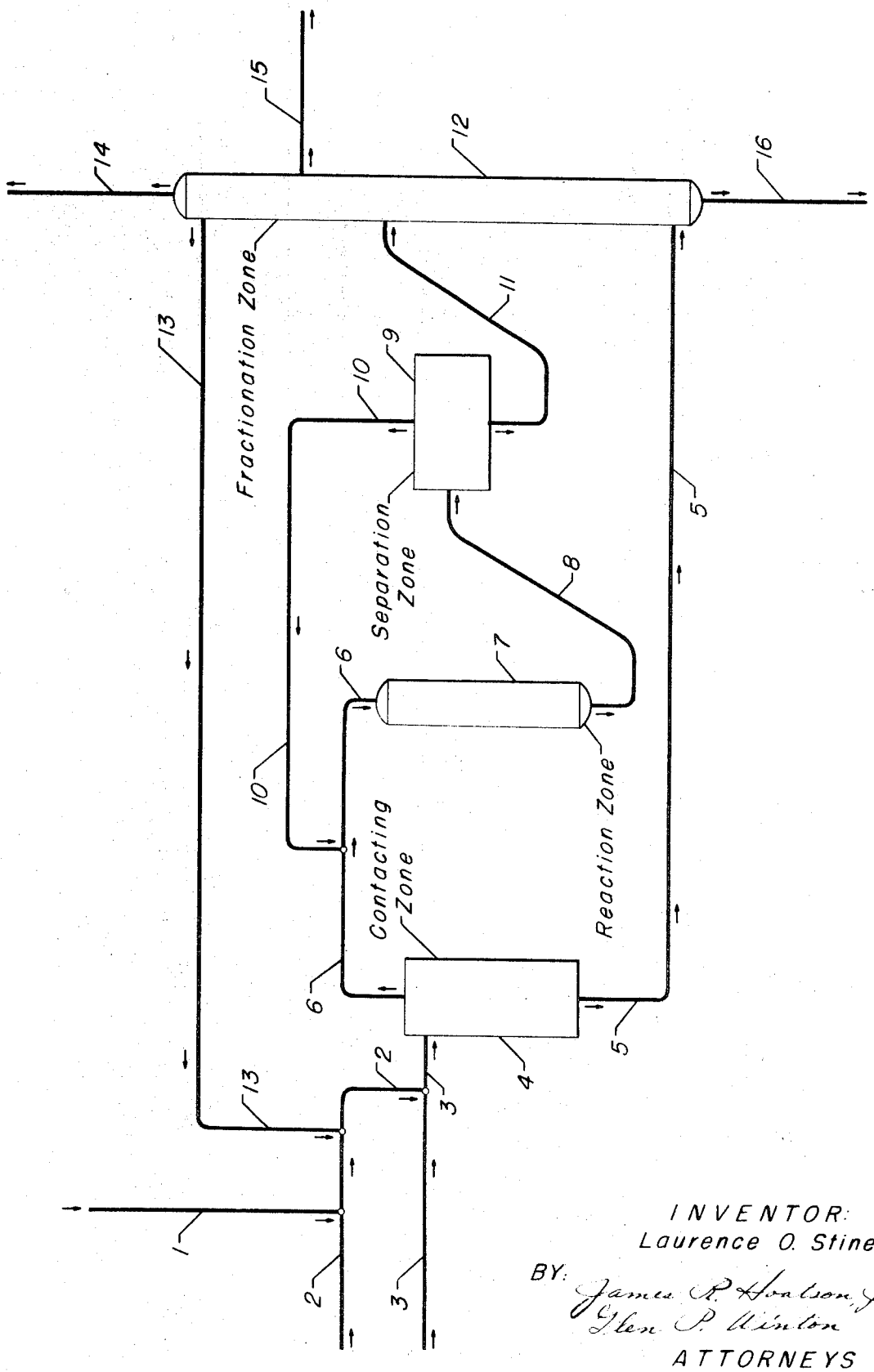
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PETROLEUM CRUDE OIL CONVERSION PROCESS

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PETROLEUM CRUDE OIL CONVERSION PROCESS

