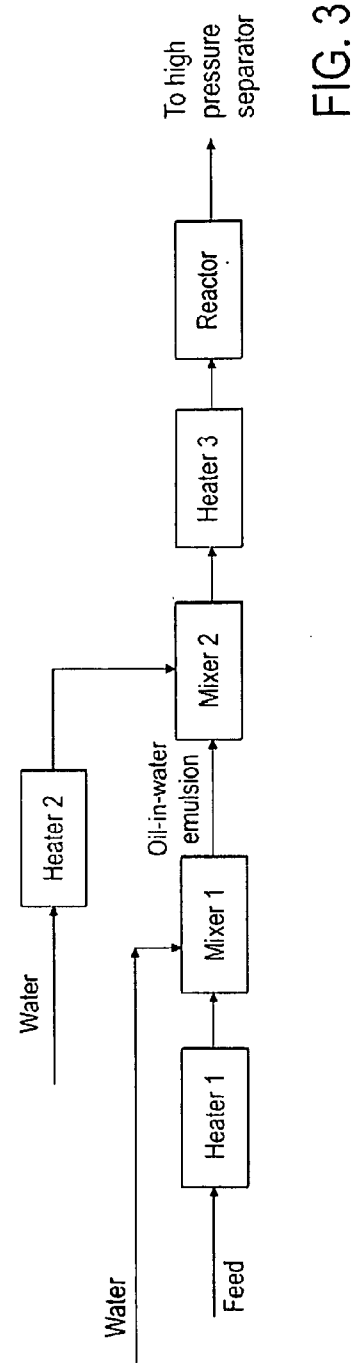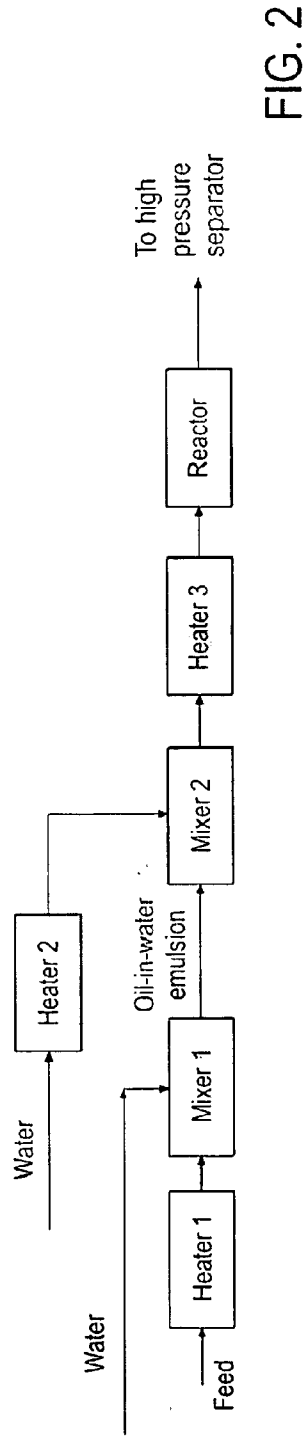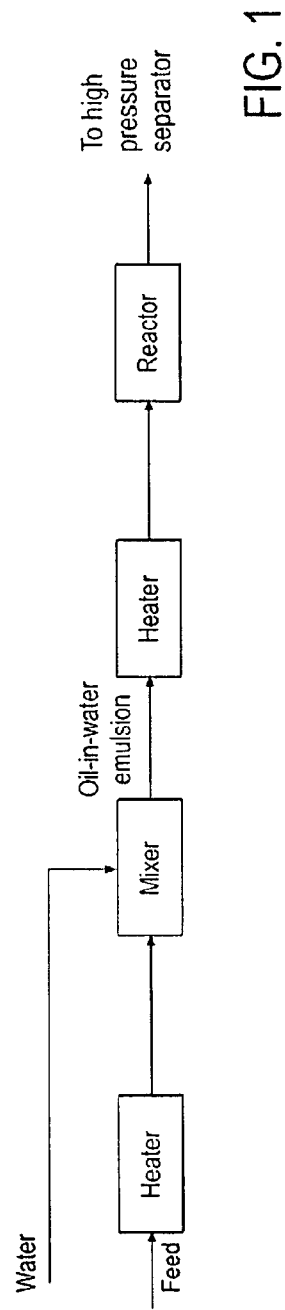(19) **United States**

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(54) **UPGRADING HEAVY HYDROCARBON OILS**

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(57) **ABSTRACT**

A process using supercritical water-oil emulsion to upgrade a heavy hydrocarbon feedstock into an upgraded hydrocarbon product or syncrude with highly desirable properties (low sulfur content, low metals content, lower density (higher API), lower viscosity, lower residuum content, etc.) is disclosed. The process does not require external supply of hydrogen nor does it use externally supplied catalysts.

