recover the bitumen from the oil sands. This indicates that the compression/decompression cycles of the pressure cycle process is more effective than without pressure cycles, and the separation of bitumen from oil sands takes longer without pressure cycles.

9.

[00113] The pH influence on separation efficiency is also evaluated. When pH is not controlled during bitumen extraction, pH of the tailings water can be about 8 after processing. In order to study influence of pH on recovery efficiency, caustic reagent solution (4 M NaOH) was added in the extraction system. Separation efficiencies of three levels of pH (pH= 9-10, 10-11, and 11-15) were tested. For 1:1 solid loading (volume ratio) and 5 cycles under overheated condition, the amounts of separated bitumen are compared under different pH conditions.

[00114] Figure 7 shows that adding NaOH is not beneficial for the pressure cycle process. When pH is higher than 11, the bitumen is emulsified in the aqueous phase. Although air floatation can increase the recovery of bitumen, the bitumen emulsified in water is still more than 20 wt%. Accordingly, more chemicals and additional procedures would be needed to recover bitumen. Therefore, caustic reagents are not needed for the pressure cycle process of the present invention. It was observed that
when no caustic reagent is used in the process, the solid and fines can precipitate in several minutes, and the separation of solid from hot water and bitumen froth is very simple. This allows for the quick recycling of hot water, which can dramatically decrease the amount of water and save more energy.

[00115] The bitumen extraction efficiency is greatly affected by pH. In experiments in which NaOH solution was added into hot water, the extraction efficiency decreased at pH higher than 9.5 (Figure 7). At pH 11.5, less than 40% bitumen could be collected in the extraction vessel. Theoretically, adding caustic reagents such as NaOH and Na₂CO₃ can enhance bitumen separation from sand grains, but emulsification of bitumen in water could decrease extraction efficiency (not shown). Also precipitation rate of sand grains and fines at higher pH is very slow (now shown). Since the compression/decompression process explores gas bubble separation effects to separate bitumen from oil sand grains and the separation efficiency is relatively high, caustic reagents are not necessary for extraction. It is possible to increase bitumen extraction efficiency and enhance bitumen quality using caustic reagents when the extraction temperature is low than 80 °C. However, addition of caustic reagents may impose quality concerns on water and sand, and may need to be treated.

[00116] When no caustic agent is used, the hot water can be directly recycled for next batch of extraction because precipitation of the sand and fine in hot water is fast following extraction. Also the organic concentration in the water is very low since no chemical additives (e.g., surfactant and caustics) are added to the process.

10.

[00117] Canadian high-grade oil sands containing 12.4±3.3% by weight bitumen and Canadian low-grade oil sands containing 6.4±1.2% bitumen are processed by the hot water extraction method assisted by pressure cycles. When CO₂ is injected into the Canadian high-grade oil sands and hot water mixture, even at low temperature more than 80% by weight bitumen is extracted (Figure 8A). However, bitumen extracted at relative low temperature (65 °C and 55 °C) contains more sand grains. This means the floatation rate is too fast compared to the separation rate and the bitumen containing sand grains is floated before separation of bitumen from oil sand grains occurs sufficiently. Extraction of bitumen using air or air/CO₂ mixture has relative low extraction rate (Figure 8B) but the extracted bitumen contains less sands. Pressurizing air/CO₂ mixture into the extraction vessel can adjust separation
rate and flotation rate. Thus, it is possible to inject fuel combustion exhaust into the extraction vessel because the exhaust can contain about 20% CO₂. When Canadian high-grade oil sands is extracted at temperature higher than water’s normal pressure boiling temperature, no large differences are observed using air and CO₂ as the compression gas because the bubbles generated are water vapor (boiling water) and more than 90% bitumen can be extracted.

[00118] As shown in Figure 9, the extraction efficiency of Canadian low-grade oil sands is normally higher than 80% for 20 cycles while CO₂ extraction rate is higher than that using air. Different from how the bitumen is dispersed in the Canadian high-grade oil sands, the bitumen in Canadian low-grade oil sands is prone to accumulate in the bitumen rich sand grains. Therefore, tailored contact conditions may be needed to avoid floating the bitumen rich oil sand grains without sufficient separation of bitumen from the oil sands.

11.