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Continuation-in-part of application Ser. No. 758,217, Sept. 9, 1968, now Patent No. 3,544,450, dated Dec. 1, 1970. This application June 22, 1970, Ser. No. 48,371

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ABSTRACT OF THE DISCLOSURE

A petroleum crude oil feedstock is converted into a more valuable hydrocarbon product by a combination process including the steps of contacting the feedstock in a contacting zone with a light hydrocarbon solvent, separating the resulting mixture to provide a light hydrocarbon fraction and a heavy hydrocarbon fraction, hydrorefining the light hydrocarbon fraction, passing a resulting hydrorefined effluent hydrocarbon and the heavy hydrocarbon fraction into a distillation zone, and recovering the desired hydrocarbon product from the distillation zone. The light hydrocarbon solvent contains hydrocarbon having less than six carbon atoms per molecule, and the hydrorefined effluent hydrocarbon contains species having less than six carbon atoms per molecule, whereby at least a portion of the light hydrocarbon solvent passed into the contacting zone is obtained from the distillation zone. The process has particular application to hydrotreating and hydrocracking heavy feedstocks containing a significant quantity of asphaltic materials, organo-metallic complexes, sulfur compounds, and nitrogen compounds, wherein at least about 10% by volume of the feedstock boils at a temperature in excess of about 1050° F.

CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part application based upon co-pending application Ser. No. 758,217, filed on Sept. 9, 1968, now U.S. Pat. No. 3,544,450 issued Dec. 1, 1970.

SUMMARY OF THE INVENTION

The present invention relates to an improved method for the conversion of a petroleum crude oil feedstocks into more valuable products. More particularly, the present invention relates to a method for contacting a petroleum crude oil feedstock with a light hydrocarbon solvent in a contacting zone maintained under contacting conditions wherein a heavy hydrocarbon fraction having an initial boiling point above about 650° F. is separated from a light hydrocarbon fraction having an end boiling point in the range of from about 650° F. to about 850° F. This light hydrocarbon fraction is subsequently catalytically converted into more valuable products while the heavy hydrocarbon fraction bypasses the catalytic reaction zone of the process and is subsequently processed in a fractionation zone with the hydrorefined effluent.

As used herein, the term "petroleum crude oil feedstock" is meant to include heavy oils extracted from tar sands, topped or reduced crudes, vacuum residuum (vacuum tower bottoms products), and especially those petroleum crude oils referred to as "black oils" which contain a significant quantity of asphaltic materials and high concentrations of sulfur, as well as large quantities of nitrogenous compounds and high molecular weight organometallic complexes, principally comprising nickel and vanadium. These "black oils" include those hydrocarbon charge stocks wherein at least about 10% by volume boils above a temperature of about 1050° F.

These black oils usually have an API gravity at 60° F. of less than 20.0, and sulfur concentrations are usually more than 1% by weight and often in excess of 3% by weight.

In brief, the present invention provides an improved method for converting such contaminated petroleum crude oils, and especially black oils, to more valuable products inasmuch as the inventive process sharply reduces the sulfur and asphaltic content of the charge passing to the hydrorefining reaction zone so that a significant proportion of the charge can be more easily converted into distillable hydrocarbons boiling below about 1050° F.

Therefore, it is an object of this invention to provide an improved process for the conversion of a petroleum crude oil feedstock, wherein a heavy fraction of the feedstock comprising major amounts of asphaltenes, organo-metallic complexes, carbon residue precursors, and dirt, is separated in a contacting zone from a light fraction of the feedstock so that the heavy fraction is caused to bypass the reactor section of the process. This heavy fraction is subsequently combined in the fractionation section of the process with that non-distillable material, if any, remaining in the effluent produced by the catalytic conversion of the light fraction.