FIG. 1

Feed → Heater → Mixer → Heater → Reactor → To high pressure separator

Water → Mixer

Oil-in-water emulsion

FIG. 2

Feed → Heater 1 → Mixer 1 → Mixer 2 → Heater 3 → Reactor → To high pressure separator

Water → Heater 1

Water → Heater 2 → Mixer 2

Oil-in-water emulsion

FIG. 3

Feed → Heater 1 → Mixer 1 → Mixer 2 → Heater 3 → Reactor → To high pressure separator

Water → Mixer 1

Water → Heater 2 → Mixer 2

Oil-in-water emulsion
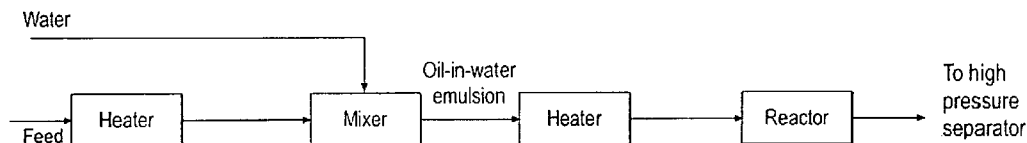
UPGRADING HEAVY HYDROCARBON OILS

FIELD OF THE INVENTION

[0001] The present invention relates to upgrading of heavy hydrocarbons such as whole heavy oil, bitumen, and the like using supercritical water.

BACKGROUND OF THE INVENTION

[0002] Oil produced from a significant number of oil reserves around the world is simply too heavy to flow under ambient conditions. This makes it challenging to bring remote, heavy oil resources closer to the markets. One typical example is the Hamaca field in Venezuela. In order to render such heavy oils flowable, one of the most common methods known in the art is to reduce the viscosity and density by mixing the heavy oil with a sufficient diluent. The diluent may be naphtha, or any other stream with a significantly higher API gravity (i.e., much lower density) than the heavy oil.

[0003] For a case such as Hamaca, diluted crude oil is sent from the production wellhead via pipeline to an upgrading facility. Two key operations occur at the upgrading facility: (1) the diluent stream is recovered and recycled back to the production wellhead in a separate pipeline, and (2) the heavy oil is upgraded with suitable technology known in the art (coking, hydrocracking, hydrotreating, etc.) to produce higher-value products for market. Some typical characteristics of these higher-value products include: lower sulfur content, lower metals content, lower total acid number (TAN), lower residuum content, higher API gravity, and lower viscosity. Most of these desirable characteristics are achieved by reacting the heavy oil with hydrogen gas at high temperatures and pressures in the presence of a catalyst. In the case of Hamaca, the upgraded crude is sent further to the end-users via tankers.

[0004] These diluent addition/removal processes and hydrogen-addition or other upgrading processes have a number of disadvantages:

[0005] 1. The infrastructure required for the handling, recovery, and recycle of diluent could be expensive, especially over long distances. Diluent availability is another potential issue.

[0006] 2. Hydrogen-addition processes such as hydrotreating or hydrocracking require significant investments in capital and infrastructure.

[0007] 3. Hydrogen-addition processes also have high operating costs, since hydrogen production costs are highly sensitive to natural gas prices. Some remote heavy oil reserves may not even have access to sufficient quantities of low-cost natural gas to support a hydrogen plant. These hydrogen-addition processes also generally require expensive catalysts and resource intensive, catalyst handling techniques, including catalyst regeneration.

[0008] 4. In some cases, the refineries and/or upgrading facilities that are located closest to the production site may have neither the capacity nor the facilities to accept the heavy oil.

