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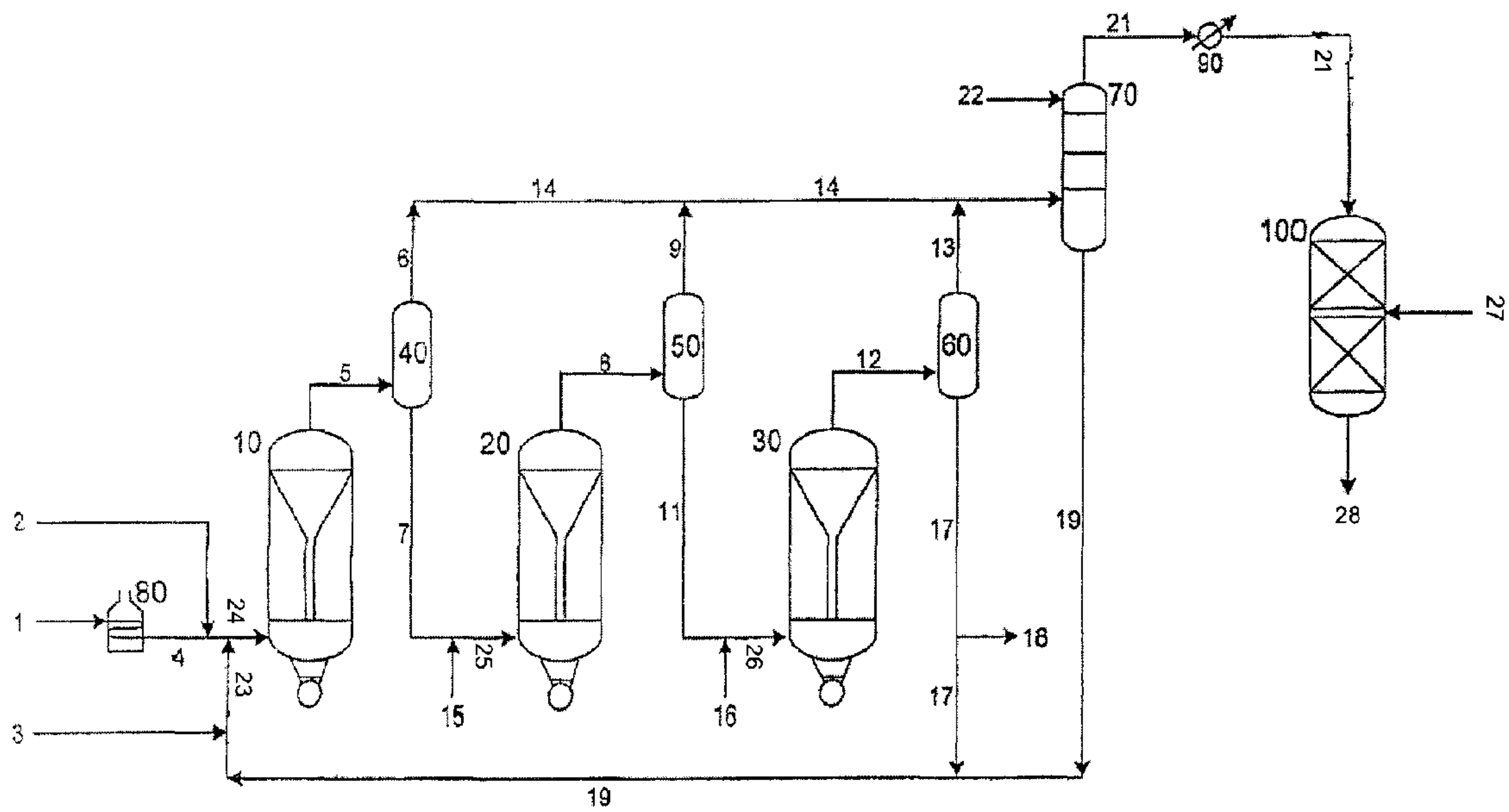
(72) **Inventeurs/Inventors:**
FARSHID, DARUSH, US;
REYNOLDS, BRUCE, US

(73) **Propriétaire/Owner:**
CHEVRON U.S.A. INC., US

(74) **Agent:** SIM & MCBURNEY

(54) **Titre : PROCEDES INTEGRES POUR VALORISER DES HUILES LOURDES ET REALISER UN HYDROFINISSAGE EN CIRCUIT**
(54) **Title: INTEGRATED HEAVY OIL UPGRADING PROCESS AND IN-LINE HYDROFINISHING PROCESS**




(57) **Abrégé/Abstract:**
A new residuum full hydroconversion slurry reactor system has been developed that allows the catalyst, unconverted oil and converted oil to circulate in a continuous mixture throughout an entire reactor with no confinement of the mixture. The mixture is partially separated in between the reactors to remove only the converted oil while permitting the unconverted oil and the slurry catalyst to continue on into the next sequential reactor where a portion of the unconverted oil is converted to lower boiling point hydrocarbons, once again creating a mixture of unconverted oil, 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 highly concentrated catalyst in unconverted oil which can be recycled directly to the first reactor. Fully converted oil can be subsequently hydrofinished for the nearly complete removal of hetoroatoms such as sulfur and nitrogen.

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(71) Applicant *(for all designated States except US)*: **CHEVRON U.S.A. INC.** [US/US]; 6001 Bollinger Canyon Road, Building T, 3rd Floor, San Ramon, CA 94583 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **FARSHID, Darush** [US/US]; 19 Hillcrest Avenue, Larkspur, CA 94939 (US). **REYNOLDS, Bruce** [US/US]; 1739 Jean Circle, Martinez, CA 94553 (US).

(74) Agents: **PRATER, Penny, L.** et al.; CHEVRON CORPORATION, LAW DEPARTMENT, Post Office Box 6006, San Ramon, CA 94583-0806 (US).