Therefore, in accordance with one embodiment of the present invention, there is provided a method for the conversion of a petroleum crude oil feedstock including the steps of contacting the feedstock with a light solvent comprising hydrocarbon having less than six carbon atoms per molecule, in a contacting zone maintained under contacting conditions wherein a heavy fraction of the feedstock is separated from a light fraction of the feedstock; passing the heavy fraction into a fractionation zone maintained under distillation conditions; passing the light fraction in admixture with a hydrogen-containing gas stream to a catalytic reaction zone maintained under conversion conditions, wherein the light fraction is at least partially converted into more valuable products; passing the effluent of the catalytic reaction zone into the fractionation zone; and withdrawing from the fractionation zone, normally gaseous components, a first fraction containing hydrocarbon having less than six carbon atoms per molecule, a second fraction containing a desired hydrocarbon product, and a third fraction comprising the heavy fraction of the feedstock.

DESCRIPTION OF THE DRAWINGS

This invention can be most clearly described and illustrated with reference to the attached drawing. While of necessity, certain limitations must be present in such schematic descriptions, no intention is meant thereby to limit the generally broad scope of this invention.

As stated hereinabove, the first step of the method of the present invention comprises contacting a petroleum crude oil feedstock with a light solvent comprising hydrocarbon having less than six carbon atoms per molecule, in a contacting zone maintained under contacting conditions wherein a heavy fraction is separated from a light fraction. In the drawing, this first step is represented as taking place in contacting zone **4**. The contacting zone must be furnished with the petroleum crude oil feedstock and the light hydrocarbon solvent. In the drawing, which illustrates a preferred embodiment of the present invention, there is provided line **1** for passage of a reaction gas, such as hydrogen, to admix with a light hydrocarbon solvent stream flowing in line **2**. The resulting mixture enters line **3** via line **2**, wherein it is combined with the petroleum crude oil feedstock passing via line 3 into contacting zone **4**.

Contacting zone **4** may be equipped with heat exchange means, heating means, and the like and is usually maintained under liquid-liquid contacting conditions in-

cluding a temperature of from about 100° F. to 500° F., preferably a temperature of from about 300° F. to 400° F., at a pressure in the range of from about atmospheric pressure to about 25 atmospheres, preferably 10 to 20 atmospheres, and at a volumetric ratio of light hydrocarbon solvent to petroleum crude oil feedstock in the range of from about 0.5 to about 5.0, and preferably at a ratio of 2.0 or less. A heavy hydrocarbon fraction of the feedstock is thus separated from a light hydrocarbon fraction of the feedstock in this contacting zone **4**.

The heavy fraction is then passed via line **5** from contacting zone **4** into fractionation zone **12**, hereinafter described, which is maintained under distillation conditions. The light fraction is passed from contacting zone **4** via line **6** into catalytic reaction zone **7**, entering zone **7** in admixture with a hydrogen-containing gas stream which enters line **6** via line **10** from a source hereinafter described. The catalytic reaction zone **7** is maintained under hydrocarbon conversion conditions wherein the light hydrocarbon fraction of the feedstock is at least partially converted into more valuable products.

In a preferred embodiment, the process of this invention is particularly applicable to the hydrorefining of a petroleum crude oil feedstock as defined hereinabove. Reaction zone **7** is of the conventional type having one or more beds of conversion catalyst disposed therein. The reaction zone may be equipped with heat transfer means, baffles, trays, heating means, etc. The reaction zone is preferably of the adiabatic or semi-adiabatic type, and the feed to the reaction zone will therefore be provided with the requisite amount of heat prior to passage thereof into the bed or beds of conversion catalyst. The actual operation of the reaction zone may be upflow, downflow, or radial flow through the catalyst.

A preferred hydrorefining catalyst which may be utilized in the process of the present invention can be characterized as a hydrotreating or a hydrocracking catalyst of the type well known in the art, comprising a metallic component possessing hydrogenation activity, which is composited with a refractory inorganic oxide carrier material which may be of either synthetic or natural origin. The precise composition and method of manufacturing the catalytic composition is not considered to be an essential element of the present process.