[00119] The bitumen quality is another important consideration. The sand concentration in the extracted bitumen increases when extraction temperature decreases (Figure 10). Compression/decompression cycling has combined bitumen separation and bitumen extraction procedures in one step. Separation and floatation are competing processes that determine the bitumen quality. Results show that if pure CO₂ is used as the extraction gas, the extracted bitumen contains a higher sand content. The sand concentration in extracted bitumen is also affected by how the bitumen is dispersed in oil sands. For Canadian high-grade bitumen, CO₂ extraction can obtain bitumen with > 70% sand. This means that bitumen and sand mixture might be well mixed together and be floated before separation occurs. If air and CO₂ mixture (2:1) is pressurized into to extraction vessel instead of using air or CO₂ alone, extracted bitumen can contain < 30% sand and the extraction rate is still high. Results show that the extraction rate and the bitumen quality are also affected by the stirring intensity. Higher agitation intensity shows relatively higher extraction rate and higher bitumen quality. So for different oil sand, the extraction parameters, including temperature, pressure, number pressure cycles, gas composition, solid/water ratio, and stirring intensity can be optimized to minimize the cost and increase the yield.

[00120] The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are
to be considered in all respects only as illustrative and not restrictive. The scope of
the invention is, therefore, indicated by the appended claims rather than by the
foregoing description. All changes which come within the meaning and range of
equivalency of the claims are to be embraced within their scope. All references
recited herein are incorporated herein in their entirety by specific reference.

[00121] The present disclosure is not to be limited in terms of the particular
embodiments described in this application, which are intended as illustrations of
various aspects. Many modifications and variations can be made without departing
from its spirit and scope, as will be apparent to those skilled in the art. Functionally
equivalent methods and apparatuses within the scope of the disclosure, in addition to
those enumerated herein, will be apparent to those skilled in the art from the
foregoing descriptions. Such modifications and variations are intended to fall within
the scope of the appended claims. The present disclosure is to be limited only by the
terms of the appended claims, along with the full scope of equivalents to which such
claims are entitled. It is to be understood that this disclosure is not limited to
particular methods, reagents, compounds compositions or biological systems, which
can, of course, vary. It is also to be understood that the terminology used herein is
for the purpose of describing particular embodiments only, and is not intended to be
limiting.

[00122] With respect to the use of substantially any plural and/or singular terms
herein, those having skill in the art can translate from the plural to the singular
and/or from the singular to the plural as is appropriate to the context and/or
application. The various singular/plural permutations may be expressly set forth
herein for sake of clarity.

[00123] It will be understood by those within the art that, in general, terms used
herein, and especially in the appended claims (e.g., bodies of the appended claims)
are generally intended as "open" terms (e.g., the term "including" should be
interpreted as "including but not limited to," the term "having" should be interpreted
as "having at least," the term "includes" should be interpreted as "includes but is not
limited to," etc.). It will be further understood by those within the art that if a
specific number of an introduced claim recitation is intended, such an intent will be
explicitly recited in the claim, and in the absence of such recitation no such intent is
present. For example, as an aid to understanding, the following appended claims
may contain usage of the introductory phrases "at least one" and "one or more" to
introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (e.g., “a” and/or “an” should be interpreted to mean “at least one” or “one or more”); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (e.g., the bare recitation of "two recitations," without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to “at least one of A, B, and C, etc.” is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (e.g., “a system having at least one of A, B, and C” would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to “at least one of A, B, or C, etc.” is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (e.g., “a system having at least one of A, B, or C” would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase “A or B” will be understood to include the possibilities of “A” or “B” or “A and B.”

[00124] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[00125] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also
encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” “greater than,” “less than,” and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 cells refers to groups having 1, 2, or 3 cells. Similarly, a group having 1-5 cells refers to groups having 1, 2, 3, 4, or 5 cells, and so forth.”

[00126] While various aspects and embodiments have been disclosed herein, other aspects and embodiments will be apparent to those skilled in the art. The various aspects and embodiments disclosed herein are for purposes of illustration and are not intended to be limiting, with the true scope and spirit being indicated by the following claims.
1. A method for extracting hydrocarbons from sands, the method comprising:
   providing sands containing a hydrocarbon;
   mixing the hydrocarbon sands with water;
   heating the water before, during, or after being mixed with the hydrocarbon sands;
   increasing the pressure within a closed vessel containing the heated hydrocarbon and water mixture in the presence of gas or by injecting with gas;
   releasing the pressure of the heated hydrocarbon and water mixture in the vessel so as to create microbubbles from the dissolved gas in the water mixture; and
   collecting the hydrocarbon from the water.