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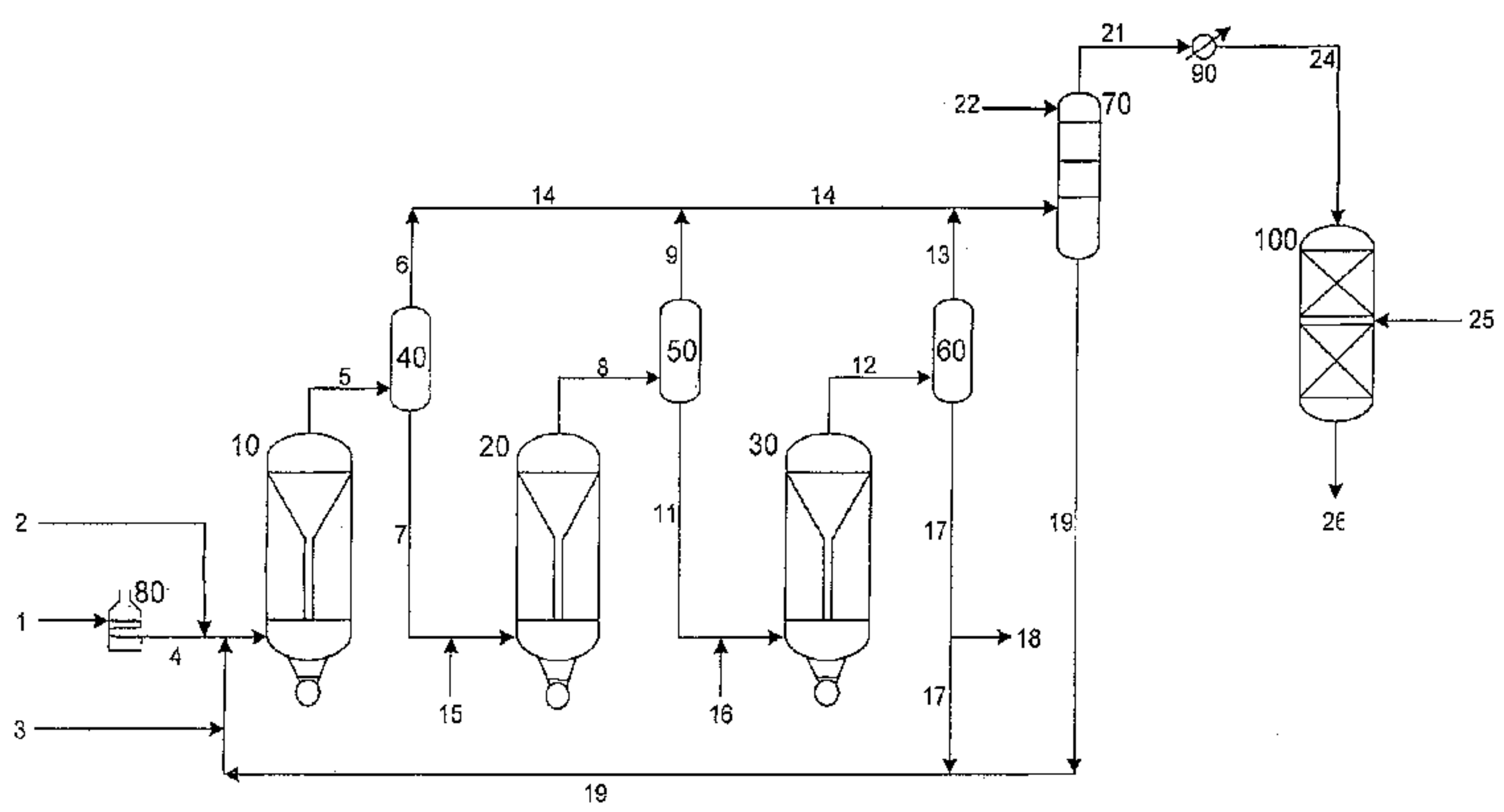
(54) **Title:** INTEGRATED HEAVY OIL UPGRADING PROCESS AND IN-LINE HYDROFINISHING PROCESS





(57) **Abstract:** A new residuum full hydroconversion slurry reactor system has been developed that allows the catalyst, unconverted oil and converted oil to circulate in a continuous mixture throughout an entire reactor with no confinement of the mixture. The mixture is partially separated in between the reactors to remove only the converted oil while permitting the unconverted oil and the slurry catalyst to continue on into the next sequential reactor where a portion of the unconverted oil is converted to lower boiling point hydrocarbons, once again creating a mixture of unconverted oil, 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 highly concentrated catalyst in unconverted oil which can be recycled directly to the first reactor. Fully converted oil can be subsequently hydrofinished for the nearly complete removal of hetoroatoms such as sulfur and nitrogen.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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.*

# INTEGRATED HEAVY OIL UPGRADING PROCESS AND IN-LINE HYDROFINISHING PROCESS

## FIELD OF THE INVENTION

The instant invention relates to a process for upgrading heavy oils using a slurry catalyst composition. In one embodiment, upgrading is followed by hydrofinishing.

## BACKGROUND OF THE INVENTION

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.

The following patents are directed to the preparation of highly active slurry catalyst compositions and their use in processes for upgrading heavy oil:

U.S. Patent Application Publication No. 2006/0058175 is directed to the preparation of a catalyst composition suitable for the hydroconversion of heavy oils. The catalyst 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 oil having a lower viscosity than the first oil. An active catalyst composition is thereby formed.

U.S. Patent Application Publication No. 2006/0058174 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 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. Patent Application Publication No. 2006/0054533 is directed to a process employing slurry catalyst 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.

U.S. Patent Application Publication No. 2006/0054534 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 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. Patent Application Publication No. 2006/0054535 is directed to a process for upgrading heavy oils 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 hydrogen gas and a second hydrocarbon oil having a lower viscosity than the first oil. An active catalyst composition is thereby formed.

## SUMMARY OF THE INVENTION

A process for the hydroconversion of heavy oils with a slurry which results in almost complete removal of sulfur or nitrogen from the final product, said process employing at least two upflow reactors in series with a separator optionally located in between each reactor, said process comprising the following steps:

(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 the first reactor, which is maintained at slurry hydroconversion conditions, including elevated temperature and pressure;

(c) removing a vapor mixture containing product, gases, unconverted material and slurry catalyst from the top of the first reactor and passing it to a first separator;

(d) in the first separator, removing a vapor stream comprising product and gases overhead to a lean oil contactor and passing a liquid bottoms material, comprising unconverted material and slurry catalyst, to the bottom of the second reactor, which is maintained at hydroconversion conditions, including elevated temperature and pressure;

(e) removing a vapor mixture containing product, gases, unconverted material and slurry catalyst from the top of the second reactor and passing it to a second separator;

(f) in the second separator, removing a vapor stream comprising product and gases overhead to the lean oil contactor and passing a liquid bottoms material, comprising unconverted material and slurry catalyst to further processing;

(g) contacting the stream comprising product and gases countercurrently with lean oil in a lean oil contactor wherein entrained catalyst and any unconverted material is removed by contact with a lean oil which exits as bottoms while products and gases are passed overhead;

(h) passing the overhead material of step (g) to a hydroprocessing unit for the removal of sulfur and nitrogen.

The slurry upgrading process of this invention converts nearly 98% of vacuum residue to lighter products ( in the boiling range below 1000F). Some of these products require further processing due to their high nitrogen, high sulfur and high aromatics content, as well as low API. The instant invention employs hydrofinishing downstream of the slurry upgrading process, resulting in almost complete removal of sulfur and nitrogen from the final product.

