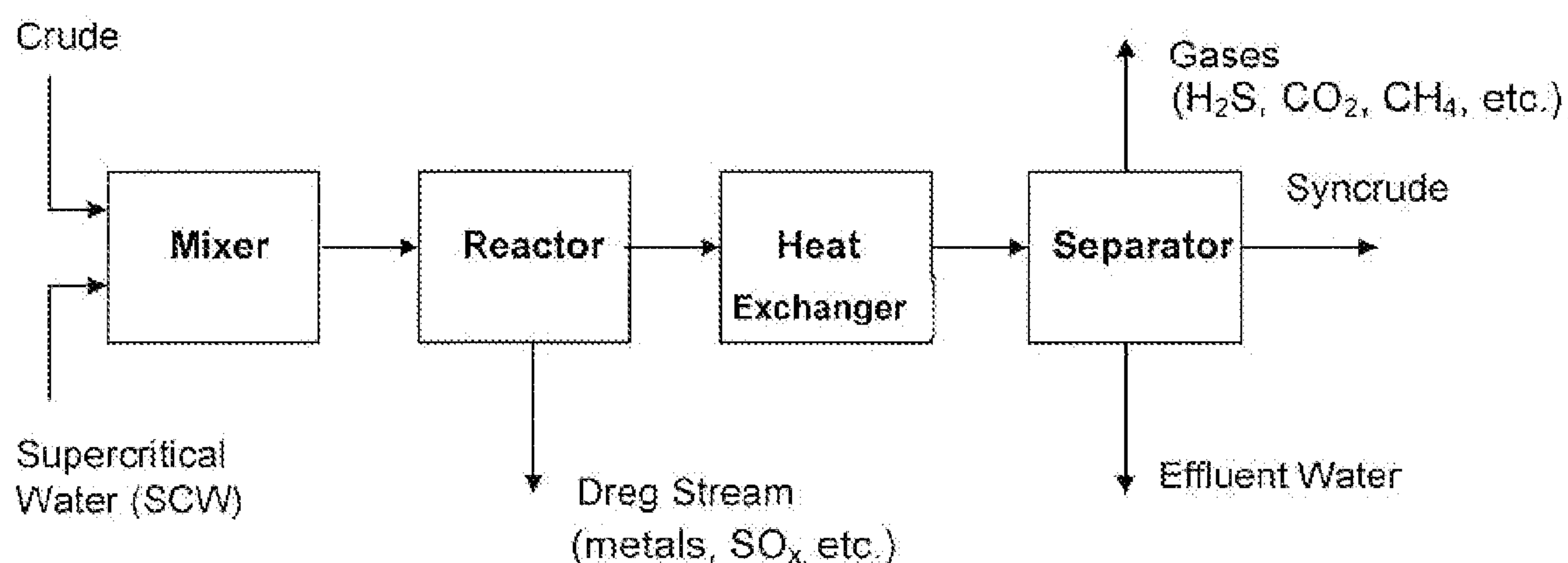


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Point, CA (US)(51) **Int. Cl.**
C10G 31/00 (2006.01)(52) **U.S. Cl.** **208/177**(57) **ABSTRACT**

A reactor for conducting a process 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.) is described. The reactor is operable under continuous) semi-continuous or batch mode and is equipped with means to enable momentum, heat and mass transfer in and out of and within the reactor.

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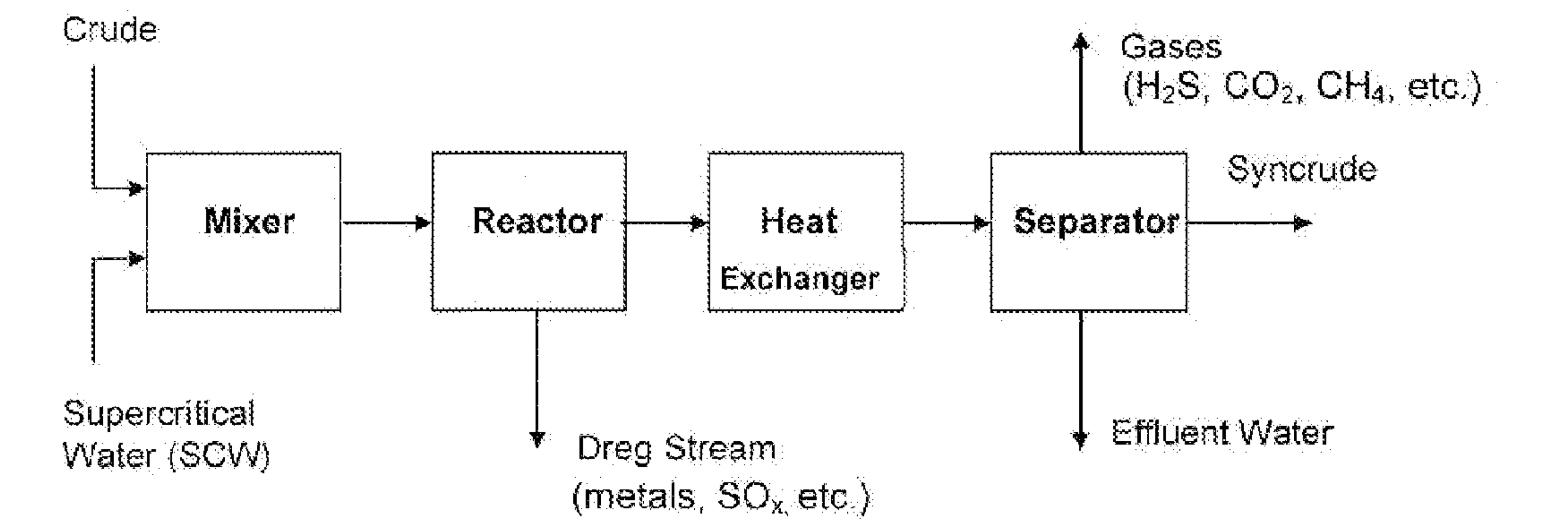


