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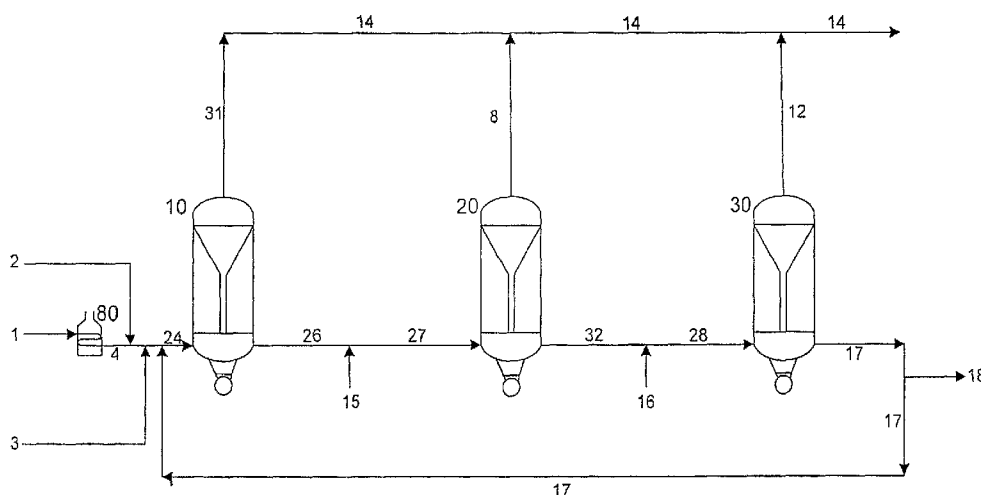
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(54) Title: PROCESS FOR UPGRADING HEAVY OIL USING A REACTOR WITH A NOVEL REACTOR SEPARATION SYSTEM



(57) Abstract: Applicants have developed a new residuum full hydroconversion slurry reactor system that allows the catalyst, unconverted oil, hydrogen, and converted oil to circulate in a continuous mixture throughout an entire reactor with no confinement of the mixture. The mixture is separated internally, within one of more of the reactors, to separate only the converted oil and hydrogen into a vapor product while permitting the unconverted oil and the slurry catalyst to continue on into the next sequential reactor as a liquid product. A portion of the unconverted oil is then converted to lower boiling point hydrocarbons in the next reactor, once again creating a mixture of unconverted oil, hydrogen, converted oil, and slurry catalyst. Further hydroprocessing may occur in additional reactors, fully converting the oil. The oil may alternately be partially converted, leaving a concentrated catalyst in unconverted oil which can be recycled directly to the first reactor.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

5 PROCESS FOR UPGRADING HEAVY OIL USING A REACTOR
 WITH A NOVEL REACTOR SEPARATION SYSTEM

FIELD OF THE INVENTION

10 The instant invention relates to a process for upgrading heavy oils using a slurry catalyst composition.

BACKGROUND OF THE INVENTION

15 There is an increased interest at this time in the processing of heavy oils, due to larger worldwide demand for petroleum products. Canada and Venezuela are sources of heavy oils. Processes which result in complete conversion of heavy oil feeds to useful products are of particular interest.

20 U.S. Patent No. 6,278,034 recites a hydrogenation process which employs a reactor having an internal means of separating gaseous product from a slurry of oil and catalyst.

 The following patent applications, which are incorporated by reference, are
25 directed to the preparation of highly active slurry catalyst compositions and their use in processes for upgrading heavy oil:

 U.S. Serial No. 10/938,202 is directed to the preparation of a catalyst
composition suitable for the hydroconversion of heavy oils. The catalyst
30 composition is prepared by a series of steps, involving mixing a Group VIB metal oxide and aqueous ammonia to form an aqueous mixture, and sulfiding the mixture to form a slurry. The slurry is then promoted with a Group VIII metal. Subsequent steps involve mixing the slurry with a hydrocarbon oil and combining the resulting mixture with hydrogen gas and a second hydrocarbon
35 oil having a lower viscosity than the first oil. An active catalyst composition is thereby formed.