However, a particularly suitable catalyst for use in the inventive process comprises a refractory inorganic oxide carrier material such as alumina, silica, zirconia, magnesia, titania, boria, strontia, hafnia, etc., and mixtures thereof including silica-alumina, silica-zirconia, silica-magnesia, silica-titania, alumina-zirconia, silica-alumina-boron phosphate, alumina-magnesia, alumina-titania, magnesia-zirconia, titania-zirconia, magnesia-titania, silica-alumina-zirconia, silica-alumina-magnesia, silica-alumina-titania, silica-magnesia-zirconia, silica-alumina-boria. It is preferred to utilize a carrier material containing at least a portion of silica, and it is particularly preferred to utilize a composition of alumina and silica.

Suitable metallic components for hydrogenation activity are those selected from the group consisting of the metals of Groups IV–B and VIII of the Periodic Table. Thus, the catalytic composition may comprise one or more metallic components selected from the group consisting of molybdenum, tungsten, chromium, iron, cobalt, nickel, platinum, palladium, iridium, osmium, rhodium, ruthenium, and mixtures thereof. The concentration of the catalytically active metallic component or components is primarily dependent upon the particular metal utilized, as well as upon the composition characteristics of the light fraction of the crude oil feedstock which enters reaction zone **7** via line **6**. The Group VI–B metal, such as chromium, molybdenum or tungsten, is usually preferred in an amount of from about 0.5% to about 10.0% by weight of the catalyst. The Group VII metal, which may be divided into the iron subgroup and the noble metal subgroup, is preferred in an amount of about 0.1% to about 10.0% by weight of the total catalyst. When an iron subgroup metal such as iron, cobalt or nickel, etc. is employed, it is preferred in an amount of from about 0.2% to about 10.0% by weight. When a noble metal subgroup metal such as platinum, palladium, or iridium, etc., is employed, it is preferred to utilize an amount within the range of from about 0.1% to about 5.0% by weight of the total catalyst.

When utilizing a hydrorefining catalyst such as described above, reaction zone **7** is maintained under hydrorefining conversion conditions including a temperature of from about 600° F. to about 1,000° F. as normally measured at the inlet to each fiixed bed of catalyst disposed within reaction zone **7**. The reaction zone effluent passing via line **8** from reaction zone **7** to separation zone **9** will normally be at a temperature which is higher than that of the reactor inlet due to the exothermic nature of the reactions being effected within the catalyst bed. For purposes of temperature control, hydrogen is passed into reaction zone **7** via lines **10** and **6**, as hereinafter described. Additional hydrogen may also enter line **6** via lines **1**, **2**, and **3**. The hydrogen is passed to the reaction zone in an amount which is usually less than about 10,000 s.c.f./bbl., and at a selected operating pressure which is usually maintained in the range of from about 1,000 to 4,000 p.s.i.g. The liquid hourly space velocity (being defined as the volume of liquid hydrocarbon change per hour per volume of catalyst disposed within the reaction zone) is maintained, typically, in the range of from about 0.25 to about 4.0.

As set forth hereinabove, the light fraction of the crude oil feedstock passing from contacting zone **4** into reaction zone **7**, is at least partially converted into more valuable products in reaction zone **7**. The resulting effluent from reaction zone **7** is passed via line **8** into separation zone **9**. This effluent stream, typically, contains normally gaseous inorganic components, such as hydrogen and hydrogen sulfide, normally gaseous hydrocarbons, and normally liquid hydrocarbons which are separated into liquid and vapor phases in separation zone **9**, which is a reactor effluent separation zone of typical prior art configuration maintained under typical phase separation conditions. Separation zone **9** may comprise a series of high pressure, low temperature separation vessels from which a net hydrogen-rich vapor or gas stream is withdrawn via line **10** and recycled via lines **10** and **6** to reaction zone **7**, while a net hydrocarbon-containing liquid stream is passed via line **11** from separation zone **9** to fractionation zone **12**. It is contemplated within the scope of this invention that any number of hot flash and/or cold flash systems utilized in conjunction with a series of hot and/or cold separators maintained in series flow or parallel flow or a combination of both flows, at different temperatures and pressures, may be included within the generally broad scope of separation zone **9**.