In accordance with another aspect, there is provided a process for the hydroconversion of heavy oils with an active slurry catalyst composition admixed in a hydrocarbon oil, which results in almost complete removal of sulfur or nitrogen from the final product, said process employing at least two upflow reactors in series with a separator located in between each reactor, said process comprising the following steps:

(a) providing the active slurry catalyst composition admixed in a hydrocarbon oil, formed by combining a slurry comprising Group VIB and Group VIII metals and a hydrocarbon oil having a viscosity of at least 2 cSt (or 32.8 SSU) @ 212°F;

(b) combining a heated heavy oil feed, the active slurry catalyst composition admixed in the hydrocarbon oil and a hydrogen-containing gas to form a mixture;

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

(d) removing a vapor mixture containing product, gases, unconverted material and slurry catalyst from the top of the first reactor and passing it to a first separator;

(e) in the first separator, removing a vapor stream comprising product and gases overhead to a lean oil contactor and passing a liquid bottoms material, comprising unconverted material and slurry catalyst, to the bottom of the second reactor, which is maintained at hydroconversion conditions, including elevated temperature and pressure;

(f) removing a vapor mixture containing product, gases, unconverted material and slurry catalyst from the top of the second reactor and passing it to a second separator;

(g) in the second separator, removing a vapor stream comprising product and gases overhead to the lean oil contactor and passing a liquid bottoms material, comprising unconverted material and slurry catalyst to further processing;

(h) contacting the vapor stream comprising product and gases countercurrently with lean oil in a lean oil contactor wherein entrained catalyst and any unconverted material is removed by contact with a lean oil which exits as bottoms while products and gases are passed overhead;

(i) passing the overhead material of step (h) to a hydroprocessing unit for the removal of sulfur and nitrogen,

wherein greater than 99% sulfur and nitrogen removal and 98% conversion to lighter products is achieved; hydroprocessing conditions employed in each reactor comprise a total pressure in the range from 1500 through 3500 psia and temperature from 700 through 900 °F; and hydrofinishing conditions in the hydroprocessing unit comprise temperatures in the range from 400 and 800

°F, space velocities in the range from 0.1 to 3 LHSV, and pressures in the range from 200 to 3000 psig, and

wherein the active slurry catalyst composition is formed by the following steps:

(a) mixing a Group VIB metal oxide and aqueous ammonia to form a Group VIB metal compound aqueous mixture;

(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;

(c) promoting the slurry with a Group VIII metal compound;

(d) mixing the slurry of step (c) with hydrocarbon oil having a viscosity of at least 2 cSt 212 °F to form an 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, thereby forming an active catalyst composition admixed with a liquid hydrocarbon; and

(f) recovering the active catalyst composition.

In accordance with a further aspect, there is provided a process for the hydroconversion of heavy oils with an active slurry catalyst composition admixed in a hydrocarbon oil, said process resulting in almost complete removal of sulfur or nitrogen from the final product, wherein at least two upflow reactors in series are employed with a separator located internally in both reactors, said process comprising the following steps:

(a) providing the active slurry catalyst composition admixed in a hydrocarbon oil, formed by combining a slurry comprising Group VIB and Group VIII metals and a hydrocarbon oil having a viscosity of at least 2 cSt (or 32.8 SSU

@ 212°F;

(b) combining a heated heavy oil feed, the active slurry catalyst composition admixed in the hydrocarbon oil and a hydrogen-containing gas to form a mixture;

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

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

(e) passing the vapor stream of step (d) overhead to a lean oil contactor, and passing the liquid stream, comprising unconverted material and slurry catalyst, from the first reactor as a bottoms stream;

(f) combining the bottoms stream of step (e) with additional feed oil resulting in an intermediate mixture;

(g) passing the intermediate mixture of step (f) to the bottom of the second reactor, which is maintained at hydroprocessing conditions, including elevated temperature and pressure;

(h) separating internally in the second reactor a stream comprising product, gases unconverted material and slurry catalyst into two streams, a vapor stream comprising products, hydrogen and other gases, and a liquid stream comprising unconverted material and slurry catalyst;

(i) passing the vapor stream of step (h) overhead to a lean oil contactor, and passing the liquid stream of step (h) from the second reactor as a bottoms stream for further processing; and

(j) passing the overhead effluent of the lean oil contactor of step (i) to a hydroprocessing unit for the removal of sulfur and nitrogen;

wherein greater than 99% sulfur and nitrogen removal and 98% conversion to lighter products is achieved, and

wherein the active slurry catalyst composition is formed by the following steps:

(a) mixing a Group VIB metal oxide and aqueous ammonia to form a Group VIB metal compound aqueous mixture;

(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;

(c) promoting the slurry with a Group VIII metal compound;

(d) mixing the slurry of step (c) with hydrocarbon oil having a viscosity of at least 2 cSt 212 °F to form an 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, thereby forming an active catalyst composition admixed with a liquid hydrocarbon; and

(f) recovering the active catalyst composition.

In accordance with another aspect, there is provided a process for the hydroconversion of heavy oils employing an active slurry catalyst composition, said process employing at least two upflow reactors in series with no interstage separation, said process comprising the following steps:

(a) providing the active slurry catalyst composition, formed from combining a slurry comprising Group VIB and Group VIII metals and a hydrocarbon oil having a viscosity of at least 2 cSt (or 32.8 SSU) @ 212°F;

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

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

(d) passing from the first reactor, a stream comprising product and gases, unconverted material and slurry catalyst to a second reactor maintained at hydroprocessing conditions for further processing and subsequent separation into vapor and liquid streams, with hydroprocessing of the vapor stream comprising product for removal of sulfur and nitrogen;

wherein greater than 99% sulfur and nitrogen removal and 98% conversion to lighter products is achieved, and

wherein the active slurry catalyst composition is formed by the following steps:

(a) mixing a Group VIB metal oxide and aqueous ammonia to form a Group VIB metal compound aqueous mixture;

(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;

(c) promoting the slurry with a Group VIII metal compound;

(d) mixing the slurry of step (c) with hydrocarbon oil having a viscosity of at least 2 cSt 212 °F to form an 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, thereby forming an active catalyst composition admixed with a liquid hydrocarbon; and

(f) recovering the active catalyst composition.

## BRIEF DESCRIPTION OF THE FIGURES

Figure 1 depicts a process scheme of this invention which employs three reactors, followed by a hydrofinishing reactor.

Figure 2 depicts a process scheme for this invention, employing three reactors.

Figure 3 depicts a process scheme of this invention which employs a fixed bed pretreating reactor upstream of three reactors employing a catalyst slurry, within the same process loop.

## DETAILED DESCRIPTION OF THE INVENTION

The instant invention is directed to a process for catalyst activated slurry hydrocracking, as depicted in Figure 1. Stream 1 comprises a heavy feed, such as vacuum residuum. This feed enters furnace 80 where it is heated, exiting in stream 4. Stream 4 combines with a hydrogen containing gas (stream 2), and a stream comprising an active slurry composition(stream 23), resulting in a mixture(stream 24). Stream 24 enters the bottom of the first reactor 10. Vapor stream 5 exits the top of the reactor and comprises products, gases, slurry, and unconverted material. Stream 5 passes to hot high pressure separator 40, which is preferably a flash drum. A vapor stream comprising products and gases is removed overhead as stream 6. Stream 6 is passed to a lean oil contactor for further processing. Liquid stream 7 is removed through the bottom of the separator 40. Stream 7 contains slurry in combination with unconverted oil.

Stream 7 is combined with a gaseous stream comprising hydrogen (stream 15) to create stream 25. Stream 25 enters the bottom of second reactor 20. Vapor stream 8, comprising products, gases, slurry and unconverted material, exits the second reactor overhead and passes to separator 50, which is preferably a flash drum. Products and gases are removed overhead as stream 9 and passed to the lean oil contactor for further processing. Liquid stream 11 is removed through the bottom of the flash drum. Stream 11 contains slurry in combination with unconverted oil.

Stream 11 is combined with a gaseous stream comprising hydrogen (stream 16) to create stream 26. Stream 26 enters the bottom of third reactor 30. Stream 12, which exits third reactor 30 passes to separator 60, preferably a flash drum. Product and gases are removed overhead from separator 60 as stream 13. Liquid stream 17 is removed through the bottom of the separator 60. Stream 17 comprises slurry in combination with unconverted oil. A portion of this stream may be drawn off through stream 18.