5 U.S. Serial No. 10/938,003 is directed to the preparation of a slurry catalyst composition. The slurry catalyst composition is prepared in a series of steps, involving mixing a Group VIB metal oxide and aqueous ammonia to form an aqueous mixture and sulfiding the mixture to form a slurry. The slurry is then promoted with a Group VIII metal. Subsequent steps involve mixing the slurry
10 with a hydrocarbon oil, and combining the resulting mixture with hydrogen gas (under conditions which maintain the water in a liquid phase) to produce the active slurry catalyst.

U.S. Serial No. 10/938,438 is directed to a process employing slurry catalyst
15 compositions in the upgrading of heavy oils. The slurry catalyst composition is not permitted to settle, which would result in possible deactivation. The slurry is recycled to an upgrading reactor for repeated use and products require no further separation procedures for catalyst removal.

20 U.S. Serial No. 10/938,200 is directed to a process for upgrading heavy oils using a slurry composition. The slurry composition is prepared in a series of steps, involving mixing a Group VIB metal oxide with aqueous ammonia to form an aqueous mixture and sulfiding the mixture to form a slurry. The slurry is then promoted with a Group VIII metal compound. Subsequent steps
25 involve mixing the slurry with a hydrocarbon oil, and combining the resulting mixture with hydrogen gas (under conditions which maintain the water in a liquid phase) to produce the active slurry catalyst.

U.S. Serial No. 10/938,269 is directed to a process for upgrading heavy oils
30 using a slurry composition. The slurry composition is prepared by a series of steps, involving mixing a Group VIB metal oxide and aqueous ammonia to form an aqueous mixture, and sulfiding the mixture to form a slurry. The slurry is then promoted with a Group VIII metal. Subsequent steps involve mixing the slurry with a hydrocarbon oil and combining the resulting mixture with
35 hydrogen gas and a second hydrocarbon oil having a lower viscosity than the first oil. An active catalyst composition is thereby formed.

5

SUMMARY OF THE INVENTION

A process for the hydroconversion of heavy oils, said process employing an upflow reactor with a separator located internally to do phase separation. At least one reactor with an internal separator may be employed, although it is more common to use reactors in series. A hydroconversion process with
10 reactors in series may employ the following steps:

- 15 (a) combining a heated heavy oil feed, an active slurry catalyst composition and a hydrogen-containing gas to form a mixture;
- (b) passing the mixture of step (a) to the bottom of a reactor, which is maintained at hydroprocessing conditions, including elevated temperature and pressure;
- 20 (c) separating internally in the reactor a stream comprising reaction products, hydrogen gas, unconverted oil, and slurry catalyst into two streams, a vapor stream comprising reaction products and hydrogen, and a liquid stream comprising unconverted material and slurry catalyst.
- 25 (d) passing the vapor stream overhead to further processing, and passing at least a portion of the liquid stream, to the next reactor in series.

30 This invention is intended to perform phase separation within one or more reactors in the process scheme depicted, so that a single vapor phase product is the only product leaving the top of the reactor. A liquid phase product is the only stream leaving the lower portion of the reactor (through the bottom or side) for further processing. If internal separation occurs, there is no
35 need for a hot high pressure separator or flash drum to separate the phase following their exit from the reactor.

- 5 The instant invention further employs a reactor differential pressure control system that regulates the vapor product leaving the top of the reactor, thus making a control valve on the feed stream to the next reactor unnecessary.

BRIEF DESCRIPTION OF THE FIGURE

10

The Figure shows the process scheme of this invention as applied to a multiple reactor system in series.