[0009] 5. Coking is often used at refineries or upgrading facilities. Significant amounts of by-product solid coke are rejected during the coking process, leading to lower liquid hydrocarbon yield. In addition, the liquid products from, a coking plant often need further hydrotreating. Further, the volume of the product from the coking process is significantly less than the volume of the feed crude oil.

[0010] A process according to the present invention overcomes these disadvantages by using supercritical water to upgrade a heavy hydrocarbon feedstock into an upgraded hydrocarbon product or syncrude with highly desirable properties (low sulfur content, low metals content, lower density (higher API), lower viscosity, lower residuum content, etc.). The process neither requires external supply of hydrogen nor must it use catalysts. Further, the process in the present invention does not produce an appreciable coke by-product.

[0011] In comparison with the traditional processes for syncrude production, advantages that may be obtained by the practice of the present invention include a high liquid hydrocarbon yield; no need for externally-supplied hydrogen; no need to provide catalyst; significant increases in API gravity in the upgraded hydrocarbon product; significant viscosity reduction in the upgraded hydrocarbon product; and significant reduction in sulfur, metals, nitrogen, TAN, and MCR (micro-carbon residue) in the upgraded hydrocarbon product.

[0012] Various methods of treating heavy hydrocarbons using supercritical water are disclosed in the patent literature. Examples include U.S. Pat. Nos. 3,948,754, 3,948,755, 3,960,706, 3,983,027, 3,988,238, 3,989,618, 4,005,005, 4,151,068, 4,557,820, 4,559,127, 4,594,141, 4,840,725, 5,611,915, 5,914,031 and 6,887,369 and EP671454.

[0013] U.S. Pat. No. 4,840,725 discloses a process for conversion of high boiling liquid organic materials to lower boiling materials using supercritical water in a tubular continuous reactor. The water and hydrocarbon are separately preheated and mixed in a high-pressure feed pump just before being fed to the reactor.

[0014] U.S. Pat. No. 6,887,369 discloses a supercritical water pretreatment process using hydrogen or carbon monoxide preferably carried out in a deep well reactor to hydrotreat and hydrocrack carbonaceous material. The deep well reactor is adapted from underground oil wells, and consists of multiple, concentric tubes. The deep well reactor described in the patent is operated by introducing feed streams in the core tubes and returning reactor effluent in the outer annular section.

SUMMARY OF THE INVENTION

[0015] The present invention relates to a process for upgrading hydrocarbons comprising mixing hydrocarbons with a fluid comprising water in a mixing zone to form an emulsion; heating the emulsion to a temperature above the critical temperature of water; reacting the emulsion in a reaction zone under supercritical water conditions in the absence of externally added hydrogen for a residence time sufficient to allow upgrading reactions to occur; withdrawing a single-phase reaction product from the reaction zone; and separating the reaction product into gas, effluent water, and upgraded hydrocarbon phases.

BRIEF DESCRIPTION OF THE DRAWING

[0016] FIG. 1 is a process flow diagram of an embodiment of the present invention.

[0017] FIG. 2 is a process flow diagram of an embodiment of the present invention.

[0018] FIG. 3 is a process flow diagram of an embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] The present process is related to processes described in commonly assigned U.S. patent application Ser. Nos.

11/555,048; 11/555,130; 11/555,196; and 11/555,211, all of which were filed on Oct. 31, 2006 and which are incorporated by reference herein. These patent applications relate to various aspects of heavy oil upgrading technology using supercritical water. The present disclosure also relates to processes using supercritical water to upgrade hydrocarbons and in a way to make fuller use of the potential of supercritical water and minimize by products produced by side reactions by focusing on the solvent oil mixing and contacting. This is accomplished by using the herein disclosed technology to enhance solvent-oil mixing/contacting through formation of emulsion so that the performance of upgrading process can be significantly improved.

Reactants

[0020] Water and hydrocarbons, preferably heavy hydrocarbons are the two reactants employed in a process according to the present invention.

