

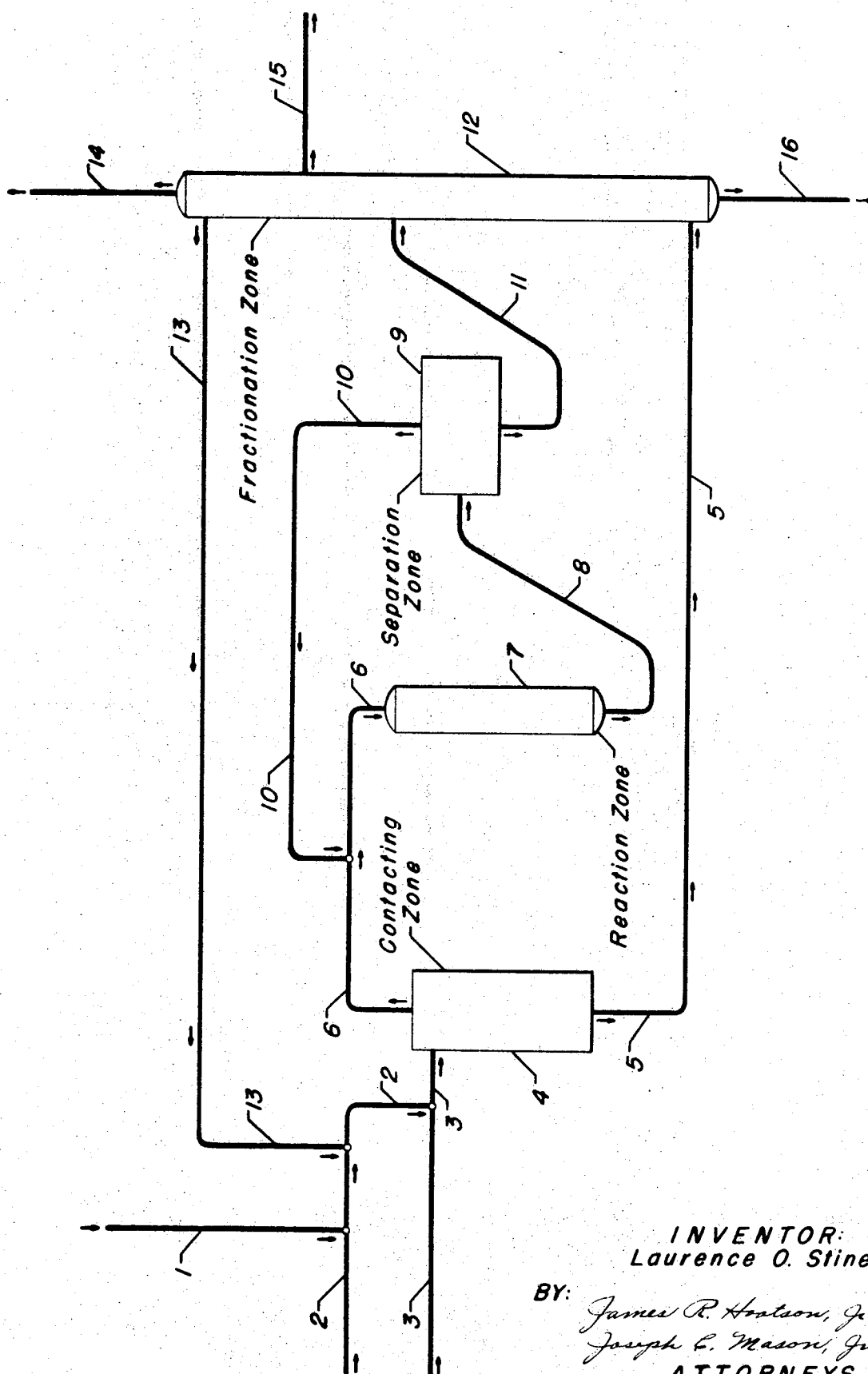
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PETROLEUM CRUDE OIL CONVERSION PROCESS

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PETROLEUM CRUDE OIL CONVERSION PROCESS
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7 Claims

ABSTRACT OF THE DISCLOSURE

A petroleum crude oil feedstock is converted into more valuable products by a combination process including the steps of contacting, separation, catalytic conversion and further separation and recovery.