FIG.1

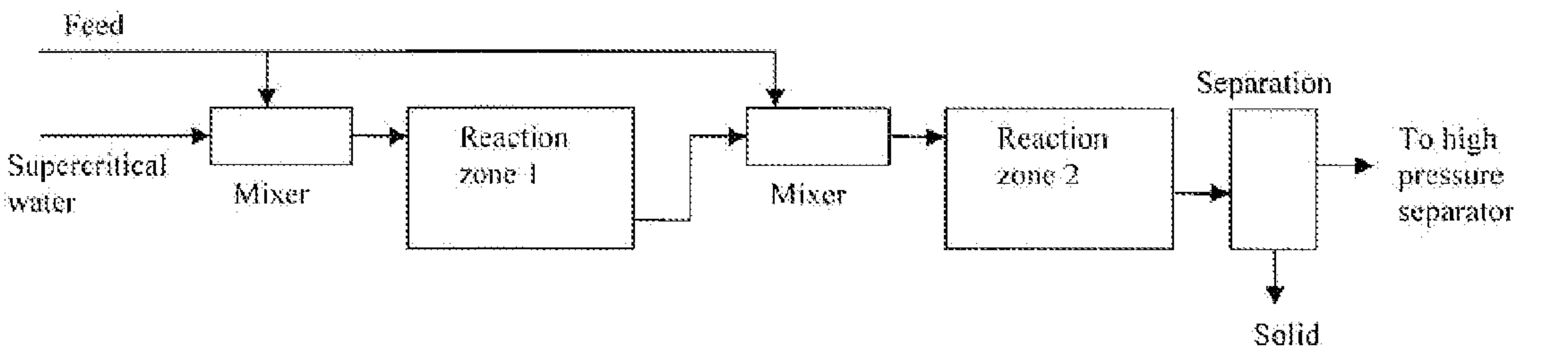


FIG.2

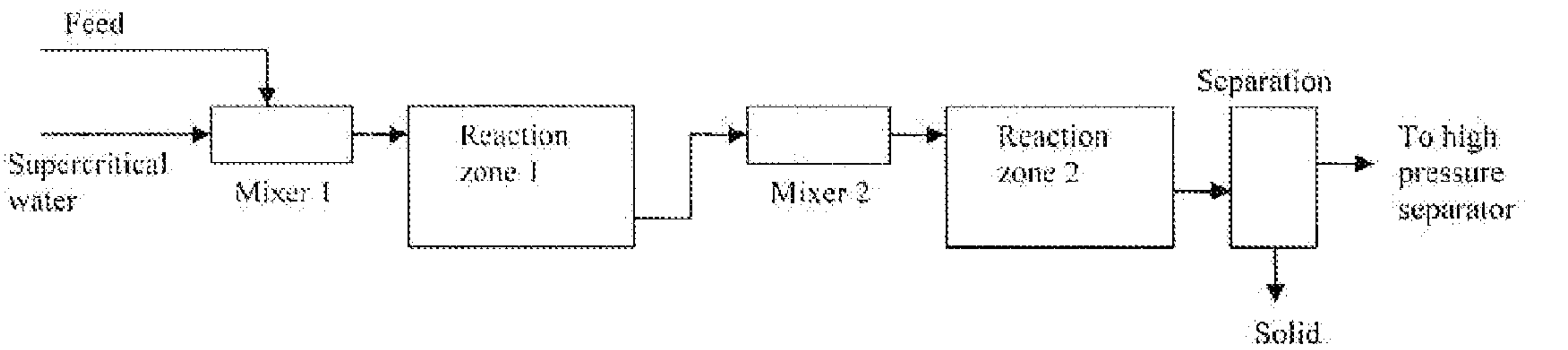


FIG.3

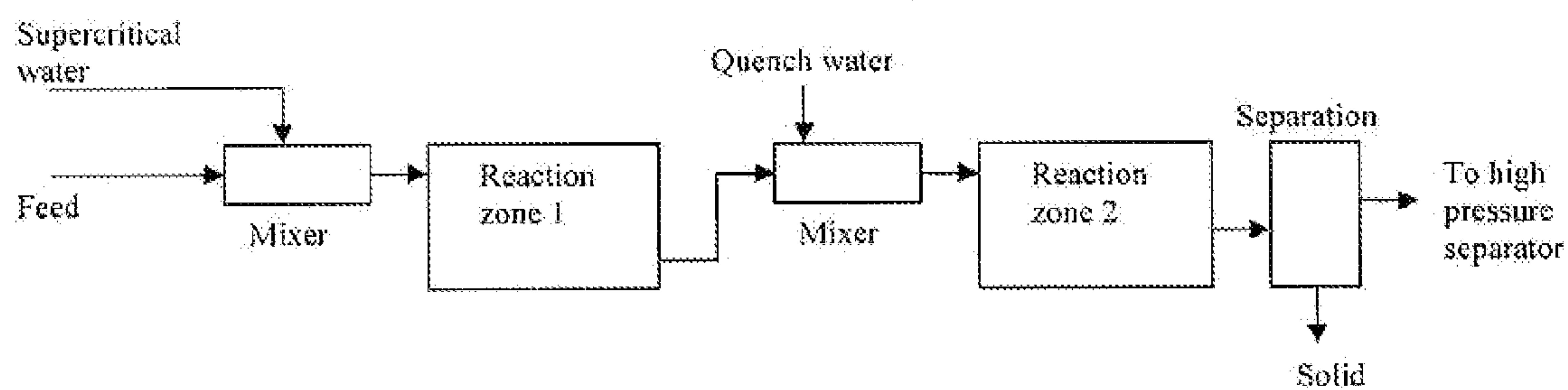


Fig.4

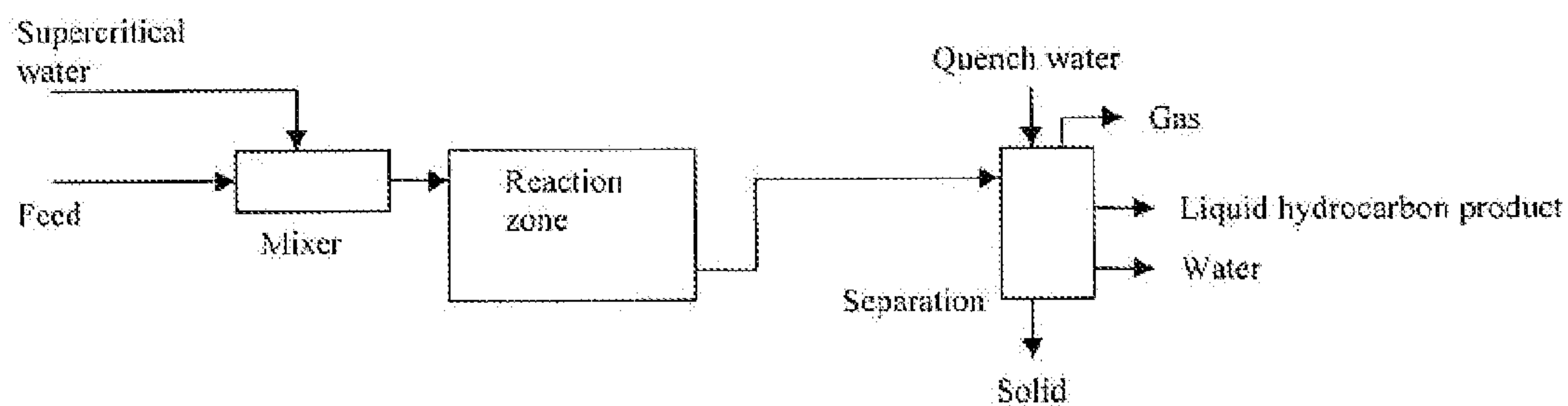


Fig.5

REACTOR AND PROCESS FOR UPGRADING HEAVY HYDROCARBON OILS

FIELD OF THE INVENTION

[0001] The present invention relates to upgrading of hydrocarbons, especially 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. These diluent addition/removal processes and hydrogen-addition or other upgrading processes have a number of disadvantages:

[0004] 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.

[0005] 2. Hydrogen-addition processes such as hydrotreating or hydrocracking require significant investments in capital and infrastructure.

[0006] 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.

[0007] 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.

[0008] 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.

[0009] 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.

[0010] 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.

[0011] 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, 5,1914,031 and 6,887,369 and EP671454.

[0012] 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.

[0013] U.S. Pat. No. 5,914,031 discloses a three zone reactor design so that the reactant activity, reactant solubility and phase separation of products can be optimized separately by controlling temperature and pressure. However, all the examples given in the patent were obtained using batch operation.

[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.

[0015] Although the above-mentioned patents disclosed and claimed various methods and processes for heavy oil upgrading using supercritical water, such as operating range of temperature, and pressure, water to oil ratio, etc, none has disclosed the design of the reactor or design related process controls for heavy oil upgrading using supercritical water. In fact, most of the examples disclosed in the patents were obtained through batch tests using an autoclave. Although there are numerous references to reactor design for processes involving supercritical water, most of them are for the application of waste treatment and none of those references has addressed the design of a reactor for both heavy oil and supercritical water, which is fundamentally different from processes of waste treatment using supercritical water, as discussed below.