Overhead vapor streams 6, 9 and 13 create stream 14, which passes to lean oil contactor 70. Stream 22, containing a lean oil such as vacuum gas oil, ' enters the top portion of lean oil contactor 70 and flows downward. (1) removing any possible entrained catalyst and (2) reducing heavy materials(high boiling range oil including small amounts of vacuum residue).

Products and gases (vapor stream 21) exit lean oil contactor 70 overhead, while liquid stream 19 exits at the bottom. Stream 19 comprises a mixture of slurry and unconverted oil. Stream 19 is combined with stream 17, which also comprises a mixture of slurry and unconverted oil. Fresh slurry is added in stream 3, and stream 23 is created. Stream 23 is combined with the feed to first reactor 10.

Stream 21 enters steam exchanger (or generator) 90, for cooling prior to hydrofinishing. The purpose of the steam exchanger is to control the hydrofinisher reactor inlet temperature as needed. Stream 21 enters the top bed of the hydrofinisher 100, a fixed bed reactor, preferably having multiple beds of active hydrotreating catalyst. Hydrogen (stream 27) is inserted as interbed quench if multiple beds are used. Hydrofinished product is removed as stream 28.

The hydrofinishing unit further refines products from the slurry upgrader to high quality products by removing impurities and stabilizing the products by saturation. Greater than 99 wt % sulfur and nitrogen removal may be achieved. Reactor effluent is cooled by means of heat recovery and sent to the product recovery section as in any conventional hydroprocessing unit.

Conditions for hydrofinishing hydrocarbons are well known to those of skill in the art, Typical conditions are between 400 and 800 F, 0.1 to 3 LHSV, and 200 to 3000 psig. Catalysts useful for the hydrofinishing reaction are preferably combinations of nickel, cobalt and molybdenum supported on zeolites or amorphous material.

Alternate embodiments, not pictured, include a series of reactors in which one or more of the reactors contains internal separation means, rather than an external separator or flash drum following the reactor. In another embodiment, there is no interstage separation between one or more of the reactors in series.

The process for the preparation of the catalyst slurry composition used in this invention is set forth in U.S. Patent Application Publications Nos. 2006/0058174 and 2006/0058175. The catalyst composition is useful for but not limited to hydrogenation upgrading processes such as thermal hydrocracking, hydrotreating, hydrodesulphurization, hydrodenitrification, and hydrodemetalization. The feeds suitable for use in this invention are set forth in U.S. Patent Application Publication No. 2006/0054535 and 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. Suitable feeds also include > atmospheric residuum, vacuum residuum and tar from a solvent deasphlating unit.

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 U.S. Patent Application Publication No. 2007/0140927.

A liquid recirculation reactor is an upflow reactor to which is fed heavy hydrocarbon oil admixed with slurry catalyst and a hydrogen rich gas at elevated pressure and temperature, for hydroconversion

Hydroconversion includes processes such as hydrocracking and the removal of heteroatom contaminants (such sulfur and nitrogen). In slurry catalyst use, catalyst particles are extremely small (1-10 micron). Pumps are not generally needed for recirculation, although they may be used. Sufficient motion of the catalyst is usually established without them.

Figure 2 illustrates another embodiment directed to a process for catalyst activated slurry hydrocracking. Stream 1 comprises a heavy feed, such as vacuum residuum. This feed enters furnace 80 where it is heated, exiting in stream 4. Stream 4 combines with a hydrogen containing gas (stream 2), and a stream comprising an active slurry composition (stream 23), resulting in a mixture (stream 24). Stream 24 enters the bottom of the first reactor 10. Vapor stream 5 exits the top of the reactor 10, comprising slurry, products and hydrogen, and unconverted material. Stream 5 passes to separator 40, which is preferably a flash drum. Products and hydrogen are removed overhead as stream 6. Liquid stream 7 is removed through the bottom of the flash drum. Stream 7 contains slurry in combination with unconverted oil.

Stream 7 is combined with a gaseous stream comprising hydrogen (stream 15) to create stream 25. Stream 25 enters the bottom of second reactor 20. Vapor stream 8, comprising products, hydrogen, slurry and unconverted material passes to separator 50, preferably a flash drum. Product and hydrogen, in a vapor stream is removed overhead as stream 9. Liquid stream 11 is removed through the bottom of the flash drum. Stream 11 contains slurry in combination with unconverted oil.

Stream 11 is combined with a gaseous stream comprising hydrogen (stream 16) to create stream 26. Stream 26 enters the bottom of third reactor 30.

Vapor stream 12, comprising products, hydrogen, slurry and unconverted material passes overhead from reactor 30 to separator 60, preferably a flash drum. Products and hydrogen are removed overhead as vapor stream 13. Liquid stream 17 is removed through the bottom of the flash drum. Stream 17 contains slurry in combination with unconverted oil. A portion of this stream may be drawn off through stream 18.

Overhead streams 6, 9 and 13 create stream 14, which passes to high pressure separator 70. Stream 21, comprising a lean oil such as vacuum gas oil enters the top portion of high pressure separator 70. Products and hydrogen exit lean oil contactor 70 overhead as vapor stream 22, while liquid stream 19 exits at the bottom. Stream 19 comprises a mixture of slurry and unconverted oil. Stream 19 is combined with stream 17, which also comprises a mixture of slurry and unconverted oil. Fresh slurry is added in stream 3, and stream 23 is created. Stream 23 is combined with the feed to first reactor 10.

The instant invention is directed to a process for catalyst activated slurry hydrocracking with upstream in-line pretreating, as depicted in Figure 3. Stream 1 comprises a heavy feed, such as vacuum residuum. This feed enters furnace 80 where it is heated, exiting in stream 4. Stream 4 combines with a hydrogen containing gas (stream 2) resulting in a mixture (stream 101). Stream 101 enters the top of the pretreater reactor 100. The pretreater is either a fixed bed hydrotreating unit or a deasphalting unit. In a deasphalting unit, solvent generally flows countercurrent to the feed. Deasphalting is not depicted. Stream 102 leaves the bottom of the pretreater and proceeds to hot high pressure separator 110, which is preferably a flash drum. Product and hydrogen is removed overhead as a vapor stream, stream 103. Stream 103 joins with stream 22. Unconverted material exits the bottoms flash drum 110 as liquid stream 104. Stream 104 combines with stream 106. Stream 106 is composed of recycle slurry catalyst (stream 19) as well as make-up slurry catalyst (stream 3). Streams 104 and 106 combine to form stream 107.

Stream 107 enters the bottoms of upflow reactor 10, which is preferably a liquid recirculating reactor. Stream 5, a vapor stream exits the reactor overhead and comprises slurry, products, hydrogen and unconverted material. Stream 5 passes to hot high pressure separator 40, which is preferably a flash drum. Product and hydrogen is removed overhead in a vapor stream as stream 6. Liquid stream 7 is removed through the bottom of the flash drum. Stream 7 contains slurry in combination with unconverted oil.