DETAILED DESCRIPTION OF THE INVENTION

15

The instant invention is directed to a process for catalyst activated slurry hydrocracking. Interstage separation of gaseous reaction products and liquid streams comprising unconverted oil and catalyst is effective in maintaining heat balance in the process. In the Figure, stream 1 comprises a heavy feed, such as vacuum residuum. Other feeds may include atmospheric residuum, vacuum residuum, tar from a solvent deasphalting unit, atmospheric gas oils, vacuum gas oils, deasphalted oils, olefins, oils derived from tar sands or bitumen, oils derived from coal, heavy crude oils, synthetic oils from Fischer-Tropsch processes, and oils derived from recycled oil wastes and polymers.

25

The feed enters furnace 80 where it is heated, exiting in stream 4. Stream 4 combines with a hydrogen containing gas (stream 2), recycle slurry (stream 17), and a stream comprising an active slurry composition (stream 3), resulting in a mixture (stream 24). Stream 24 enters the bottom of the first reactor 10. Vapor Stream 31 exits the top of the reactor comprising primarily reaction products and hydrogen, due to a separation apparatus inside the reactor (not shown). Liquid stream 26, which contains slurry in combination with unconverted oil, exits the bottom, or side, of reactor 10.

35

Stream 26 is combined with a gaseous stream comprising hydrogen (stream 15) to create stream 27. Stream 27 enters the bottom of second reactor 20.

5. Vapor stream 8, comprising primarily reaction products and hydrogen, exits the top of the reactor 20 and joins the vapor product from reactor 20. Liquid stream 27, which contains slurry in combination with unconverted oil, exits the bottom, or side, of reactor 20.
- 10 Stream 32 is combined with a gaseous stream comprising hydrogen (stream 16) to create stream 28. Stream 28 enters the bottom of reactor 30. Vapor stream 12, comprising primarily reaction products and hydrogen, exits the top of the reactor and joins the vapor product from the first two reactors. in stream 14. Liquid stream 17, which contains slurry in combination with unconverted
- 15 oil, exits the bottom, or side, of reactor 30. A portion of this stream may be drawn off as stream 18 or recycled back to the first reactor 10, as stream 17..

Overhead streams from reactors 10, 20 and 30 (streams 31, 8 and 12 respectively) create stream 14, which passes to downstream equipment for

20 further processing.

The preferred type of reactor in the instant invention is a liquid recirculating reactor, although other types of upflow reactors may be employed. Liquid recirculating reactors are discussed further in copending application S.N.

25 _____ (T-6493), which is incorporated by reference.

A liquid recirculation reactor is an upflow reactor which feeds heavy hydrocarbon oil and a hydrogen rich gas at elevated pressure and temperature for hydroconversion. Process conditions for the liquid

30 recirculating reactor include pressures in the range from 1500 through 3500 psia, preferably 2000 through 3000 psia. Temperatures are in the range from 700 through 900F, preferably 775 through 850F.

Hydroconversion includes processes such as hydrocracking and the removal

35 of heteroatom contaminants (such sulfur and nitrogen). In slurry catalyst use, catalyst particles are extremely small (1-10 micron). Pumps may be used for recirculation of slurry, although they not required to be used.

- 5 The process for the preparation of the catalyst slurry composition used in this invention is set forth in U.S. Serial No. 10/938003 and U.S. Serial No. 10/938202 and is incorporated by reference. The catalyst composition is useful for but not limited to hydrogenation upgrading processes such as hydrocracking, hydrotreating, hydrodesulphurization, hydrodenitrification, and
- 10 hydrodemetalization.