[0021] Any heavy hydrocarbon can be suitably upgraded by a process according to the present invention. Preferred are heavy hydrocarbons having an API gravity of less than 20°. Among the preferred heavy hydrocarbons are heavy crude oil, heavy hydrocarbons extracted from tar sands, commonly called tar sand bitumen, such as Athabasca tar sand bitumen obtained from Canada, heavy petroleum crude oils such as Venezuelan Orinoco heavy oil belt crudes, Boscan heavy oil, heavy hydrocarbon fractions obtained from crude petroleum oils, particularly heavy vacuum gas oils, vacuum residuum as well as petroleum tar, tar sands and coal tar. Other examples of heavy hydrocarbon feedstocks which can be used are oil shale, shale oil, and asphaltenes.

Water

[0022] Any source of water may be used in the fluid comprising water in practicing the present invention. Sources of water include but are not limited to drinking water, treated or untreated wastewater, river water, lake water, seawater produced water or the like.

[0023] Mixing/Emulsion Formation

[0024] A heavy hydrocarbon feed and the fluid comprising water are contacted in a mixing zone to form an emulsion prior to entering the reaction zone.

[0025] Forming an emulsion allows the present process to utilize the advantage of the high interfacial area of emulsions to improve water-oil contacting. As it was pointed in the above-identified related applications, surroundings the heavy hydrocarbon molecules by water molecules during heating and reaction processes avoids over cracking the hydrocarbon feed into light hydrocarbons and polymerizing the hydrocarbon feed into coke.

[0026] One way to achieve the goal of surrounding the heavy hydrocarbon molecules by water molecules is to form an emulsion, i.e. a kinetically or thermodynamically stable dispersion of an oil phase and an aqueous phase, with or without added surfactant. The high interfacial area of emulsion will provide sufficient contact and mixing of oil with water to achieve a high yield of liquid hydrocarbons.

[0027] For applications of emulsion technology generally, one big challenge is breaking the emulsion when needed to achieve phase separation after the emulsion has served the purpose for which it was formed. The technical and economic challenges of emulsion-breaking technology has prevented emulsion technology from being used more broadly because

the costs of breaking up the emulsion to separate the target product often outweigh the benefits of performance enhancement provided by emulsion. However, for heavy oil upgrading using supercritical water as herein described, the emulsion is destroyed during the upgrading process through vaporization of the water and release of hydrocarbon product. Therefore, in accordance with the present process the advantages of emulsion use are obtained having to incur the costs associated with the application of breaking, the emulsion to separate the product.

[0028] The structure and droplet size of the emulsion can be optimized based on process performance requirement and operation cost. There are several ways to form water-oil emulsion known to those of ordinary skill in this technology including high shear equipment such as nozzle, etc. Surfactants or other agents (emulsifiers) may be needed to form a stable emulsion with required structure and droplet size. The emulsion may be either an oil-in-water emulsion or a water-in-oil emulsion.

[0029] A surfactant or a mix of surfactants may be included in the heavy oil/water feedstock emulsion to increase the stability of the emulsion. Suitable surfactants include both water and oil soluble surfactants. A suitable surfactant or mixtures of surfactants include surfactants having a hydrophilic-lipophilic balance in the range of between about 2 and about 10 and mixtures thereof. When a single surfactant is used, sufficient amounts are used to obtain a stable emulsion. Typically this concentration of single surfactant falls in the range of between about 50 ppm and about 2% of the emulsion. It has been found that when a combination of surfactants is used, the total amount of surfactant added is typically less than the amount used for any single surfactant. Thus, when a combination of surfactants are used to achieve a stabilized emulsion, the total surfactant concentration typically falls in the range of between about 100 ppm and about 1% of the emulsion. Suitable emulsifiers include fatty acid soaps such as calcium dioleate, fatty amides such as the reaction products of oleic acid and diethylamine thiamine, a variety of polymeric emulsifiers containing alcohol or carboxylic acid groups or organophilic clays, and certain organic-silicone-based polymers.

[0030] FIG. 1 shows one embodiment. The water and oil are pumped to a mixer where an oil-in-water emulsion is formed. In an embodiment the emulsion has a ratio of oil to water from 10:1 to 1:5. The oil-in-water emulsion; can be prepared in any convenient way suitable for making a fine dispersion of an aqueous phase in a continuous oil phase, but preferably it is prepared by strong physical agitation of the aqueous and oil components optionally in the presence of a suitable oil-in-water emulsifier. Other ways to form oil-water emulsions include using a micro channel mixer or high shear equipment such as nozzles, etc. As noted previously, surfactants or other agents may be needed to form a stable emulsion with the required structure and droplet size.