Stream 7 is combined with a gaseous stream comprising hydrogen (stream 15) to create stream 25. Stream 25 enters the bottom of second reactor 20. Stream 8, a vapor stream comprising slurry, products, hydrogen and unconverted material, passes overhead from reactor 20 to separator 50, preferably a flash drum. Products and hydrogen are removed overhead as vapor stream 9 Liquid stream 11 is removed through the bottom of the flash drum Stream 11 contains slurry in combination with unconverted oil. Stream 11 is combined with a gaseous stream comprising hydrogen (stream 16) to create stream 26. Stream 26 enters the bottom of third reactor 30.Vapor stream 12 passes overhead from reactor 30 to hot high pressure separator 60, preferably a flash drum. Product and hydrogen is removed overhead as vapor stream 13. Stream 17 is removed through the bottom of the flash drum 60. Liquid stream 17 contains slurry in combination with unconverted oil. A portion of this stream may be drawn off through stream 18.

Overhead vapor streams 6, 9 and 13 create stream 14, which passes to lean oil contactor 70. Stream 22, containing a lean oil such as vacuum gas oil, enters the top portion of lean oil contactor 70 and flows downward (1) removing any possible entrained catalyst and (2) reducing heavy materials (high boiling range oil including small amounts of vacuum residue). Product. and hydrogen (stream 23) exits lean oil contactor 70 as vapor overhead, while liquid stream 19 exits at the bottom. Stream 23 combines with product stream 103 to form stream 22, which is sent to hydrofinishing.

Stream 19 comprises a mixture of slurry and unconverted oil. Stream 19 is combined with stream 17, which also comprises a mixture of slurry and unconverted oil. Fresh slurry is added in stream 3, and stream 106 is created. Stream 106 is combined with the feed to first reactor 10 (stream 104) to create stream 107.

The heavy product fraction is hydrofinished to eliminate any remaining olefins. The hydrofinisher further refines products from the slurry upgrader to high quality products by removing impurities and stabilizing the products. Greater than 99 wt % sulfur and nitrogen removal may be achieved. Reactor effluent is cooled by means of heat recovery and sent to the product recovery section as in any conventional hydroprocessing unit.

Conditions for pretreating hydrocarbons are well known to those of skill in the art. Pretreating may involve hydrotreating or deasphalting. Hydrotreating is a well-known form of feed pretreatment, and usually occurs in fixed bed hydrotreating reactors having one or more beds. Hydrotreating is generally disclosed in U.S. Patent No. 6,890,423 and is discussed in Gary and Handwerk, *Petroleum Refining* (2nd ed. 1984). Typical hydrotreating conditions vary over a wide range. In general, the overall LHSV is about 0.25 to 2.0, preferably about 0.5 to 1.0. The hydrogen partial pressure is greater than 200 psia, preferably ranging from about 500 psia to about 2000 psia. Hydrogen recirculation rates are typically greater than 50 SCF/Bbl, and are preferably between 1000 and 5000 SCF/Bbl. Temperatures range from about 300[deg] F. to about 750[deg] F., preferably ranging from 450[deg] F. to 600[deg] F. Catalysts useful in hydrotreating operations are well known in the art. Suitable catalysts include noble metals from Group VIIIA (according to the 1975 rules of the International Union of Pure and Applied Chemistry), such as platinum or palladium on an alumina or siliceous matrix, and unsulfided Group VIIIA and Group VIB, such as nickel-molybdenum or nickel-tin on an alumina or siliceous matrix. The non-noble metal (such as nickel-molybdenum) hydrogenation metals are usually present in the final catalyst composition as oxides, or more preferably or possibly, as sulfides when such compounds are readily formed from the particular metal involved. Preferred non-noble metal catalyst compositions contain in excess of about 5 weight percent, preferably about 5 to about 40 weight percent molybdenum and/or tungsten, and at least about 0.5, and generally about 1 to about 15 weight percent of nickel and/or cobalt determined as the corresponding oxides. The noble metal (such as platinum) catalyst may contain in excess of 0.01 percent metal, preferably between 0.1 and 1.0 percent metal. Combinations of noble metals may also be used, such as mixtures of platinum and palladium.

Pretreating may alternately employ deasphalting, if the feed to be employed contains asphalt. Deasphalting is usually accomplished by the use of propane as a solvent, although other solvents may include lower-boiling paraffinic hydrocarbons such as ethane, butane or pentane. Deasphalting techniques are well known in the refining arts, but are discussed in the text *Petroleum Refining*. Deasphalting is disclosed generally in patents such as U.S. Patent Nos. 6,264,826 and 5993,644.

Alternate embodiments for the slurry reactor system, which are not pictured, include a series of reactors in which one or more of the reactors contains internal separation means, rather than an external separator or flash drum following the reactor.

Example

**In-line hydrofinishing Performance**

| | Feed from slurry hydrocracker to Hydrofinisher | Full Range Product from Hydrofinisher | Jet Fuel Cut from Hydrofinisher | Diesel Cut from Hydrofinisher |
|---|---|---|---|---|
| | | | | |
| API | 34.8 | 38.9 | | |
| Sulfur, wppm | 3300 | 6 | < 2 | 3 |
| Nitrogen, wppm | 2500 | 23 | 6 | 8 |
| Smoke Point, mm | | | 19 | |
| Cetane Index | | | | 44 |

It is apparent from the Table above that hydrofinishing of the product of slurry hydrocracking provides dramatic reduction of sulfur and nitrogen content. In both full range product and in individual product cuts, such as jet fuel and diesel.

WHAT IS CLAIMED IS:

1. A process for the hydroconversion of heavy oils with an active slurry catalyst composition admixed in a hydrocarbon oil, which results in almost complete removal of sulfur or nitrogen from the final product, said process employing at least two upflow reactors in series with a separator located in between each reactor, said process comprising the following steps:

(a) providing the active slurry catalyst composition admixed in a hydrocarbon oil, formed by combining a slurry comprising Group VIB and Group VIII metals and a hydrocarbon oil having a viscosity of at least 2 cSt (or 32.8 SSU) @ 212°F;

(b) combining a heated heavy oil feed, the active slurry catalyst composition admixed in the hydrocarbon oil and a hydrogen-containing gas to form a mixture;

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

(d) removing a vapor mixture containing product, gases, unconverted material and slurry catalyst from the top of the first reactor and passing it to a first separator;

(e) in the first separator, removing a vapor stream comprising product and gases overhead to a lean oil contactor and passing a liquid bottoms material, comprising unconverted material and slurry catalyst, to the bottom of the second reactor, which is maintained at hydroconversion conditions, including elevated temperature and pressure;

(f) removing a vapor mixture containing product, gases, unconverted material and slurry catalyst from the top of the second reactor and passing it to a second separator;

(g) in the second separator, removing a vapor stream comprising product and gases overhead to the lean oil contactor and passing a liquid bottoms material, comprising unconverted material and slurry catalyst to further processing;

(h) contacting the vapor stream comprising product and gases countercurrently with lean oil in a lean oil contactor wherein entrained catalyst and any unconverted material is removed by contact with a lean oil which exits as bottoms while products and gases are passed overhead; and

(i) passing the overhead material of step (h) to a hydroprocessing unit for the removal of sulfur and nitrogen,

wherein greater than 99% sulfur and nitrogen removal and 98% conversion to lighter products is achieved; hydroprocessing conditions employed in each reactor comprise a total pressure in the range from 1500 through 3500 psia and temperature from 700 through 900 °F; and hydrofinishing conditions in the hydroprocessing unit comprise temperatures in the range from 400 and 800 °F, space velocities in the range from 0.1 to 3 LHSV, and pressures in the range from 200 to 3000 psig, and

wherein the active slurry catalyst composition is formed by the following steps:

(a) mixing a Group VIB metal oxide and aqueous ammonia to form a Group VIB metal compound aqueous mixture;

(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;

(c) promoting the slurry with a Group VIII metal compound;

(d) mixing the slurry of step (c) with hydrocarbon oil having a viscosity of at least 2 cSt 212 °F to form an 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, thereby forming an active catalyst composition admixed with a liquid hydrocarbon; and

(f) recovering the active catalyst composition.