5 WHAT IS CLAIMED IS:

1. A process for the hydroconversion of heavy oils, said process employing upflow reactors with a separator located internally in at least one reactor, said process comprising the following steps:

10

- (a) combining a heated heavy oil feed, an active slurry catalyst composition and a hydrogen-containing gas to form a mixture;

15

- (b) passing the mixture of step (a) to the bottom of the first reactor, which is maintained at hydroprocessing conditions, including elevated temperature and pressure;

20

- (c) separating internally in the first reactor a stream comprising reaction product, hydrogen gases, unconverted material and slurry catalyst into two streams, a vapor stream comprising reactor products and hydrogen, and a liquid stream comprising unconverted material and slurry catalyst;

25

- (d) passing the vapor stream overhead to further processing, and passing the liquid stream, comprising unconverted material and slurry catalyst, from the first reactor as a bottoms stream;

30

- (e) passing at least a portion of the liquid stream of step (d) to the bottom of the second reactor, which is maintained at hydroprocessing conditions, including elevated temperature and pressure;

35

- 5 (f) separating internally in the second reactor a stream
comprising reaction product, hydrogen gases,
unconverted material and slurry catalyst into two streams,
a vapor stream comprising reactor products and
hydrogen, and a liquid stream comprising unconverted
10 material and slurry catalyst;
- (g) passing the vapor stream overhead to further processing,
and passing the liquid stream, comprising unconverted
material and slurry catalyst, from the second reactor as a
15 bottoms stream To further processing.
2. The process of claim 1, wherein the liquid stream of step (g) is recycled
to step (a), the mixture of step (a) further comprising recycled
unconverted material and slurry catalyst.
20
3. The process of claim 1, wherein the bottom of a third reactor which is
maintained at slurry hydroprocessing conditions, including elevated
temperature and pressure
- 25 4. The process of claim 1, in which the recirculating reactor employs a
pump.
5. The process of claim 1, in which hydroprocessing conditions employed
in each reactor comprise a total pressure in the range from 1500 to
30 3500 psia, and a reaction temperature of from 700 to 900F
6. The process of claim 5, in which the preferred total pressure is in the
range from 200 through 3000 psia and the preferred temperature is in
the range from 775 through 850F-
35
7. The hydroconversion process of claim 1, wherein the heavy oil is
selected from the group consisting of atmospheric residuum, vacuum

- 5 residuum, tar from a solvent deasphalting unit, atmospheric gas oils,
vacuum gas oils, deasphalted oils, olefins, oils derived from tar sands
or bitumen, oils derived from coal, heavy crude oils, synthetic oils from
Fischer-Tropsch processes, and oils derived from recycled oil wastes
and polymers.
- 10
8. The hydroconversion process of claim 1, wherein the process is
selected from the group consisting of hydrocracking, hydrotreating,
hydrodesulphurization, hydrodenitrification, and hydrodemetalization.
- 15 9. The process of claim 1, wherein the active slurry catalyst composition
of claim 1 is prepared by the following steps:
- (a) mixing a Group VIB metal oxide and aqueous ammonia
 to form a Group VI B metal compound aqueous mixture;
- 20 (b) sulfiding, in an initial reaction zone, the aqueous mixture
 of step (a) with a gas comprising hydrogen sulfide to a
 dosage greater than 8 SCF of hydrogen sulfide per pound
 of Group VIB metal to form a slurry;
- 25 (c) promoting the slurry with a Group VIII metal compound;
- (d) mixing the slurry of step (c) with a hydrocarbon oil having
 a viscosity of at least 2 cSt @ 212°F to form an
30 intermediate mixture;
- (e) combining the intermediate mixture with hydrogen gas in
 a second reaction zone, under conditions which maintain
 the water in the intermediate mixture in a liquid phase,
35 thereby forming an active catalyst composition admixed
 with a liquid hydrocarbon; and

5 (f) recovering the active catalyst composition.

10. The process of claim 1, in which at least 90wt% of the feed is converted to lower boiling products.

10 11. The hydroconversion process of claim 1, wherein the heavy oil is selected from the group consisting of atmospheric residuum, vacuum residuum, tar from a solvent deasphalting unit, atmospheric gas oils, vacuum gas oils, deasphalted oils, olefins, oils derived from tar sands or bitumen, oils derived from coal, heavy crude oils, synthetic oils from
15 Fischer-Tropsch processes, and oils derived from recycled oil wastes and polymers.

Figure 1

