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(54) Process for hydroconversion of heavy hydrocarbonaceous feeds.

(57) A process for converting a heavy hydrocarbonaceous chargestock to lower boiling products, at hydroconversion conditions and in the presence of hydrogen, wherein a presulfided catalyst precursor concentrate is introduced with the chargestock into a hydroconversion zone. The hydroconversion is conducted at a temperature from about 425°C to 510°C and a hydrogen partial (gauge) pressure of from about 50 to 5,000 psig (0.345 to 34.475 MPa).

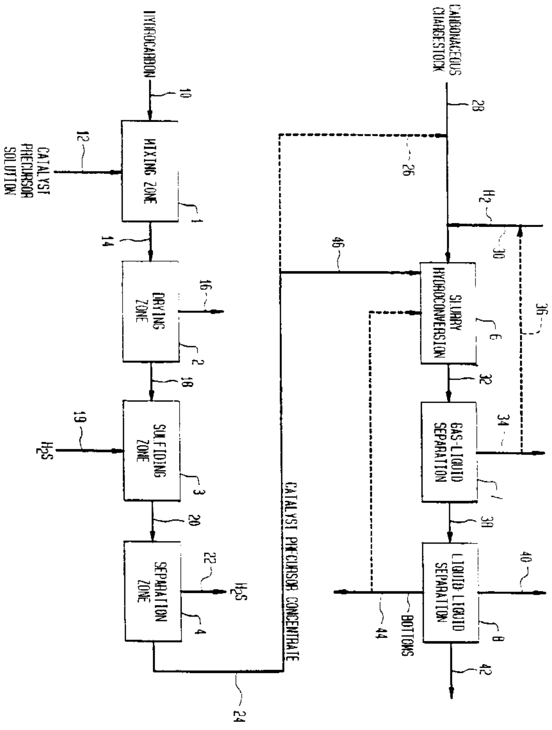

FIG. 1

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FIELD OF THE INVENTION

This invention relates to an improvement in a slurry hydro- conversion process for heavy hydrocarbonaceous feedstocks wherein a concentrate of a presulfided catalyst precursor concentrate of molybdenum, formed in a portion of process feed, is used as a source of catalyst. The presulfided precursor concentrate can be added directly to the hydroconversion reactor or it can be premixed with process feed prior to introduction to the reactor provided that the temperature of the concentrate, prior to addition or to premixing, is maintained below about 315° C.

BACKGROUND OF THE INVENTION

There is substantial interest in the petroleum industry in converting heavy hydrocarbonaceous feedstocks to lower boiling liquids. One type of process suitable for hydroconversion of heavy feedstocks is a slurry process using a catalyst prepared in a hydrocarbon oil from (a thermally decomposable, metal compound) catalyst precursor. The catalyst is formed in situ in the hydroconversion zone. See for example, U.S. Patent Nos. 4,226,742 and 4,244,839.

Further, U.S. Patent Nos. 4,740,295 and 4,740,489, teach a method wherein a catalyst is prepared from a phosphomolybdic acid precursor concentrate. The precursor concentrate is sulfided prior to the final catalyst formation. This presulfiding step is taught to produce a catalyst having greater control over coke formation. The presulfiding agent in these two patents requires a hydrogen-sulfide containing gas or a hydrogen-sulfide precursor and the resulting catalyst concentrate is used for hydroconversion of heavy hydrocarbonaceous materials to lower boiling products.

The term "hydroconversion" with reference to a hydrocarbonaceous oil, is used herein to designate a catalytic process conducted in the presence of hydrogen in which at least a portion of the heavy constituents of the oil is converted to lower boiling products. The simultaneous reduction of the concentration of nitrogenous compounds, sulfur compounds and metallic constituents of the oil may also result.

All boiling points referred to herein are atmospheric pressure equivalent boiling points unless otherwise specified.

The process of introducing a catalyst precursor in the form of a concentrate mixed in a hydrocarbonaceous oil into a hydroconversion zone containing a heavy hydrocarbonaceous chargestock is disclosed in U.S. Patent No. 5,053,376, which is incorporated herein by reference. This procedure has certain advantages when compared with a process wherein the catalyst precursor is introduced into the hydroconversion zone without first forming a concentrate; that is, by introducing the catalyst precursor directly into the feed or directly into the reactor. The advantages include: (i) ease of mixing the precursor with a small stream instead of the whole feed; (ii) the ability to store the precursor concentrate for future use and/or activity certification either on site or at another site; and (iii) the ability to use a hydrocarbonaceous oil, other than the feedstock, as dispersing medium for the catalyst precursor, when hydrocarbonaceous oil other than the feedstock can be more optimum for developing catalyst activity. U.S. Patent No. 5,053,376 teaches the use of elemental sulfur as a sulfiding agent.