2. The process of claim 1, wherein the hydroprocessing unit is operated at hydrofinishing conditions.

3. The process of claim 1, wherein the hydroprocessing unit is a fixed

bed reactor which comprises at least one catalyst bed.

4. The process of claim 3, wherein quench gas is introduced between beds to control bed inlet temperatures.

5. The process of claim 3, wherein at least one catalyst bed of the hydroprocessing unit comprises hydrofinishing catalyst.

6. The process of claim 5, wherein hydrofinishing catalyst comprises combinations selected from the group consisting of cobalt, nickel and molybdenum, on a zeolitic or amorphous support.

7. The process of claim 1, wherein the inlet temperature to the hydroprocessing unit is controlled.

8. The process of claim 7, wherein a steam exchanger is employed to control the inlet temperature of the hydroprocessing unit.

9. The process of claim 1, wherein the bottoms material of step (g) is recycled to step (b), the mixture of step (b) further comprising recycled unconverted material and slurry catalyst.

10. The process of claim 1, wherein the bottoms material of step (g) is passed to the bottom of a third reactor which is maintained at hydroconversion conditions, including elevated temperature and pressure.

11. The process of claim 1, in which at least one of the reactors is a liquid recirculating reactor.

12. The process of claim 11, in which the recirculating reactor employs a pump.

13. The process of claim 1, in which the total pressure is in the range from 2000 through 3000 psia and temperature is in the range from 775 through 850 °F.

14. The process of claim 1, wherein the separator located between each reactor is a flash drum.

15. 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 deasphlating 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.

16. The hydroconversion process of claim 1, wherein the process is selected from the group consisting of hydrocracking, hydrotreating, hydrodesulphurization, hydrodenitrification, and hydrodemetalization.

17. A process for the hydroconversion of heavy oils with an active slurry catalyst composition admixed in a hydrocarbon oil, said process resulting in almost complete removal of sulfur or nitrogen from the final product, wherein at least two upflow reactors in series are employed with a separator located internally in both reactors, said process comprising the following steps:

(a) providing the active slurry catalyst composition admixed in a hydrocarbon oil, formed by combining a slurry comprising Group VIB and Group VIII metals and a hydrocarbon oil having a viscosity of at least 2 cSt (or 32.8 SSU @ 212°F;

(b) combining a heated heavy oil feed, the active slurry catalyst composition admixed in the hydrocarbon oil and a hydrogen-containing gas to form a mixture;

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

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

(e) passing the vapor stream of step (d) overhead to a lean oil contactor, and passing the liquid stream, comprising unconverted material and slurry catalyst, from the first reactor as a bottoms stream;

(f) combining the bottoms stream of step (e) with additional feed oil resulting in an intermediate mixture;

(g) passing the intermediate mixture of step (f) to the bottom of the second reactor, which is maintained at hydroprocessing conditions, including elevated temperature and pressure;

(h) separating internally in the second reactor a stream comprising product, gases unconverted material and slurry catalyst into two streams, a vapor stream comprising products, hydrogen and other gases, and a liquid stream comprising unconverted material and slurry catalyst;

(i) passing the vapor stream of step (h) overhead to a lean oil contactor, and passing the liquid stream of step (h) from the second reactor as a bottoms stream for further processing; and

(j) passing the overhead effluent of the lean oil contactor of step (i) to a hydroprocessing unit for the removal of sulfur and nitrogen;

wherein greater than 99% sulfur and nitrogen removal and 98% conversion to lighter products is achieved, and

wherein the active slurry catalyst composition is formed by the following steps:

(a) mixing a Group VIB metal oxide and aqueous ammonia to form a Group VIB metal compound aqueous mixture;

(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;

(c) promoting the slurry with a Group VIII metal compound;

(d) mixing the slurry of step (c) with hydrocarbon oil having a viscosity of at least 2 cSt 212 °F to form an 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, thereby forming an active catalyst composition admixed with a liquid hydrocarbon; and

(f) recovering the active catalyst composition.

18. A process for the hydroconversion of heavy oils employing an active slurry catalyst composition, said process employing at least two upflow reactors in series with no interstage separation, said process comprising the following steps:

(a) providing the active slurry catalyst composition, formed from combining a slurry comprising Group VIB and Group VIII metals and a hydrocarbon oil having a viscosity of at least 2 cSt (or 32.8 SSU) @ 212°F;

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

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

(d) passing from the first reactor, a stream comprising product and gases, unconverted material and slurry catalyst to a second reactor maintained at hydroprocessing conditions for further processing and subsequent separation into vapor and liquid streams, with hydroprocessing of the vapor stream comprising product for removal of sulfur and nitrogen;

wherein greater than 99% sulfur and nitrogen removal and 98% conversion to lighter products is achieved, and

wherein the active slurry catalyst composition is formed by the following steps:

(a) mixing a Group VIB metal oxide and aqueous ammonia to form a Group VIB metal compound aqueous mixture;

(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;

(c) promoting the slurry with a Group VIII metal compound;

(d) mixing the slurry of step (c) with hydrocarbon oil having a viscosity of at least 2 cSt 212 °F to form an 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, thereby forming an active catalyst composition admixed with a liquid hydrocarbon; and

(f) recovering the active catalyst composition.

19. The process of claim 18, in which additional hydrogen is added to the stream of step (d) prior to its entrance to the second reactor.