[0031] Considering the high viscosity of the feed oil, a pre-heater may be needed to heat the oil to certain temperature to facilitate the emulsion formation. The temperature of heavy oil feed should be kept in the range of about 100° to 200° C. to avoid thermal cracking but still high enough to maintain reasonable pressure drop. The oil-in-water emulsion will have lower viscosity than feed oil (heavy oil), and its flow behavior will be more similar to water than feed oil. It is obvious that lower viscosity is advantageous to lower power consumption for pumps. Other advantages of having water as

the external, continuous phase will include reduced fouling of the pipes and reactor from the oil phase, and improved heat transfer to the reactor feed.

[0032] The oil-in-water emulsion is sent to heater to be heated up to temperature required for oil upgrading (higher than supercritical water conditions). Oil-in-water emulsion provide very high interfacial area for water-oil contact, and this is of critical importance to achieve high upgrading performance because the abundance of water molecules surrounding the hydrocarbon molecules will significantly suppress condensation reactions and therefore reduce formation of coke and solid product.

[0033] FIG. 2 shows another embodiment. A second water stream is added to the process so that water to oil ratio for emulsion formation and for the upgrading process can be adjusted independently to optimize the performance. The temperature of second water stream can also be adjusted to achieve optimized performance. The viscosity of oil-in-water emulsion would be much lower than feed oil, which makes the mixing of those two streams much easier.

[0034] FIG. 3 shows yet another embodiment. Water-in-oil emulsion, which also has the advantage of high water-oil interfacial area, was formed at the mixer. Then the emulsion will meet with and heated up by a water stream with temperature higher then critical point. Since the water has a lower boiling point than feed oil, water inside the oil shell will quickly evaporate to break up the oil shell and therefore achieve very good water-oil mixing.

Reaction Conditions

[0035] After the reactants have been mixed to form an emulsion, they are passed into a reaction zone in which they are allowed to react under temperature and pressure conditions of supercritical water, i.e. supercritical water conditions, in the absence of externally added hydrogen, for a residence time sufficient to allow upgrading reactions to occur. The reaction is preferably allowed to occur in the absence of externally added catalysts or promoters, although the use of such catalysts and promoters is permissible in accordance with the present invention.

[0036] "Hydrogen" as used herein in the phrase, "in the absence of externally added hydrogen" means hydrogen gas. This phrase is not intended to exclude all sources of hydrogen that are available as reactants. Other molecules such as saturated hydrocarbons may act as a hydrogen source during the reaction by donating hydrogen to other unsaturated hydrocarbons. In addition, H_2 may be formed in-situ during the reaction through steam reforming of hydrocarbons and water-gas-shift reaction.

[0037] The reaction zone preferably comprises a reactor, which is equipped with a means for collecting the reaction products (syncrude, water, and gases), and a bottom section where any metals or solids (the "dreg stream") may accumulate.

[0038] Supercritical water conditions include a temperature from 374° C. (the critical temperature of water) to 1000° C., preferably from 374° C. to 600° C. and most preferably from 374° C. to 400° C., a pressure from 3,205 (the critical pressure of water) to 10,000 psia, preferably from 3,205 psia 7 to 7,200 psia and most preferably from 3,205 to 4,000 psia, an oil/water volume ratio from 1:0.1 to 1:10, preferably from 1:0.5 to 1:3 and most preferably about 1:1 to 1:2.

[0039] The reactants are allowed to react under these conditions for a sufficient time to allow upgrading reactions to

occur. Preferably, the residence time will be selected to allow the upgrading reactions to occur selectively and to the fullest extent without having undesirable side reactions of coking or residue formation. Reactor residence times may be from 1 minute to 6 hours, preferably from 8 minutes to 2 hours and most preferably from 10 to 40 minutes.

Reaction-Product Separation

[0040] After the reaction has, progressed sufficiently, a single phase reaction product is withdrawn from the reaction zone, cooled, and separated into gas, effluent water, and upgraded hydrocarbon phases. This separation is preferably done by cooling the stream and using one or more two-phase separators, three-phase-separators, or other gas-oil-water separation device-known in the art. However, any method of separation can be used in accordance with the invention. As noted previously, the emulsion has been broken as a result of the very high temperature reaction.