Fractionation zone **12** may be of a conventional type and is utilized for obtaining an overhead fraction containing normally gaseous constituents such as hydrogen, methane, ethane, etc., a first intermediate fraction comprising hydrocarbon having less than six carbon atoms per molecule, a second intermediate fraction containing desired valuable hydrocarbon product, such as gasoline or jet fuel, and a bottoms fraction comprising a major portion of the heavy fraction as removed via line **5** from contacting zone **4**. The fractionation zone **12** may be a series of fractional distillation columns. In the preferred embodiment of this invention, fractionation zone **12** is represented as being a single distillation column and is operated at conditions of temperature and pressure so that the desired fractions can be recovered therefrom.

Referring to the drawing, an overhead fraction containing normally gaseous constituents is removed from fractionation zone **12** via line **14**. A first intermediate

fraction comprising hydrocarbon having less than six carbon atoms per molecule is removed from fractionation zone **12** via line **13**, and at least a portion is recycled via line **13** to line **2** for subsequent passage to contacting zone **4** via lines **2** and **3**. A second intermediate fraction containing desired valuable hydrocarbon product is removed from fractionation zone **12** and sent to product storage (not shown) via line **15**. The bottoms fraction comprising a major portion of the heavy fraction from the contacting zone **4** is removed from fractionation zone **12** via line **16**. This bottoms fraction may be discarded, burned as fuel, treated for metals recovery, sent to furher processing or, if desired, recycled in part through means (not shown) back to line **3** for further contacting in contacting zone **4**.

PREFERRED EMBODIMENTS

From the foregoing discussion, the method of operation of the present invention, as well as the advantages thereof, will be readily apparent to those skilled in the art.

In particular, it is to be noted that by having the heavy fraction of the crude oil feedstock which is separated within contacting zone **4** completely bypass the hydrorefining reaction zone **7**, the asphaltenes, organo-metallic complexes, carbon residue precursors and the like do not become involved in the hydrorefining reaction and longer catalyst life is obtained in reaction zone **7**. In addition, higher and more selective yields of the desired more valuable product or products can be achieved when processing the light fraction of the feedstock within reaction zone **7** under conditions which include substantial freedom from asphalteness, organo-metallic complexes, and carbon residue precursors. The absence of these heavy contaminants in the hydrorefining reaction zone allows the light fraction of the feelstock to be hydrogenated at a lower catalytic severity, thereby enhancing catalyst selectivity as well as catalyst life.

Furthermore, in hydrorefining the light fraction in accordance with the inventive process in the presence of a hydrotreating or a hydrocracking catalyst, the light fraction will not only be more easily desulfurized, denitrogenated and saturated, but the resulting hydrorefining effluent will typically contain a substantial quantity of light hydrocarbon having less than six carbon atoms per molecule which will be recovered in fractionation zone **12**. Additionally, any light solvent which may be lost in the heavy fraction of the feedstock will be recovered, since the heavy fraction passes from contacting zone **4** into fractionation zone **12**. Thus the process of the present invention not only minimizes loss of the light solvent, but it is also capable of producing light solvent sufficient to compensate for any extraneous loss of light solvent from the process.

As previously noted hereinabove, the light solvent which is utilized in the contacting zone of the inventive process is a hydrocarbon solvent containing hydrocarbon species having less than six carbon atoms per molecule. It is particularly preferred that the light solvent be selected from the group consisting of propane, butane, pentane, and mixtures thereof.

In summary, a preferred embodiment of the present invention may now be characterized as a method for the conversion of a petroleum crude oil feedstock into a more valuable hydrocarbon product which comprises: (a) contacting the feedstock with a light solvent containing hydrocarbon having less than six carbon atoms per molecule, in a contacting zone maintained under contacting conditions wherein a heavy hydrocarbon fraction is separated from a light hydrocarbon fraction; (b) passing the heavy hydrocarbon fraction to a fractionation zone maintained under distillation conditions, and passing the light hydrocarbon fraction in admixture with a hydrogen-containing gas stream to a hydrorefining reaction zone containing a hydrorefining catalyst maintained under hydrorefining conversion conditions wherein the light hydrocarbon fraction is at least partially converted into a more valuable product; (c) passing an effluent stream containing hydrogen, normally gaseous hydrocarbon and normally liquid hydrocarbon from the reaction zone to a separation zone maintained under separation conditions; (d) passing a hydrogen-containing gas stream from the separation zone to the reaction zone and a hydrocarbon-containing liquid stream from the separation zone to the fractionation zone; (e) withdrawing from the fractionation zone a first fraction containing normally gaseous components, a second fraction containing hydrocarbon having less than six carbon atoms per molecule, a third fraction containing desired more valuable hydrocarbon product, and a fourth fraction comprising at least a major portion of the heavy hydrocarbon fraction specified in Step (b); and, (f) passing at least a portion of the second fraction into the contacting zone to provide at least a part of the light solvent.