[0016] It has long been known in the art that supercritical water can be used for waste treatment, especially for treating wastewater containing organic contaminants. Therefore, there are numerous disclosures in the literature on reactor design for waste treatment using supercritical water, tended to address the following issues:

[0017] (1) Solid handling. Waste streams typically contain both organic and inorganic materials. Although organic materials can be destroyed quickly through supercritical water oxidation, inorganic materials are insoluble in supercritical water. Several patents address this concern. For example, U.S. Pat. Nos. 5,560,823 and 5,567,698 incorporated by reference herein disclose a reversible flow reactor having two reaction zones which are alternately used for supercritical water oxidation while the remaining reaction zone is flushed with subcritical effluent from the active reaction zone. U.S. Pat. No. 6,264,844, incorporated by reference herein, discloses a tubular reactor for supercritical water oxidation. The velocity of the reaction mixture is sufficient to prevent settling of solid. Inorganic salts in the effluent mixture, which are insoluble at conditions of supercritical temperature and pressure for water, are dissolved in a liquid water phase during cooling down of the effluent mixture at an outlet end of the reactor.

[0018] (2) Oxidizer management. U.S. Pat. Nos. 5,384,051 and 5,558,783, incorporated by reference herein, disclose a reactor design for supercritical wastewater oxidation. It contains a reaction zone inside the containment vessel and a permeable liner around the reaction zone. An oxidizer is mixed with a carrier fluid such as water. The mixture is heated and pressurized to supercritical conditions, and then introduced to the reaction zone gradually and uniformly by forcing it radially inward through the permeable liner and toward the reaction zone. The permeable liner permits the continuous, gradual, uniform dispersion of a reactant and therefore promotes an even and efficient reaction. The liner also isolates the pressure vessel from high temperature and oxidizing conditions found in the reaction zone, allowing a reduction in cost of the pressure vessel. EP 1489046 discloses a double-vessel design with a reaction vessel placed inside a pressure vessel. Reaction takes place inside the reactor vessel at high temperature, pressure and corrosive environments. The outer pressure vessel will only see water.

[0019] (3) Containment of toxic material. Some waste stream contains contaminants that are extremely harmful to humans and the environment, therefore the possibility of releasing of such harmful material has to be addressed in the reactor design. U.S. Pat. No. 6,168,771, incorporated by reference herein, discloses a reactor design including an autoclave inside a pressure vessel. The pressure between autoclave and pressure vessel is essentially equal to that inside the autoclave, therefore eliminating possible leaking of toxic material inside the autoclave.

[0020] Although heavy oil upgrading using supercritical water may be considered similar in some respects to waste treatment using supercritical water, and can be implemented using various elements of reactors designed for waste treatment, there are significant differences in requirement for reactor design for heavy hydrocarbon upgrading from that for waste treatment. Specifically, the following are among

the many issues to be addressed in designing a reactor in which to conduct an effective process for heavy oil upgrading using supercritical water:

[0021] (1) Importance of selectivity. For waste treatment, the only performance target is conversion. In other words, the reaction is non-selective total oxidation and there is no need to worry about selectivity, which makes the reactor design much easier. For heavy oil upgrading, the feed is a mixture containing broad range of materials, and the reactions involved are much more complex. We need not only to consider conversion, but also more importantly to pursue high selectivity, since non-selective reactions will lead to low-value byproducts such as solid coke or gases. Obviously, reactor design for selective reactions in a complex system is very different and much more challenging than that for non-selective total oxidation.

[0022] (2) High concentration of feed. Typically the organic component concentration in the waste stream is low, and in many situations the concentration is only in the ppm range. For oil upgrading, it is preferable to run the reaction using the lowest possible water to oil ratio to reduce capital and operating cost. The oil concentration is typically several orders of magnitude higher in upgrading as opposed to waste treatment.

[0023] (3) High density and viscosity One distinguishing feature of heavy oil is high density and viscosity. In fact, this is one of the primary reasons that the oil has to be upgraded. The density of heavy oil is very close to liquid water, and viscosity can be as high as 10,000 cp. High density and viscosity, together with high concentration make the dispersion of heavy oil into supercritical water an important consideration.

SUMMARY OF THE INVENTION

[0024] The present invention relates to an apparatus for upgrading a hydrocarbon by reaction with a fluid comprising water under supercritical water conditions comprising; means for dispersing and mixing the fluid comprising water and the hydrocarbon under conditions which disfavor thermal cracking and formation of coke; means for injecting a dispersed water-hydrocarbon mixture into a reaction zone under supercritical water conditions; a reaction zone having means for maintaining a uniform temperature within said reaction zone, means for controlling the residence time in the reaction zone within determined limits and means for avoiding the settling of inorganic solids within the reaction zone; and means for recovering an upgraded hydrocarbon.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] FIG. 1 is a process flow diagram of one embodiment of a process employing an apparatus of the present invention.

[0026] FIG. 2 is a process flow diagram of another embodiment of a process employing an apparatus of the present invention.

[0027] FIG. 3 is a process flow diagram of another embodiment of a process employing an apparatus of the present invention.

[0028] FIG. 4 is a process flow diagram of another embodiment of a process employing an apparatus of the present invention.

[0029] FIG. 5 is a process flow diagram of another embodiment of a process employing an apparatus of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reactants

[0030] Water and hydrocarbons, preferably heavy hydrocarbons are the two reactants employed in a process according to the present invention.

