UPGRADING HEAVY HYDROCARBON OILS

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 disclosed. The process does not require external supply of hydrogen nor does it use externally supplied catalysts.
FIG. 1

Crude

Mixer

Reactor

Heat Exchanger

Syncrude

Effluent Water

Supercritical Water (SCW)

Dreg Stream (metals, SOx, etc.)

Gases (H2S, CO2, CH4, etc.)
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 (cracking, hydrocracking, hydroisomerization, 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:
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.

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

[0005] 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.

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.

[0006] 5. Coking is often used at refineries or upgrading facilities. Significant amounts of by-product solid coke are rejected during the coking process, readings 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.

[0007] 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 syn crude with highly desirable properties (low sulfur content, low metals content, lower density (higher API), low viscosity, low 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.

[0008] In comparison with the traditional processes for syn crude 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.


[0010] 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.

[0011] 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

[0012] The present invention relates to a process for upgrading hydrocarbons comprising mixing hydrocarbons with a fluid comprising water in a mixing zone to form a mixture; passing the mixture to a reaction zone; reacting the mixture in the 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

[0013] FIG. 1 is a process flow diagram of an embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reactants

[0014] Water and hydrocarbons, preferably heavy hydrocarbons are the two reactants employed in a process according to the present invention.
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, Boscana 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

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

In accordance with the invention, the heavy hydrocarbon feed and the fluid comprising water are contacted in a mixing zone prior to entering the reaction zones. 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.

The oil and water should be heated and mixed so that the combined stream will reach supercritical water conditions in the reaction zone. Various heating sequences may be employed to accomplish this result. For example, oil and water streams may be heated separately at different temperatures so that supercritical water mixes with and heats the remaining oil so that the entire stream will reach supercritical conditions in the reaction zone. Other methods of mixing and heating sequences may be used as will be recognized by those skilled in the art.

Reaction Conditions

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.

"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, H₂ may be formed in-situ during the reaction through steam reforming of hydrocarbons and water-gas-shift reaction.

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.

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 the 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.

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.

Reaction Product Separation

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.

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 (CO₂ and H₂S), 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.

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.

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 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.

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.

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

Thermal Cracking: CₓHᵧ→lighter hydrocarbons
Steam Reforming: CₓHᵧ + 2xH₂O = xCO₂ + (2x+y/2)H₂
Water-Gas-Shift: CO + H₂O = CO₂ + H₂
Demetalization: $\text{C}_8\text{H}_{18}\text{Ni}_2 + \text{H}_2\text{O}/\text{H}_2 \rightarrow \text{NiO}/\text{Ni(OH)}_2 + \text{lighter hydrocarbons}$

Desulfurization: $\text{C}_8\text{H}_{18}\text{S}_2 + \text{H}_2\text{O}/\text{H}_2 \rightarrow \text{H}_2\text{S} + \text{lighter hydrocarbons}$

[0030] 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.

[0031] The following Examples are illustrative of the present inventions but are not intended to limit the invention in any way beyond what is contained in the claims which follow.

**EXAMPLE 1**

Showing Typical Laboratory Process

[0032] FIG. 1 shows a process flow diagram for a laboratory unit for practicing some embodiments of the invention. Oil and supercritical water are contacted in a mixer prior to entering the reactor. The reactor is equipped with an inner tube for collecting the products (syncrude, unreacted water, and gases), 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 clunk-shell 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 3,200-4,000 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.

[0033] 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 Product Syncrude

[0034] 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. 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 supercritical 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.

[0035] 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.

[0036] 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.

[0037] 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 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.

[0038] Undiluted Boscan 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: 9 API gravity at 60/60; 1,140 CST viscosity@40° C.; 8.0 wt % C/H ratio; 16 wt % MCRT; 5.8 wt % Sulphur; and 1,280 ppm Vanadium. The undiluted Boscan crude oil after the supercritical 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.

[0039] 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.

[0040] 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
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 a mixture;
   (b) passing the mixture to a reaction zone;
   (c) reacting the mixture in the reaction zone under super-
       critical water conditions in the absence of externally
       added hydrogen 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 hydrocar-
   bons are heavy hydrocarbons selected from the group con-
   sisting of whole heavy petroleum crude oil, tar sand bitu-
   men, 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 fluid
   comprising water enters the mixing zone at a temperature
   greater than the critical temperature of water.

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 supercriti-
   cal 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 supercriti-
   cal 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 supercriti-
   cal 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 20 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 for upgrading hydrocarbons comprising:
    (a) mixing hydrocarbons with a fluid comprising water in
        a mixing zone to form a mixture;
    (b) passing the mixture to a reaction zone;
    (c) reacting the mixture in the reaction zone under super-
        critical water conditions in the absence of externally
        added hydrogen and 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.

11. A process according to claim 10, wherein the hydro-
    carbons 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.

12. A process according to claim 10, wherein the fluid
    comprising water enters the mixing zone at a temperature
    greater than the critical temperature of water.

13. A process according to claim 10, wherein the condi-
    tions in the mixing zone include a temperature greater than
    the critical temperature of water and a pressure greater than
    the critical pressure of water.

14. A process according to claim 10, wherein the supercriti-
    cal 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.

15. A process according to claim 10, wherein the supercriti-
    cal 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.

16. A process according to claim 10, wherein the supercriti-
    cal 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 20 to 40 minutes.

17. A process according to claim 10, wherein the water is
    drinking water, treated wastewater, untreated wastewater,
    river water, lake water, seawater, produced water or their
    mixtures.

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