BACKGROUND OF THE INVENTION

This invention relates to a method for the conversion of a petroleum crude oil feedstock into more valuable products. Further, this invention specifically relates to a method for contacting a petroleum crude oil feedstock with a C_6 - C_8 containing naphtha stream in a contacting zone maintained under contacting conditions wherein a heavy fraction stream having an initial boiling point above about 650° F. is separated from a light fraction stream having an end boiling point of from above about 650° F. to 850° F. This light fraction stream is subsequently catalytically converted into more valuable products while the heavy fraction stream bypasses the catalytic reaction portion of the process and is subsequently separated in a fractionation zone.

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 organo-metallic complexes principally comprising nickel and vanadium. These "black oils" include those hydrocarbon charge stocks of which 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 further, sulfur concentrations are usually more than 1% by weight and often in excess of 3% by weight.

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

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

Therefore, in accordance with one embodiment of my invention, there is provided a method for the conversion of a petroleum crude oil feedstock including the steps of contacting this feedstock with a C_6 - C_8 containing naphtha stream in a contacting zone maintained under contacting conditions, wherein a heavy fraction stream is separated

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from a light fraction stream with the heavy fraction stream, being then passed into a fractionation zone maintained under distillation conditions, and the light fraction stream in admixture with a hydrogen containing gas stream being passed to a catalytic reaction zone maintained under conversion conditions, wherein the light fraction stream is at least partially converted into more valuable products and, from the effluent of the catalytic reaction zone, normally gaseous components, and normally gaseous and normally liquid conversion products, including a C_6 - C_8 containing naphtha stream are separated and recovered.

DESCRIPTION OF THE DRAWING

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 C_6 - C_8 containing naphtha stream in a contacting zone maintained under contacting conditions wherein a heavy fraction stream is separated from a light fraction stream. 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 C_6 - C_8 containing naphtha stream. In the drawing, which illustrates a preferred embodiment of my invention, there is provided line 1 for passage of a reaction gas such as hydrogen to admix with a C_6 - C_8 containing naphtha stream in line 2 for admixture 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 contacting conditions including a temperature of from about 100° F. to 500° F., and preferably a temperature of from about 300° F. to 400° F., and a pressure in the range of from about atmospheric to about 25 atmospheres, preferably 10 to 20 atmospheres, and a C_6 - C_8 containing naphtha stream to petroleum crude oil feedstock ratio of from about 0.5 to 5.0, and preferably from about .0 to 2.0. A heavy fraction stream is thus separated from a light fraction stream in this contacting zone.

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

In a preferred embodiment, the process of this invention is particularly applicable to the hydrotreating of a petroleum crude oil feedstock as defined hereinabove. Reaction zone 7 is of the conventional type with the conversion catalyst disposed therein in the reaction zone. The reaction zone may be equipped with heat transfer means, baffles, trays, heating means, etc. The reaction zone is preferably of the adiabatic type and thus feed to the reaction zone will preferably be provided with the requisite amount of heat prior to passage thereof to said reaction zone. The actual operation of the reaction zone may be upflow, downflow, or radial flow. A preferred hydrotreating catalyst which may be utilized in the process of the present invention can be characterized as comprising a metallic component possessing hydrogenation activity, which component is composited with a refractory inorganic oxide carrier material which may be of either syn-

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thetic 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 my invention would comprise 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 composite 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 the characteristics of the charge stock. 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 VIII metals, which may be divided into two subgroups, namely the iron subgroup and the noble metal subgroup, are preferred in an amount of about 0.1% to about 10% 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 hydrotreating catalyst such as described above, reaction zone 7 is maintained under hydrotreating conversion conditions including a temperature of from about 600° F. to about 1,000° F. as measured at the inlet to the fixed bed of the catalyst disposed within reaction zone 7. The reaction zone effluent passing via line 8 to separation zone 9 will be at a higher temperature than that of the reactor inlet due to the exothermic nature of the reactions being effected. Hydrogen, via lines 6 and 10, as hereinafter described, as well as via lines 1, 2, and 3, is passed to the reaction zone in an amount usually less than about 10,000 s.c.f./bbl., and at the 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 charge per hour per volume of catalyst disposed within the reaction zone) is maintained in the range of from about 0.25 to about 4.0.

As set forth hereinabove, the light fraction stream from contacting zone 4 is at least partially converted into more valuable products in reaction zone 7. The effluent passing from reaction zone 7 via line 8, is passed to separation zone 9. This effluent stream contains normally gaseous components, normally gaseous hydrocarbons, and normally liquid hydrocarbons which pass directly to separation zone 9 which is maintained under separation conditions hereinafter defined.