2. A method as in claim 1, wherein the hydrocarbon is a bitumen.

3. A method as in claim 1, wherein the hydrocarbon is a tar.

4. A method as in claim 1, wherein the hydrocarbon includes molecules that can be processed into fuel.

5. A method as in claim 1, wherein the gas is selected from the group consisting of air, N₂, O₂, CO₂, Ar, BF₃, CH₄, C₂H₂, C₂H₄, H₂S, C₂H₆, C₃H₆, C₃H₈, 1-butene, 1,3-butadiene, vinyl chloride, 1,1,1,2-tetrafluoroethane, isobutane, n-butane, isobutene, or any mixtures thereof.

6. A method as in claim 1, wherein the gas includes carbon dioxide.

7. A method as in claim 1, wherein the sands and water are conditioned in batch tumblers or conditioning drums or are mixed during transport through a pipeline.

8. A method as in claim 1, wherein the process is performed with at least one of the following:
increasing the pressure to a range of about 10 to about 210 psi followed by
reducing the pressure by at least 10 psi;
maintaining the temperature between about 20 degrees C to about 120
degrees C;
cycling the pressure for about 2 to about 30 pressure cycles;
solid water volume ratio is from 0.1:1 to 2:1;
increasing the pressure at a rate of compression that is about 5 to about 300
seconds to reach maximum pressure; or
decreasing the pressure at a rate of decompression that is about 0.01 to about
300 seconds to vent to reach ambient pressure or any other lowered pressure.

9. A method as in claim 1, further comprising introducing the
hydrocarbon and water into primary separation vessel (PSV).

10. A method as in claim 9, further comprising settling the mixture into
stratified layers in the PSV: impure bitumen froth on the top; a combination of
bitumen, sand, clay and water in the middle (middlings); and sand precipitated to the
bottom.

11. A method as in claim 10, further comprising pumping the precipitated sand into a settling basin with water to form tailings.

12. A method as in claim 11, further comprising separating the hydrocarbon from the tailings.

13. A method as in claim 10, further comprising further separating and cleaning the middlings by gas injection and steam de-aeration.

14. A method as in claim 13, further comprising recovering the hydrocarbon from the middlings.

15. A method as in claim 10, further comprising recovering the hydrocarbon from the froth.
16. A method as in claim 1, wherein the process is substantially devoid of adding caustic agents to the hydrocarbon and water mixture.

17. A method for extracting hydrocarbons from particle, the method comprising:
   providing a particle containing a hydrocarbon;
   mixing the hydrocarbon-containing particle sands with water;
   heating the water before, during, or after being mixed with the hydrocarbon-containing particle;
   increasing the pressure of the heated mixture within a closed vessel;
   releasing the pressure in the vessel so as to create microbubbles in the mixture that liberate the hydrocarbon from the particle; and
   collecting the hydrocarbon from the water and particle.

18. A method as in claim 17, wherein the pressure is increased by decreasing the volume of the vessel.

19. A method as in claim 17, wherein the pressure is increased by increasing the number of molecules in the vessel.

20. A method as in claim 17, wherein the pressure is increased by increasing the temperature in the vessel.

21. A method as in claim 17, wherein the pressure is increased by injecting a gas into the vessel.

22. A method as in claim 21, wherein the gas is selected from the group consisting of air, N₂, O₂, CO₂, Ar, BF₃, CH₄, C₂H₂, C₂H₄, H₂S, C₂H₆, C₃H₆, C₃H₈, 1-butene, 1,3-butadiene, vinyl chloride, 1,1,1,2-tetrafluoroethane, isobutane, n-butane, isobutene, or any mixtures thereof.