Figure 1

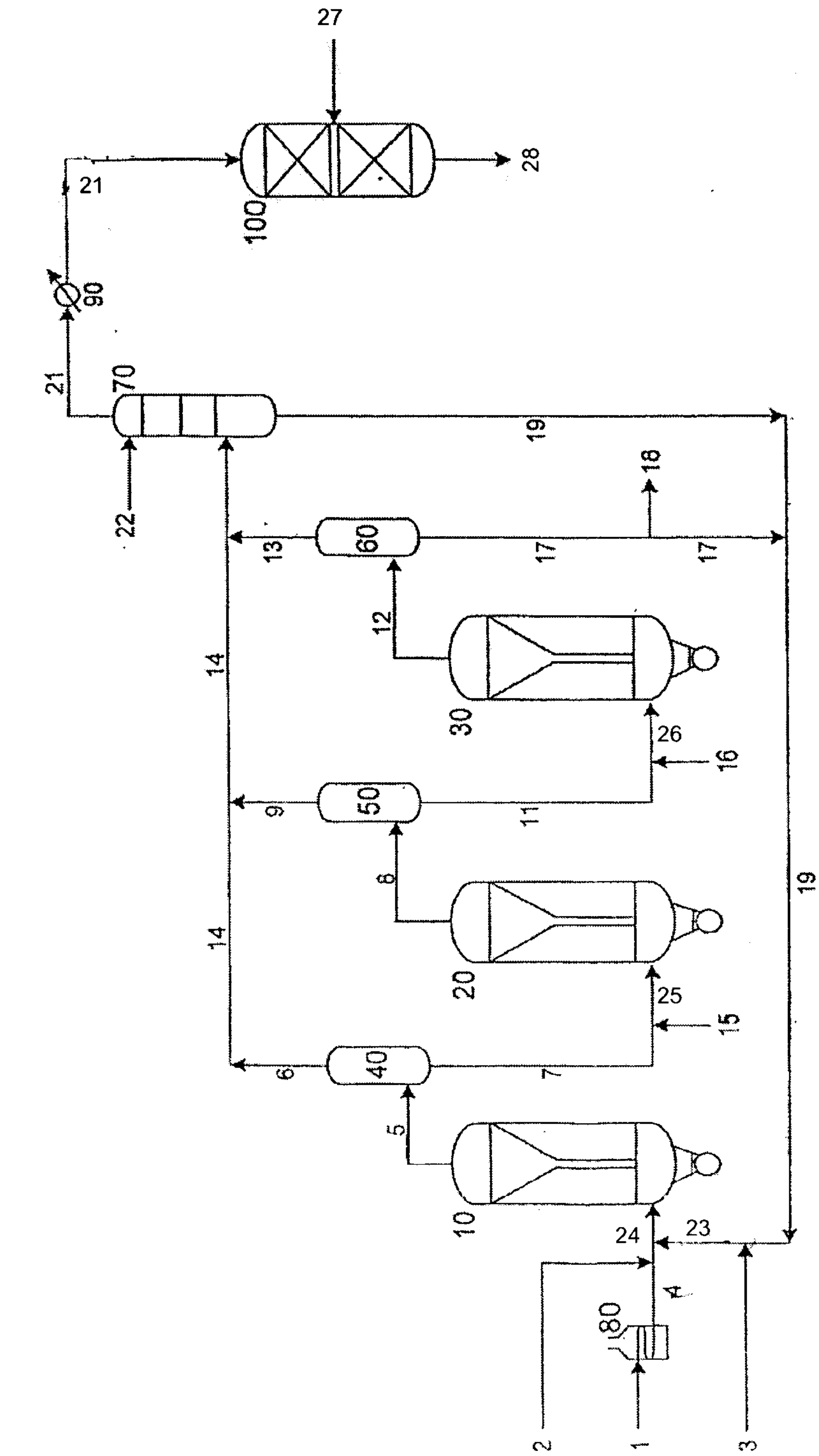
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Figure 2

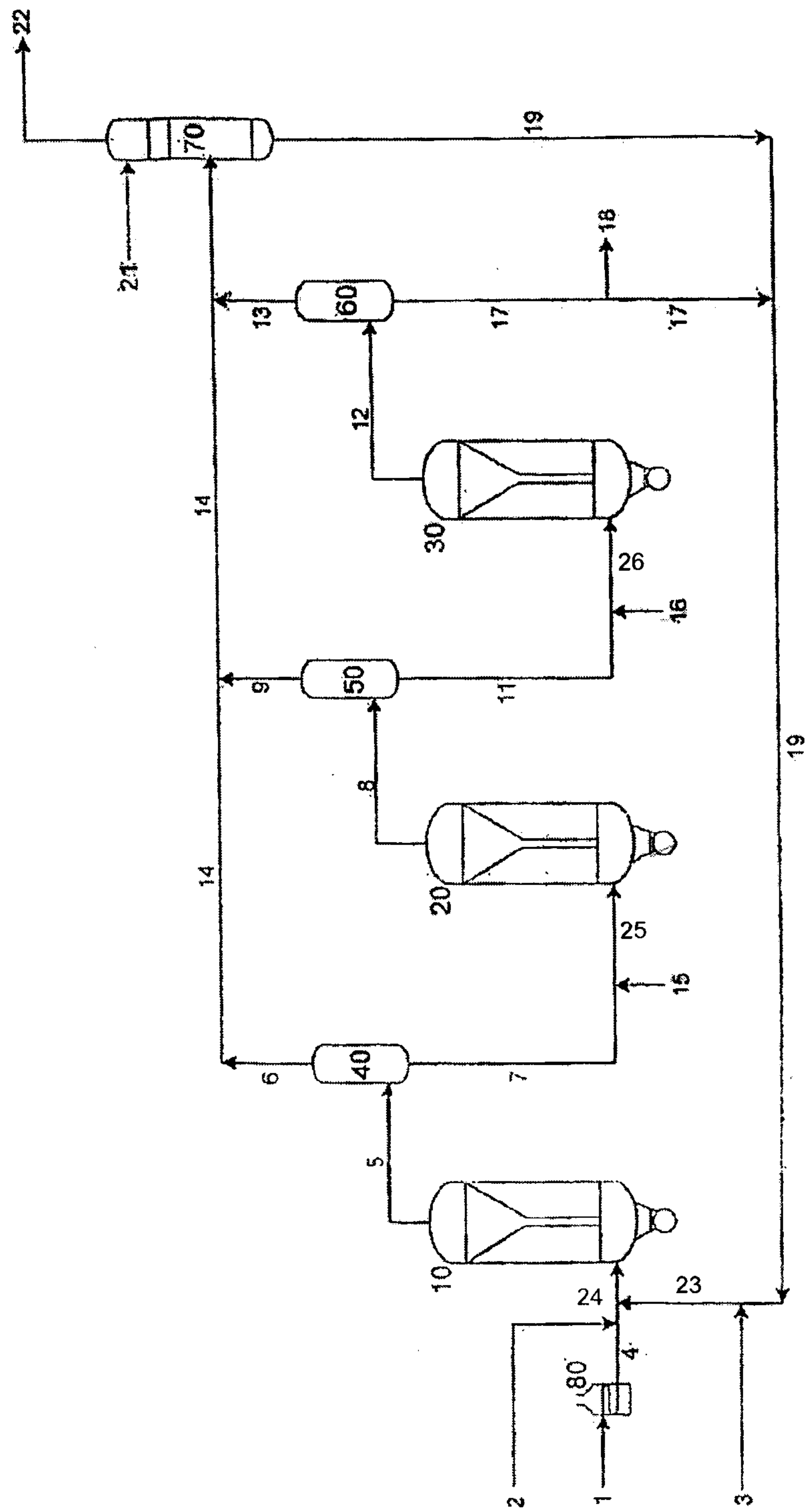
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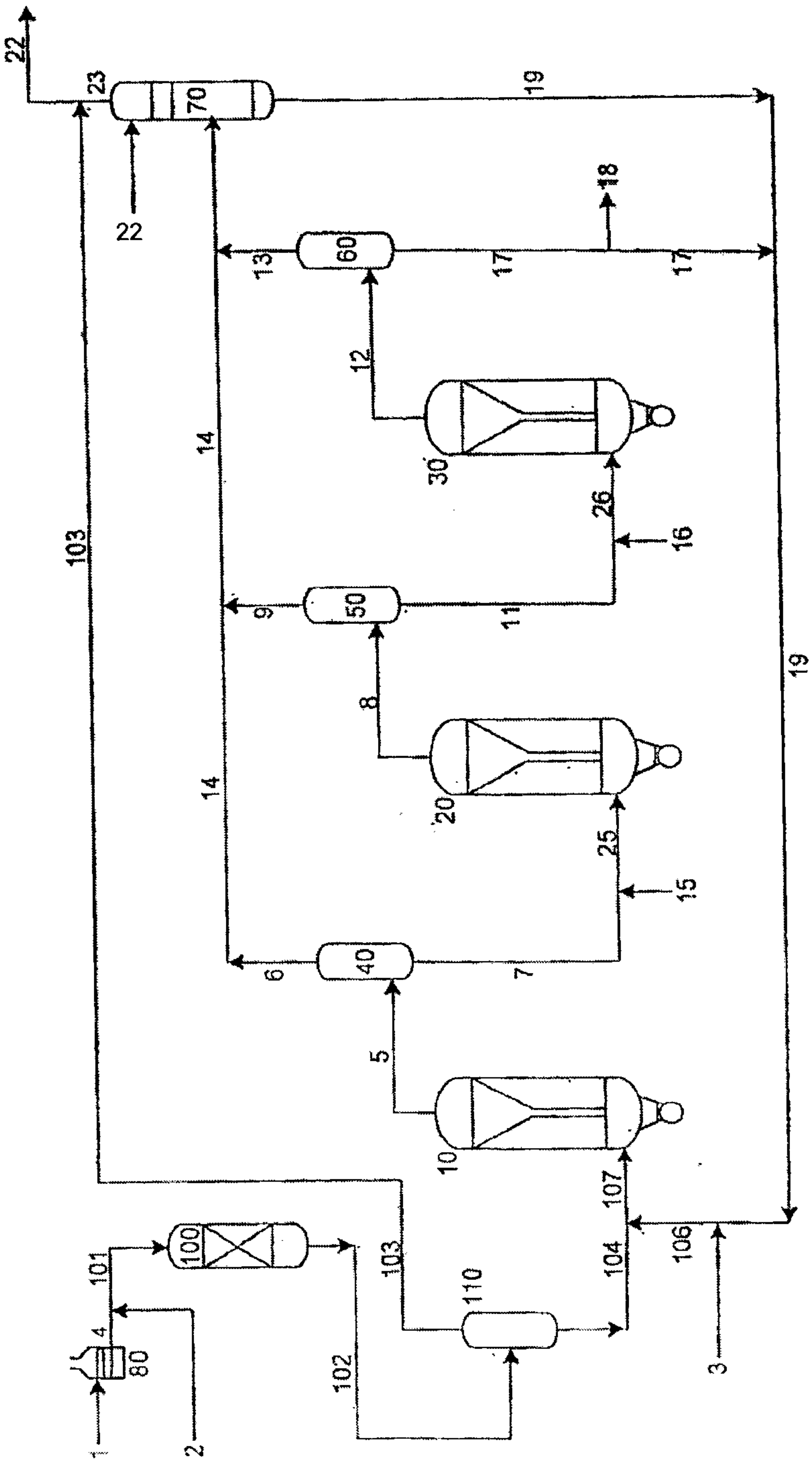
Figure 3