Separation zone 9 may be a series of high pressure, low temperature separation vessels from which a hydrogen-rich gas stream via line 10 is withdrawn, and recycled via lines 10 and 6 to reaction zone 7. A hydrocarbon-containing stream is then passed via line 11 from separation zone 9 to fractionation zone 12. It is also contemplated within the scope of this invention that any number of hot flash

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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 pressure is included within the generally broad scope of my separation zone 9.

Fractionation zone 12 may be of a conventional type and is utilized for obtaining an overhead fraction containing normally gaseous hydrocarbons, a first intermediate fraction comprising a C_6 - C_8 containing naphtha fraction, a second intermediate fraction containing desired valuable hydrocarbon product, and a bottoms fraction fraction comprising a major portion of the heavy fraction as removed from contacting zone 4. The fractionation zone 12 may be a series of fractional distillation columns. In the present preferred embodiment of this invention, fractionation zone 12 is represented as being a single distillation column and operated at conditions of temperature and pressure so that the desired fractions can be recovered therefrom. In the drawing, an overhead fraction containing normally gaseous hydrocarbon is removed from fractionation zone 12 via line 14. A first intermediate fraction comprising a C_6 - C_8 containing naphtha fraction is removed from fractionation zone 12 via line 13 and recycled to line 2 for 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 storage (not shown) via line 15. The bottoms fraction comprising a major portion of the heavy fraction stream from the contacting zone is removed from fractionation zone 12 via line 16. This bottoms fraction may be discarded, treated for metals recovery or, if desired, recycled through means not shown back to line 3 for further contacting in contacting zone 4.

Thus, by having the heavy fraction stream from contacting zone 4 completely bypass the hydrotreating reaction zone, the asphaltenes, organo-metallic complexes, carbon residue precursors and the like do not become involved in the hydrotreating reaction and longer catalyst life and higher, more selective yields of product can be achieved when processing the light fraction stream obtained by contacting the petroleum oil feedstock with the C_6 - C_8 containing naphtha stream in the contacting zone.

The invention claimed:

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

- (a) contacting said feedstock with a C_6 - C_8 naphtha and separating the resulting mixture into a heavy fraction and a light fraction;
- (b) subjecting said light fraction to catalytic hydrotreating 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 fraction around said reaction zone and introducing the heavy fraction into said distillation zone; and
- (e) withdrawing from said distillation zone a first fraction comprising C_6 - C_8 naphtha, a second intermediate fraction comprising desired valuable hydrocarbon product, and a bottoms fraction comprising a major portion of said heavy fraction as specified in step (d).

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

3. The method according to claim 1 wherein said contacting is effected at a temperature of from about 100° F. to 500° F. and a pressure in the range of from about atmospheric to about 25 atmospheres and a C_6 - C_8 containing naphtha stream to crude oil feedstock ratio of from about 0.5 to 5.0.

4. The method according to claim 1 wherein at least a portion of said first intermediate fraction is recycled to step (a) as said C_6 - C_8 naphtha.

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

- (a) contacting said feedstock with a C_6-C_8 containing naphtha stream in a contacting zone maintained under contacting conditions wherein a heavy fraction stream is separated from a light fraction stream;
- (b) passing said heavy fraction stream to a lower section of a fractionation zone maintained under distillation conditions and passing said light fraction stream 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 fraction stream is at least partially converted into more valuable products;
- (c) passing an effluent stream containing normally gaseous components, normally gaseous hydrocarbons and normally liquid hydrocarbons from said reaction zone directly to a separation zone maintained under separation conditions wherein said hydrogen-containing gas stream is recycled to said reaction zone and a hydrocarbon-containing stream is passed to said fractionation zone;
- (d) withdrawing from said fractionation zone an overhead fraction containing normally gaseous hydrocarbons, a first intermediate fraction comprising a C_6-C_8

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containing naphtha fraction, a second intermediate fraction containing desired valuable hydrocarbon product, a bottoms fraction comprising a major portion of said heavy fraction as specified in Step (b); and,

- (e) passing at least a portion of said first intermediate fraction into admixture with said C_6-C_8 containing naphtha stream as specified in Step (a).
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 of from about 100° F. to 500° F. and a pressure in the range of from about atmospheric to about 25 atmospheres and a C_6-C_8 containing naphtha stream to crude oil feedstock ratio of from about 0.5 to 5.0.

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