[0031] Any 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

[0032] 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.

Mixing

[0033] In accordance with the invention, the heavy hydrocarbon feed and a fluid comprising water that has been heated to a temperature higher than its critical temperature are contacted in a mixing zone prior to entering the reaction zone. In accordance with the invention, mixing may be accomplished in many ways and is preferably accomplished by a technique that does not employ mechanical moving parts. Such means of mixing may include, but are not limited to, use of static mixers, spray nozzles, sonic or ultrasonic agitation, or thermal siphons.

[0034] The oil and water should be heated and mixed so that the combined stream will reach supercritical conditions in the reaction zone.

[0035] It was found that by avoiding excessive heating of the feed oil, the formation of byproduct such as solid residues is reduced significantly. One aspect of this invention is to employ a heating sequence so that the temperature and pressure of the hydrocarbons and water will reach supercritical reaction conditions in a controlled manner. This will avoid excessive local heating of oil, which will lead to solid formation and lower quality product. In order to achieve better performance, the oil should only be heated up with sufficient amount of water present and around the hydrocarbon molecules. This requirement can be met by mixing oil with water before heating.

[0036] In one embodiment of the present invention, water is heated to a temperature higher than its critical temperature, and then mixed with oil. The temperature of heavy oil feed should be kept in the range of about 100° C. to 200° C. to avoid thermal cracking but still high enough to maintain a reasonable pressure drop. The water stream temperature

should be high enough to make sure that after mixing with oil, the temperature of the oil-water mixture is still higher than the water supercritical temperature. In this embodiment, the oil is actually heated up by water. An abundance of water molecules surrounding the hydrocarbon molecules will significantly suppress condensation reactions and therefore reduce formation of coke and solid product.

[0037] The required temperature of the supercritical water stream, T_{SCW} , can be estimated based on reaction temperature, T_R , and water to oil ratio. Since the heat capacity of water changes significantly in the range near its critical conditions, for a given reaction temperature, the required temperature for the supercritical water stream increases almost exponentially with decreasing water-to-oil ratio. The lower the water-to-oil ratio, the higher the T_{SCW} . The relationship, however, is very nonlinear since higher T_{SCW} leads to a lower heat capacity (far away from the critical point).

[0038] In another embodiment, water is heated up to supercritical conditions. Then the supercritical water mixed with heavy oil feed in a mixer. The temperature of heavy oil feed should be kept in the range of about 100° C. to 200° C. to avoid thermal cracking but still high enough to maintain reasonable pressure drop. After mixing with heavy oil, the temperature of the water-oil mixture would be lower than critical temperature of water; therefore a second heater is needed to raise the temperature of the mixture stream to above the critical temperature of water. In this embodiment, the heavy oil is first partially heated up by water, and then the water-oil mixture is heated to supercritical conditions by the second heater.

[0039] Other methods of mixing and heating sequences based on the above teachings may be used to accomplish these objectives as will be recognized by those skilled in the art.

Reaction Conditions

[0040] After the reactants have been mixed, 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.

[0041] "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.

[0042] The reaction zone preferably comprises a reactor, which is equipped with a means for collecting the reaction products (syncrude, water, and gases), and a section, preferably at the bottom, where any metals or solids (the "dreg stream") may accumulate.

[0043] 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 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.

[0044] 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 20 to 40 minutes.

The Reactor

[0045] A reactor designed for heavy oil upgrading using supercritical water in accordance with the present invention will preferably include the following features:

[0046] The reactor will have means for adequate oil-water mixing and dispersion. Contrary to the conventional thermal cracking in an uncontrolled fashion that will lead to excessive formation of light hydrocarbon and therefore lower liquid hydrocarbon yield at the temperature and pressure under supercritical water conditions, heavy hydrocarbons will hydrothermally crack into lighter components. Furthermore, hydrocarbon radicals formed from thermal cracking will also recombine and polymerize and eventually become coke. Water molecules, especially under supercritical conditions, can quench and stabilize hydrocarbon radicals and therefore prevent them from over cracking and polymerization. To avoid over cracking into light hydrocarbons and coke formation, the heavy hydrocarbon molecules are preferably surrounded by water molecules to the greatest practical extent. Therefore, the reactor includes means to assure adequate mixing of oil with water for the purpose of achieving a high yield of liquid hydrocarbons. Such means should be chosen so as to be able to handle heavy oil feed which has low API gravity and high viscosity at high oil to water ratio. Depending on specific applications such means can include, among others (a) nozzles; (b) static mixer; (c) stirring vessel; (d) micro-channel device; and sonic and ultrasonic device.

[0047] The reaction zone in accordance with the present invention will preferably:

[0048] (1) Provide an appropriate residence time to achieve high conversion and liquid yield. Controlling the residence time narrowly within determined limits is a very important factor for heavy oil upgrading using supercritical water. The desired products of heavy oil upgrading are liquid hydrocarbons. Insufficient residence time will lead to low conversion and hence low liquid hydrocarbon yield. On the other hand, excess conversion will lead to low value by products such as light hydrocarbon gas and coke. In order to achieve highly selective conversion to liquid hydrocarbons, it is critical to maintain adequate residence time.