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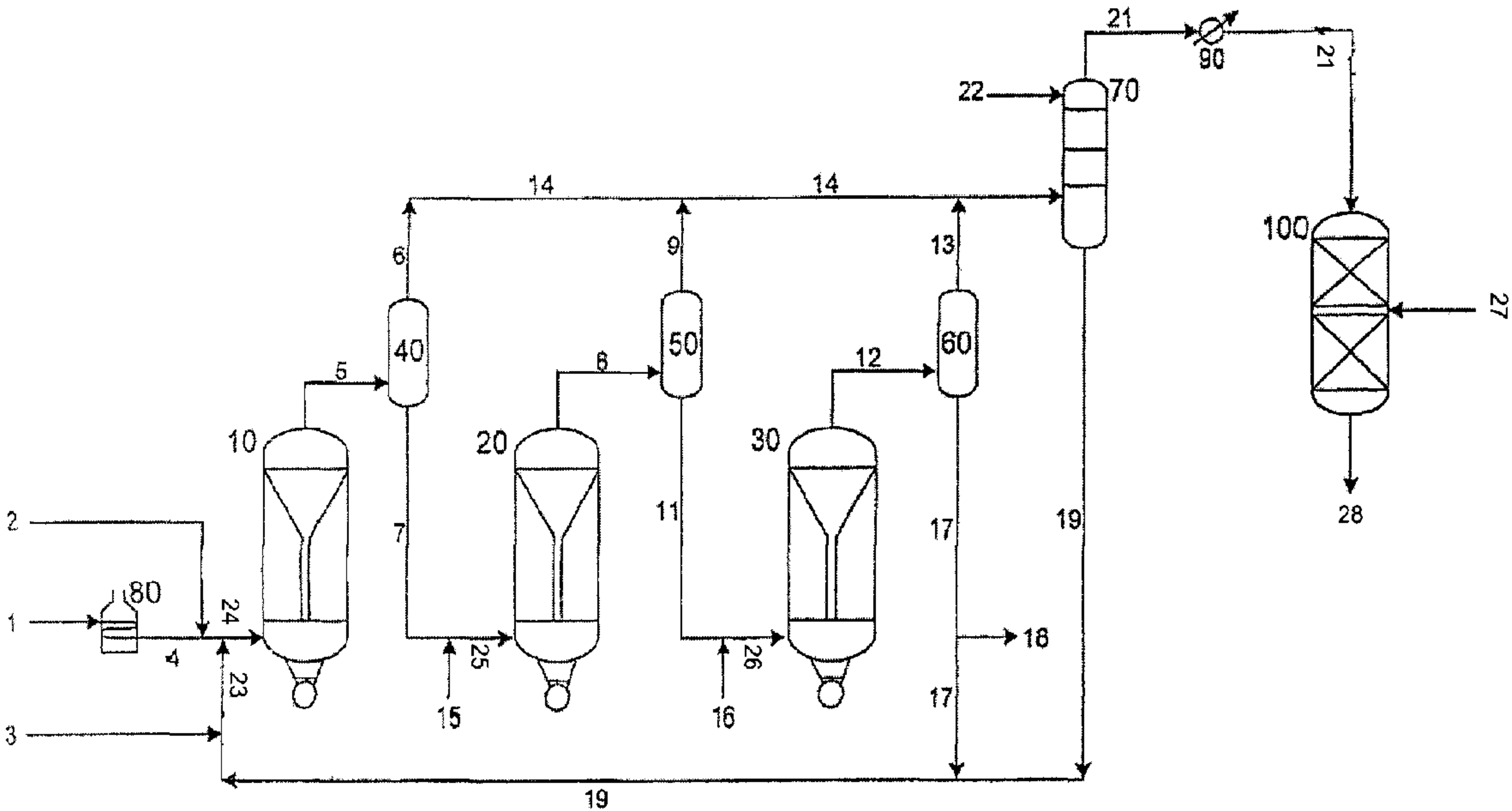

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