A catalyst precursor concentrate is usually presulfided and converted to a catalyst concentrate comprised of solid catalyst particles dispersed in a hydrocarbonaceous oil. At least a portion of this catalyst is then introduced into the hydrocarbonaceous chargestock to be hydroconverted, with or without coal. Typically, a catalyst concentrate that contains from about 0.2 wt.% up to 0.7 wt.% Mo is added to the process feedstock to obtain a blend of feed and concentrate that contains from about 0.005 wt.% (50 wppm) to about 0.100 wt.% (1000 wppm) Mo. This invention is concerned only with introducing a presulfided catalyst precursor concentrate into a hydroconversion zone and not a catalyst concentrate.

Attempts to increase the molybdenum content of presulfided, preformed catalyst concentrates results in loss of catalyst activity when the concentration is increased above about 0.7 wt.% molybdenum (see Figure 2). The problem appears to derive from association of small catalyst particles as the concentration of catalyst particles increases, thus resulting in loss of catalyst dispersibility.

The presence of higher molybdenum levels in a concentrate is valued in that such levels minimize the size of the preparation facilities as well as the volume of the concentrate stream that must be blended with process feed to maintain a given level of Mo in the reactor. Reduction of stream volume makes the maintenance of heat balance simpler and reduces the amount of gas oil entering the reactor in the case where an atmospheric residuum is used as the vehicle for the concentrate preparation. Reduction of the volume of gas oil results in reduction in gas production and in consumption of hydrogen.

It has now been found that this concentration limit of about 0.7 wt.% Mo can be overcome by eliminating the catalyst preforming step and feeding only the presulfided precursor concentrate into the hydro-conversion zone. When a presulfided precursor concentrate is used, the concentration of Mo in the concentrate can be raised to 1.5 wt.%, and above, without sacrifice in activity of the catalyst that is ultimately formed when blends of precursor concentrate and process feed (overall Mo content of 50 to 1000 wppm) are subjected to hydroconversion conditions (Figure 2).

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a process for hydroconverting a hydrocarbonaceous chargestock to lower boiling products, which comprises reacting the hydrocarbonaceous charge-stock with a presulfided catalyst precursor concentrate in the presence of hydrogen at hydroconversion conditions, the presulfided catalyst precursor concentrate having been prepared by the steps which comprise: (a) forming a mixture of a hydrocarbonaceous oil comprising constituents boiling above about 565° C and an aqueous solution of a precursor containing a molybdenum polyacid precursor in an amount to provide from about 0.2 wt.% to 5 weight percent molybdenum, calculated as elemental molybdenum, based on the hydrocarbonaceous oil to produce a water-containing catalyst precursor concentrate, (b) drying the water-containing catalyst precursor concentrate to remove water and produce a substantially water-free catalyst precursor concentrate, and (c) contacting the resultant catalyst precursor concentrate with added hydrogen sulfide at a temperature from about 10° C up to but not including the temperature of catalyst formation, and a hydrogen sulfide partial pressure ranging from about 14.7 psia to about 200 psia to produce a presulfided catalyst precursor concentrate.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a schematic flow plan of one embodiment of the invention.

Figure 2 is a graph comparing the catalyst activity of presulfided precursor concentrate and presulfided-preformed catalyst concentrate as the wt.% molybdenum in the concentrate increases from 0.2 wt.% to 1.5 wt.%.

Figure 3 is a graph comparing the wt.% of catalyst solids in the catalyst concentrate stream as a function of catalyst preforming temperature. The threshold temperature for catalyst solids formation is about 315° C.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the Figure 1, a heavy hydrocarbonaceous oil is introduced by line 10 into mixing zone 1. Suitable hydrocarbonaceous oils for introduction into mixing zone 1 include hydrocarbonaceous oils comprising constituents boiling above 565° C, preferably having at least 10 wt.% constituents boiling above 565° C, such as crude oils, atmospheric residua boiling above 340° C, and vacuum residua boiling above 565° C. Preferably, the hydrocarbonaceous oil has an initial boiling point above at least 340° C and comprise asphaltenes and/or resins. Most preferably, the hydrocarbonaceous oils comprise a lighter boiling oil boiling below 565° C and a heavier oil boiling above about 565° C in a blend comprising at least about 22 wt.% materials boiling above 565° C. Preferred concentrations of the 565+° C blend include from about 22 to 85 wt.% heavier oil, more preferably from about 30 to 85 wt.% heavier oil, still more preferably about 40 to 85 wt.% heavier oil, and most preferably about 45 to 75 wt.% heavier oil, based on the total weight of the blend (mixture of oils). The light oil may be a gas oil and heavier oil may be a vacuum residuum. Alternatively, an atmospheric residuum having the appropriate amount of desired constituents may be used as the oil of line 10.