[0041] The composition of gaseous product obtained by treatment of the heavy hydrocarbons in accordance with the process of the present invention will depend on feed properties and typically comprises light hydrocarbons, water vapor, acid gas (CO_2 and H_2S), methane and hydrogen. The effluent water may bemused, reused or discarded. It may be, recycled to e.g. the feed water tank, the feed water treatment system or to the reaction zone.

[0042] The upgraded hydrocarbon product, which is sometimes referred to as "syrcrude" herein may be upgraded further or processed into other hydrocarbon products using methods that are known in the hydrocarbon processing art.

[0043] The process of the present invention may be carried out as a continuous or semi-continuous process or a batch, process. In the continuous process the entire system operates with a feed stream of oil and a separate feed stream of water and reaches a steady state; whereby all the flow rates, temperatures, pressures, and composition of the inlet, outlet, and recycle streams do not vary appreciably with time.

[0044] While not being bound to any theory of operation, it is believed that a number of upgrading reactions are occurring simultaneously at the supercritical reaction conditions used in the present process.

[0045] In a preferred embodiment of the invention the major chemical/upgrading reactions are believed to be:

[0046] Thermal Cracking $C_xH_y \rightarrow$ lighter hydrocarbons

[0047] Steam Reforming: $C_xH_y + 2xH_2O = xCO_2 + (2x+y/2)H_2$

[0048] Water-Gas-Shift: $CO + H_2O = CO_2 + H_2$

[0049] Demetalization: $C_xH_yNi_w + H_2O/H_2 \rightarrow NiO/Ni(OH)_2 +$ lighter hydrocarbons

[0050] Desulfurization: $C_xH_yS_z + H_2O/H_2 = H_2S +$ lighter hydrocarbons

[0051] The exact pathway may depend on the reactor operating conditions (temperature, pressure, O/W volume ratio), reactor design (mode of contact/mixing, sequence of heating), and the hydrocarbon feedstocks

[0052] The following Examples are illustrative of the present invention, but are not intended to limit the invention in any way beyond what is contained in the claims which follow.

EXAMPLES

Example 1

Heavy Oil Upgrading Using Emulsion Mixing

[0053] The experiment was performed using a continuous system. A feed oil, which was a heavy crude with API=12.8,

which was diluted with a diluent hydrocarbon at a ratio of 5:1 (20 vol % of diluent) and water was heated to 150° C. before entering a micromixer. The heated crude was mixed with water in the micromixer to form a water-oil emulsion, which was injected into a stream of supercritical water at temperature of 400° C. The total water to oil ratio (volume at room temperature) was 3:1. The oil-supercritical water mixture was then injected into a reactor at temperature of 400° C. and pressure, of 3400 psig. The upgraded product, which formed a homogeneous phase with supercritical water, was withdrawn from the top of the reactor and send to high pressure separator which was operated at the same pressure but lower temperature to achieve oil-water separation. The dreg stream was removed from reactor bottom.

[0054] The diluted heavy crude oil properties were measured before reacting it with the supercritical water process as referred to in Example 1. The properties of the crude were as follows: 12.8 API gravity at 60/60; 1329 CST viscosity @40° C.; 13.04 wt % MCRT; 3.54 wt % sulfur; 0.56 wt % nitrogen; 3.05 mg KOH/gm acid number; 1.41 wt % water; 371 ppm Vanadium; and 86 ppm Nickel. The diluted heavy crude oil after the super critical water treatment was converted into a syncrude with the following properties: 23.4 API gravity at 60/60; 9.8 CST viscosity @40° C.; 1.9 wt % MCRT; 2.7 wt % sulfur; 2.41 mg KOH/gm acid number; 88% Vanadium reduction; and 93% Nickel reduction.

[0055] Based on reactor volume and liquid yield it was calculated that the liquid productivity was 15.61 lb/ft3.h.