[0049] (2) Provide sufficient heat transfer rate to maintain uniform temperature distribution. In comparing other supercritical water applications, heavy oil is a much more complicated feed and heavy oil upgrading is a very complex process. In addition, as indicated above, the desired liquid hydrocarbon is an intermediate product from selective, partial reaction. Therefore, it is extremely important to control reaction tempera-

ture to achieve high liquid hydrocarbon yield. Adequate control of reaction temperature can be achieved by providing enough heat transfer area, uniform feed distribution; or by quenching.

[0050] (3) Be able to handle solid formed during the reaction. During the reaction, small amounts of solid byproducts, primarily inorganic materials (metals, sulfur, coke etc), will be formed, and the reaction zone must be able to handle such solids so they will not cause operating problems and will not contaminate the liquid hydrocarbon product.

[0051] The present invention also employs a separation zone for product recovery. The effluent stream from the reaction zone contains liquid hydrocarbon product, gas, water under supercritical conditions and solids. The liquid hydrocarbons are generally separated from other components to achieve high yield. The preferred way is to remove the solid first, and then bring the fluid phase containing hydrocarbon products, supercritical water and gas byproducts out of supercritical condition by lowering temperature, pressure or both so that hydrocarbon product and water will condense into liquid phase. The solids are primarily inorganic materials formed during the reactions and can be separated from the supercritical fluid phase using separation techniques known in the art, which could be a disengaging zone in the reactor or a separate device such as settling vessel, filter, cyclone etc.

[0052] Another option for separating the solids is to bring the product stream out of supercritical regime by lowering temperature or pressure or both. Then the solid will precipitate. A potential disadvantage of this option is that some of the inorganic components in the solid may dissolve in water, which may contaminate the liquid hydrocarbon product. It should be noted that depending on the specific applications, a reactor for heavy oil upgrading using supercritical water in accordance with the present invention may have more than one of each of the three components listed above.

[0053] FIG. 1 shows an embodiment of the present invention, which has been used in a laboratory. An inline mixer is used for mixing heavy oil with water. For this specific embodiment it is a static mixer. The reaction zone comprises a spiral tube reactor with large length to diameter ratio to attain high velocity inside the reactor, which is helpful to maintain oil-water dispersion. This design also makes the fluid flow inside the reactor close to plug flow and therefore achieves narrow residence time distribution for selective conversion to desired liquid hydrocarbons. Inorganic solids in the feed and formed during the reaction will not dissolve in supercritical water. High velocity inside the reactor also prevents settling of those inorganic solids. The small diameter of the reactor body also provides large specific surface area for heat transfer to maintain uniform temperature distribution inside the reactor. The length of the reactor can be designed based on residence time needed for specific conversion. A second vessel is added to settle the solids. The temperature and pressure is maintained at the same values as those in the spiral tube so that the fluid in the second vessel is still at supercritical water conditions. Due to the larger cross-sectional area of the second vessel the fluid velocity is much lower. As a result, inorganic materials separated from the fluid will settle down in the vessel, and can be removed from the system. The fluid containing hydrocarbon products, supercritical water and gas byproducts is cooled while

maintaining at the same pressure as in the reactor, and hydrocarbon products and water are condensed in the high pressure separator.

[0054] A spiral tube with a high length to diameter ratio which may be from 50 to 10,000, preferably from 100 to 4,000 may be used as reactor body. Use of such a reactor has the advantages of high velocity, narrow residence time distribution, and large surface for heat transfer. The length to diameter ratio is a useful parameter to determine preferred reactor configurations. The diameter may be determined by velocity needed to avoid solids precipitation and then the length can be selected to provide the desired residence time. Other reactor configurations known to those in the art can be used to achieve similar effects such as a serpentine reactor.

[0055] In the embodiments shown in FIG. 1 the separation zone for removing solid and recovering hydrocarbon products is a vessel with a dip tube. Other fluid solid separation devices known in the art can be used to achieve the separation effect, which includes, but not limited to, cyclone, filter, ceramic membrane, settling tank, etc.

[0056] In the embodiment shown in FIG. 1, as well as in other embodiments described herein, the mixer, reaction and separation zones are separated. Such arrangement is convenient for laboratory research, and is used as an illustrative example. It is within the scope of the present invention and in some applications will be beneficial to integrate these three functions into one vessel.

[0057] As mentioned above, the reactor may include more than one piece of each function devices. FIG. 2 shows an example. In order to avoid over cracking of the feed to form undesired byproducts such as light hydrocarbon gases and coke, heavy hydrocarbon molecules are preferably surrounded by sufficient water molecules. Generally speaking, a higher water to oil ratio will be helpful to maintain the desired environment. However, high water to oil ratio also means high equipment and operating cost. The embodiment shown in FIG. 2 can achieve high water to oil ratio locally without increasing overall water to feed ratio. Instead of mixing all the feed oil with water at reactor inlet, this embodiment uses multiple injections of oil to maintain a desired water to oil ratio. Such a design is also helpful to control reaction temperature. By distributing feed oil more uniformly through the reactor length, reaction temperature will not increase too much due to the exothermic nature of the reactions.