23. A method as in claim 21, wherein the gas includes CO₂.
24. A method as in claim 17, wherein the process is performed with at least one of the following:
   increasing the pressure to a range of about 10 to about 210 psi followed by reducing the pressure by at least 10 psi;
   maintaining the temperature between about 20 degrees C to about 120 degrees C;
   cycling the pressure for about 2 to about 30 pressure cycles;
   a solid/water volume ratio that is from 0.1:1 to 2:1;
   increasing the pressure at a rate of compression that is about 5 to about 300 seconds to reach maximum pressure; or
   decreasing the pressure at a rate of decompression that is about 0.01 to about 300 seconds to vent to reach ambient pressure or any other lowered pressure.

25. A method as in claim 10, further comprising introducing additional hot water to separate the bitumen froth layer and solids.

26. A method for extracting hydrocarbons from oil sands, the method comprising:
   introducing water into a low-pressure vessel at about 20 to about 40% of vessel capacity;
   heating the water to over 50 degrees C and less than 120 degrees C;
   introducing oil sands into the vessel at a solid/water volume ratio of about 0.1 to about 3 volume to form a water/oil sands mixture;
   closing and pressuring the vessel with a gas to a pressure of about 25 to about 210 psi;
   maintaining the temperature of the water/oil sands mixture between about 20 degrees C to about 120 degrees C;
   decompressing the pressure in the vessel so as to generate gaseous microbubbles that release the hydrocarbon from the oil sands; and
   recovering the hydrocarbon from the water and sands.

27. A method as in claim 26, wherein the process is performed with at least one of the following:
increasing the pressure to a range of about 10 to about 150 psi followed by reducing the pressure by at least 10 psi;
maintaining the temperature between about 50 degrees C to about 110 degrees C;
cycling the pressure for about 2 to about 30 pressure cycles;
a solid/water volume ratio that is from 0.1:1 to 2:1;
increasing the pressure at a rate of compression that is about 5 to about 300 seconds to reach maximum pressure; or
decreasing the pressure at a rate of decompression that is about 0.01 to about 300 seconds to vent to reach ambient pressure or any other lowered pressure.

28. A method as in claim 27, wherein the temperature is obtained by injecting steam or a heating jacket.

29. A method as in claim 28, wherein the heated water and oil sands are mixed in a fluidic passageway and pumped into the vessel.

30. A method for extracting hydrocarbons from sands, the method comprising:
     providing sands containing a hydrocarbon;
     mixing the sand containing the hydrocarbon with water;
     cycling the pressure of the mixture in a vessel by increasing the pressure and then decreasing the pressure so as to change gas solubility in the water and form gaseous microbubbles in the mixture; and
     collecting the hydrocarbon from the water and sands.

31. A method as in claim 30, further comprising introducing a gas into the vessel, wherein the gas is selected from the group consisting of include ammonia, ozone, chlorine, air, nitrogen, oxygen, carbon monoxide, carbon dioxide, argon, helium, water vapor, BF₃, CH₄, C₂H₂, C₂H₄, H₂S, C₂H₆, C₃H₆, propane, 1-butene, 1,3-butadiene, vinyl chloride, 1,1,1,2-tetrafluoroethane, isobutane, n-butane, and sobutene and combinations thereof.
32. A method as in claim 30, wherein the process is performed with at least one of the following:

- increasing the pressure to a range of about 10 to about 150 psi followed by reducing the pressure by at least 10 psi;
- maintaining the temperature between about 50 degrees C to about 110 degrees C;
- cycling the pressure for about 2 to about 30 pressure cycles;
- a solid/water volume ratio that is from 0.1:1 to 2:1;
- increasing the pressure at a rate of compression that is about 5 to about 300 seconds to reach maximum pressure; or
- decreasing the pressure at a rate of decompression that is about 0.01 to about 300 seconds to vent to reach ambient pressure or any other lowered pressure.
FIG. 2

FIG. 3
FIG. 4

FIG. 5
FIG. 9

Recovered Bitumen (wt%) vs Cycle Number

- 65 degree C, 100 psi, CO2
- 85 degree C, 100 psi, CO2
- 65 degree C, 100 psi, Air
- 85 degree C, 100 psi, Air

FIG. 10

Sand Concentration (wt%) vs Temperature (°C)

- Utah Asphalt Ridge oil sands, Air
- Utah Asphalt Ridge oil sands, CO2
- High-grade Canadian oil sands, Air
- High-grade Canadian oil sands, CO2
- Low-grade Canadian oil sands, Air
- Low-grade Canadian oil sands, CO2