Example 2

Reference Run Using In-Line Mixer

[0056] In order to demonstrate the improved performance by using emulsion mixing, a reference run using in-line mixer to mix water and oil was performed under the same operation conditions (temperature, pressure, water to oil ratio). Feed oil (diluted heavy crude of Example 1) was preheated to 130 C, and then mixed with supercritical water in an inline mixer. Water-oil stream flow through a 20 ft spiral coil immersed in a high temperature sand bath (same as reactor temperature) to further improve water-oil contact, and then fed to the reactor. The upgraded product, which formed a homogeneous phase with supercritical water, was withdrawn from the top of the reactor and send to high pressure separator which was operated at the same pressure but lower temperature to achieve oil-water separation. The dreg stream was removed from reactor bottom.

[0057] The liquid product (syncrude) from this reference run has the following properties: 22 API gravity at 60/60; 14.7 CST viscosity @40° C.; 1.99 wt % MCRT; 2.74 wt % sulfur; 3.0 mg KOH/gm acid number; 86% Vanadium reduction; and 91% Nickel reduction. Overall the product quality is comparable with those obtained in Example 1. However, in order to achieve upgraded product with such quality, much longer residence time was needed. As a result, the liquid productivity for this was 9.2 lb/ft3.h.

[0058] By comparing results of the above two examples, it is clear that under similar operation conditions (pressure, temperature and water to oil) by using emulsion mixing the upgrading process can be significantly enhanced, demonstrated by improved liquid yield at shorter residence time while maintaining same product quality. In comparing with experimental results using in-line mixer and spiral coil or oil-ater mixing, the application of emulsion mixing fled to a

80% increase of upgraded liquid, productivity (defined as lb upgraded liquid/(ft3.h)) while maintaining the same product quality (API, viscosity, metal removing rate etc.)

[0059] There are numerous variations on the present invention which are possible in light of the teachings and supporting examples described herein. It is therefore understood that within the scope of the following claims, the invention may be practiced otherwise than as specifically described or exemplified herein.

What is claimed is:

1. A process for upgrading hydrocarbons comprising:
   (a) mixing hydrocarbons with a fluid comprising water in a mixing zone to form an emulsion;
   (b) heating the emulsion to a temperature higher than the critical temperature of water;
   (c) reacting the emulsion in a reaction zone under supercritical water conditions in the absence of externally added hydrogen and externally supplied catalyst for a residence time sufficient to allow upgrading reactions to occur;
   (d) withdrawing a single-phase reaction product from the reaction zone; and
   (e) separating the reaction product into gas, effluent water, and upgraded hydrocarbon phases.

2. A process according to claim 1, wherein the hydrocarbons are heavy hydrocarbons selected from the group consisting of whole heavy petroleum crude oil, tar sand bitumen, heavy hydrocarbon fractions obtained from crude petroleum oils, heavy vacuum gas oils, vacuum residuum, petroleum tar, coal tar and their mixtures.

3. A process according to claim 1, wherein the emulsion has oil to water ratio of from 10:1 to 1:5.

4. A process according to claim 1, wherein the conditions in the mixing zone include a temperature higher than the critical temperature of water and a pressure greater than the critical pressure of water.

5. A process according to claim 1, wherein the supercritical water conditions include a temperature from 374° C. to 1000° C., a pressure from 3,205 psia to 10,000 psia an oil/water volume ratio from 1:0.1 to 1:10 and where the residence time is from 1 minute to 6 hours.

6. A process according to claim 1, wherein the supercritical water conditions include a temperature from 374° C. to 600° C., a pressure from 3,205 psia to 7,200 psia, an oil/water volume ratio from 1:0.5 to 1:3 and where the residence time is from 8 minutes to 2 hours.

7. A process according to claim 1, wherein the supercritical water conditions include a temperature from 374° C. to 400° C., a pressure from 3,205 psia to 4,000 psia, an oil/water volume ratio from 1:1 to 1:2 and where the residence time is from 10 to 40 minutes.

8. A process according to claim 1, wherein the mixture in the reaction zone is reacted in the absence of any catalyst or promoter.

9. A process according to claim 1, wherein the water is drinking water, treated wastewater, untreated wastewater, river water, lake water, seawater, produced water or their mixtures.

10. A process according to claim 1, wherein a surfactant or emulsifier is added to the mixing zone in step (a)

11. A process according to claim **1**, wherein an oil-water emulsion is formed using a micro-channel mixer in step (a)

12. A process according to claim **1**, wherein an oil-water emulsion is water-in-oil

13. A process according to claim **1**, wherein an oil-water emulsion is oil-in-water

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