[0058] Only two injections were shown in FIG. 2 This is not intended as a limitation. A reactor with multiple injections may also be used. In addition, one or more settling vessels can be added to a reactor with a multiple injection configuration to achieve solid separation under supercritical conditions.

[0059] FIG. 3 shows yet another embodiment with more than one mixing and reaction zones. A second mixer, which may or may not be the same as the first mixer, is added between reaction zone to enhance the oil/supercritical water mixing. Again, multiple mixers and reaction zones can be used. The upgrading reaction is exothermic. A reactor with a large surface area helps to maintain uniform temperature distribution inside the reactor.

[0060] Depending on feed properties; heat exchange through the surface area provided by the reactor may or may not be enough. Water can be used to quench the reaction stream and thereby control the reaction temperature.

[0061] FIG. 4 shows an embodiment of using water to quench the reaction stream between two reaction zones. The amount of water used for quenching should be enough to bring down the reaction temperature while the reaction stream after quenching still maintain supercritical conditions. Multiple reaction zones and water quenching may be necessary for some feeds.

[0062] The quenching water can also be used to for product recovery, as shown in FIG. 5. After reaction the product stream is quenched by liquid water. The solid will be washed out by the water, and: due to the temperature reduction caused by quenching water and the hydrocarbons will condense as liquid.

Reaction Product Separation

[0063] 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 ones 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.

[0064] 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 be used, reused or discarded. It may be recycled to e.g. the feed water tank, the feed water treatment system or to the reaction zone.

[0065] The upgraded hydrocarbon product, which is sometimes referred to as "syncrude" herein may be upgraded further or processed into other hydrocarbon products using methods that are known in the hydrocarbon processing art.

[0066] The process of the present invention may be carried out either as a continuous or semi-continuous process or a batch process or as a continuous process. In the continuous process the entire system operates with a feed stream of oil and a separate feed stream of supercritical 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.

[0067] While not being bound to any theory of operation, it is believed that a number of upgrading reactions are occurring simultaneously at the supercritical water conditions used in the present process. In a preferred embodiment of the invention the major chemical/upgrading reactions are believed to be:

[0068] Thermal Cracking: $\text{C}_x\text{H}_y \rightarrow \text{lighter hydrocarbons}$

[0069] Steam Reforming: $\text{C}_x\text{H}_y + 2x\text{H}_2\text{O} = x\text{CO}_2 + (2x + y/2)\text{H}_2$

[0070] Water-Gas-Shift: $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$

[0071] Demetalization: $\text{C}_x\text{H}_y\text{Ni}_w + \text{H}_2\text{O}/\text{H}_2 \rightarrow \text{NiO}/\text{Ni}(\text{OH})_2 + \text{lighter hydrocarbons}$

[0072] Desulfurization: $\text{C}_x\text{H}_y\text{S}_z + \text{H}_2\text{O}/\text{H}_2 = \text{H}_2\text{S} + \text{lighter hydrocarbons}$

[0073] 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 feedstock.

[0074] 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.

EXAMPLE 1

Process Conditions

[0075] Oil and supercritical water are contacted in a mixer prior to entering the reactor. The reactor is equipped with air inner tube for collecting the products (syncrude, excess water, and gas), and a bottom section where any metals or solids comprising a "dreg stream" of indeterminate properties or composition may accumulate. The shell-side of the reactor is kept isothermal during the reaction with a clamshell furnace and temperature controller. Preferred reactor residence times are 20-40 minutes, with preferred oil/water volume ratios on the order of 1:3. Preferred temperatures are around 374°-400° C., with the pressure at 3200-4000 psig. The reactor product stream leaves as a single phase, and is cooled and separated into gas, syncrude, and effluent water. The effluent water is recycled back to the reactor. Sulfur from the original feedstock accumulates in the dreg stream for the most part, with lesser amounts primarily in the form of H₂S found in the gas phase and water phase.

[0076] As the next examples will show, very little gas is produced in most cases. With suitable choice of operating conditions, it is also possible to reduce or nearly eliminate the "dreg stream." Elimination of the dreg stream means that a greater degree of hydrocarbon is recovered as syncrude, but it also means that metals and sulfur will accumulate elsewhere, such as in the water and gas streams.

EXAMPLE 2

Properties of the Product Syncrude

[0077] A Hamaca crude oil was diluted with a diluent hydrocarbon at a ratio of 5:1 (20 vol % of diluent:). The diluted Hamaca crude oil properties were measured before reacting it with the supercritical water process as referred to in Example 1 and FIG. 2. The properties of the crude were as follows, 12.8 API gravity at 60/60; 1329 CST viscosity @40° C.; 7.66 wt % C/H ratio, 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 Hamaca crude oil after the super critical water treatment was converted into a syncrude with the following properties: 24.1 API gravity at 60/60; 5.75 CST viscosity @40° C.; 7.40 wt % C/H ratio; 2.25 wt % MCRT; 2.83 wt % sulfur; 0.28 wt % nitrogen; 1.54 mg KOH/gm acid number; 0.96 wt % water; 24 ppm Vanadium; and 3 ppm Nickel. Substantial reductions in metals and residues were observed, with simultaneous increase in the API gravity and a significant decrease in the viscosity of the original crude oil feedstock. There were modest reductions in the Total Acid number, sulfur concentration, and nitrogen concentration which could be improved with further optimization of the reaction conditions.