The invention claimed:

1. A method for the conversion of a petroleum crude oil feedstock into a more valuable hydrocarbon product which comprises:

(a) contacting said feedstock with a light solvent containing hydrocarbon having less than six carbon atoms per molecule, and separating the resulting mixture into a heavy hydrocarbon fraction and a light hydrocarbon fraction;

(b) subjecting said light hydrocarbon fraction to catalytic hydrorefining in a reaction zone;

(c) passing the normally liquid hydrocarbon portion of the effluent from said reaction zone to a fractional distillation zone;

(d) bypassing said heavy hydrocarbon fraction around said reaction zone and introducing said heavy hydrocarbon fraction into said distillation zone; and

(e) withdrawing from said distillation zone a first fraction comprising hydrocarbon having less than six carbon atoms per molecule a second fraction comprising said desired more valuable hydrocarbon product, and a bottoms fraction comprising a major portion of said heavy hydrocarbon fraction specified in step (d).

2. The method according to claim **1** wherein at least a portion of said first fraction is recycled to step (a) to provide at least a part of said light solvent.

3. The method according to claim **1** wherein said crude oil feedstock is admixed with hydrogen.

4. The method according to claim **1** wherein said contacting is effected at a temperature of from about 100° F. to 500° F., at a pressure in the range of from about atmospheric pressure to about 25 atmospheres, and at a volumetric ratio of light solvent to crude oil feedstock in the range of from about 0.5 to 5.0.

5. A method for the conversion of a petroleum crude oil feedstock into a more valuable hydrocarbon product which comprises the steps of:

(a) contacting said feedstock with a light solvent containing hydrocarbon having less than six carbon atoms per molecule, in a contacting zone maintained under contacting conditions wherein a heavy hydrocarbon fraction is separated from a light hydrocarbon fraction;

(b) passing said heavy hydrocarbon fraction to a fractionation zone maintained under distillation conditions, and passing said light hydrocarbon fraction in admixture with a hydrogen-containing gas stream to a hydrorefining reaction zone containing a hydrorefining catalyst maintained under hydrorefining conversion conditions wherein said light hydrocarbon fraction is at least partially converted into a more valuable hydrocarbon product;

(c) passing an effluent stream containing hydrogen, normally gaseous hydrocarbon and normally liquid hydrocarbon from said reaction zone to a separation zone maintained under separation conditions;

(d) passing a hydrogen-containing gas stream from said separation zone to said reaction zone and a hydrocarbon-containing liquid stream from said separation zone to said fractionation zone;

(e) withdrawing from said fractionation zone a first fraction containing normally gaseous components, a second fraction containing hydrocarbon having less than six carbon atoms per molecule, a third fraction containing desired more valuable hydrocarbon product, and a fourth fraction comprising at least a major portion of said heavy hydrocarbon fraction specified in Step (b); and,

(f) passing at least a portion of said second fraction into said contacting zone to provide at least a part of said light solvent.

6. The method according to claim **5** wherein said crude oil feedstock is admixed with hydrogen.

7. The method according to claim **5** wherein said contacting zone is maintained at a temperature in the range of from about atmospheric pressure to about 25 atmospheres, and at a volumetric ratio of light solvent to crude oil feedstock in the range of from about 0.5 to 5.0.

8. The method according to claim **5** wherein said light solvent comprises at least one hydrocarbon selected from the group consisting of propane, butane, and pentane.

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