[0078] When the diluted Hamaca crude was sent directly to the reactor without being first heated with supercritical water, the product syncrude had the following properties; 14.0 API gravity at 60.60; 1:88 CST viscosity @40° C.; 8.7 wt % MCRT; 3.11 wt % sulfur; 267 ppm Vanadium; and 59 ppm Nickel. This comparison demonstrates the importance of the heating sequence of the present invention.

[0079] Apart from the occasional, small accumulation of a: dreg stream, there is very little coking or solid byproducts formed in the supercritical water reaction. The material balance was performed for two separate experimental runs.

[0080] In the experimental run with no dreg stream formed, the starting feedstock of diluted Hamaca crude at 60 grams produced a syncrude product of 59.25 grams which corresponds to a high overall recovery of 99 percent. It was thought that due to the absence of a dreg stream, the experimental mass; balance was impacted in the determination of the sulfur and metals. The gas phase did not contain metals species and had little sulfur compounds. It was hypothesized that a portion of the metal and sulfur may have accumulated on the walls of the reactor or downstream plumbing.

[0081] In the experimental run with a dreg stream formed, the starting feedstock of diluted Hamaca crude at 30 grams produced a syncrude product of 22.73 grams. The dreg stream that was formed accounted for 5.5 grams. The overall recovery with the dreg stream was 96.7 percent. In the dreg stream, sulfur accounted for 31% of the total sulfur with the remaining sulfur in the oil product, water phase, and gas phase. The metals content of the dreg stream accounted for 82% of the total metals with the remaining metals in the oil product. For commercial operations, it may be preferable to minimize the formation of a dreg stream, since it represents a 18% reduction in syncrude product, and generates a lower value product stream that impacts the process in terms of economics and disposal concerns.

[0082] Undiluted Boscan crude oil properties were measured before reacting it with the supercritical water process of the present invention. The properties of the crude were as follows: 9 API gravity at 60/60; 1,140 CST viscosity @40° C.; 8.0 wt % C/H ratio; 16 wt % MCRT; 5.8 wt % Sulfur; and 1,280 ppm Vanadium;. The undiluted Boscan crude oil after the super critical water treatment was converted into a syncrude with the following properties: 22 API: gravity at 60/60; 9 CST viscosity @40° C.; 7.6 wt % C/H ratio, 2.5 wt % MCRT; 4.6% sulfur; and 130 ppm Vanadium.

[0083] A simulated distillation analysis of the original crude oil vs. the syncrude products from different experimental runs shows that the syncrude prepared in accordance with the present invention clearly has superior properties than the original crude. Specifically, the syncrudes contain a higher fraction of lower-boiling fractions, 51% of the diluted Hamaca crude boils across a range of temperatures of less than 1000° F., while employing a process according to the present invention using supercritical water depending on process configurations, between 79 to 94% of the syncrude boils across a range of temperatures of less than 1000° F. 40% of the undiluted Boscan crude boils across a range of temperatures of less than 1000° F., while employing a process according to the present invention using supercritical water, 93% of the syncrude boils across a range of temperatures of less than 1000° F.

[0084] 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. An apparatus for upgrading a hydrocarbon by reaction with a fluid comprising water under supercritical water conditions comprising:

- a. means for dispersing and mixing the fluid comprising water and the hydrocarbon under conditions which disfavor thermal cracking and formation of coke.
- b. means for injecting a dispersed water-hydrocarbon mixture into is a reaction zone under supercritical water conditions;
- c. a reaction zone having means for maintaining a uniform temperature within said reaction zone; means for controlling the residence time in the reaction zone within determined limits and means for avoiding the settling of inorganic solids within the reaction zone; and
- d. means for recovering an upgraded hydrocarbon.

2. An apparatus according to claim 1, wherein the means for dispersing the fluid comprising water and the hydrocarbon comprise at least one static mixer, spray nozzle, sonic or ultrasonic agitator, thermal siphon or combinations thereof

3. An apparatus according to claim 1, wherein the reaction zone comprises a reactor having means for collecting reaction products and means for accumulating metals or solids.

4. An apparatus according to claim 1 wherein the means for recovering an upgraded hydrocarbon comprises a vessel having a dip tube a cyclone, a filter, a membrane or a packed bed.

5. An apparatus according to claim 1, wherein the reaction zone comprises a tubular reactor having a length to diameter ratio from 50 to 10,000 and a length selected to provide adequate residence time in the reaction zone.

6. An apparatus according to claim 1, wherein the reaction zone comprises a tubular reactor having a length to diameter ratio from 100 to 4,000 and a length selected to provide adequate residence time in the reaction zone.

7. An apparatus according to claim 1 wherein the reaction zone compresses a tubular reactor having a diameter selected to sustain a turbulent flow of reactants to avoid precipitation of solids and a length selected to provide adequate residence time in the reaction zone.

8. An apparatus according to claim 1, wherein the reaction zone comprises at least two reactors.

9. An apparatus according to claim 8 further comprising quenching means between said at least two reactors.

10. An apparatus according to claim 3, wherein a mixer precedes the reactor.

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