An aqueous solution of phosphomolybdic acid (or other suitable water or oil soluble molybdenum compound) is introduced into mixing zone 1 via line 12. A sufficient amount of the aqueous phosphomolybdic acid solution is introduced into mixing zone 1 to provide from about 0.2 to 5, preferably from about 0.2 to 3, more preferably 0.5 to 2 wt.% molybdenum from the phosphomolybdic acid, calculated as elemental molybdenum based on the hydrocarbonaceous oil. The resulting mixture is a water-containing catalyst precursor concentrate (i.e., wet catalyst precursor concentrate). The wet catalyst precursor concentrate is removed from mixing zone 1 via line 14 and passed to drying zone 2. In drying zone 2, bulk water is removed from the wet catalyst precursor concentrate by any suitable manner, such as heating the water-containing catalyst precursor concentrate to a temperature sufficient to vaporize the water. A temperature ranging from about 100° C to 150° C is suitable for this purpose. Water is removed from drying zone 2 via line 16.

The term "phosphomolybdic acid" is used herein to designate aqueous solutions of the reaction product of MoO_3 with dilute phosphoric acid in which the phosphorus to molybdenum atomic ratio ranges from 0.083 to 2.00, preferably from 0.083 to 1.00 and most preferably from 0.083 to 0.50. These solutions can contain one or more phosphomolybdic acid species such as the 12-molybdophosphoric acid (e.g. $H_2PMo_{12}O_{40}$ x H_2O) and the dimeric 18-molybdophosphoric acid. Moreover, the crystalline 12 and 18 acids can be used to prepare the water solutions of phosphomolybdic acid used in the process of the invention. As to phosphomolybdic acids refer to *Topics in Current Chemistry* No. 76, published by Springer-Verlag of New York, pp. 1-64, 1978.

Although phosphomolybdic acid is most often employed, other suitable molybdenum compounds convertible (under preparation conditions) to presulfided catalyst precursor concentrates include: (1) inorganic metal compounds such as carbonyls, halides, oxyhalides, poly acids such as isopolyacids and heteropolyacids (e.g., molybdosilicic acid, as well as phosphomolybdic acid); (2) molybdenum salts of organic acids such as acyclic and alicyclic aliphatic carboxylic acids and thiocarboxylic acids containing two or more carbon atoms (e.g., naphthenic acids); aromatic carboxylic acids (toluic acid); sulfonic acids (e.g., toluene-sulfonic acid); sulfinic acid; mercaptans, xanthic acids; phenols, di- and polyhydroxy aromatic compounds: (3) organomolybdenum compounds such as chelates, e.g., with 1,3-diketones, ethylenediamine, ethylenediaminetetraacetic acid, phthalocyanines, etc.; (4) molybdenum salts of organic amines such as aliphatic amines, aromatic amines and quaternary ammonium compounds.

The essentially water-free catalyst precursor concentrate is removed from drying zone 2 and is passed to sulfiding zone 3 via line 18. Of course, if an aqueous solution of catalyst precursor is not used, then the drying step can be eliminated. In sulfiding zone 3, the dry catalyst precursor concentrate is contacted with a sulfiding agent which may be a hydrogen sulfide-containing gas, hydrogen sulfide precursor, or elemental sulfur. Hydrogen may be present or absent during the sulfiding step, preferably absent. The sulfiding agent is preferably a gas comprising from 10 to 100 mole percent hydrogen sulfide. The sulfiding step is conducted at relatively low total pressures. Suitable low pressures include a total pressure ranging from about 0 to 450 psig, preferably a pressure ranging from about 0 to 100 psig. The hydrogen sulfide partial pressure may range from about 14.7 psia to 200 psia, preferably from 20 psia to 100 psia. Suitable temperatures in the sulfiding zone include a temperature of at least about 10° C up to, but not including the temperature at which the precursor will be converted to a catalyst, preferably the temperature will be from about 10° C to 315° C, more preferably from about 40° C to 150° C. Suitable contact times will range from about 5 minutes to 120 minutes, depending on the sulfiding temperature employed. Contact of the essentially dry catalyst precursor concentrate with the sulfiding agent at the given conditions produces a presulfided catalyst precursor concentrate.

If elemental sulfur is used, it may be used either as a sublimed powder, or as a concentrated dispersion of sublimed powder, such as commercial Flowers of Sulfur, in heavy hydrocarbonaceous oil. Allotropic forms of elemental sulfur, such as orthorhombic and monoclinic sulfur are also suitable. The preferred physical form of sulfur is the sublimed powder (flowers of sulfur), although sulfur may also be introduced as molten sulfur and as sulfur vapor. The amount of sulfur added into mixing zone 1 is such that the atomic ratio of sulfur to molybdenum is from about 1/1 to 8/1, preferably from about 2/1 to 7/1 and more preferably from about 3/1 to 6/1. Preferably, sulfur is dispersed in the hydrocarbonaceous oil prior to addition of the molybdenum compound, e.g., the aqueous solution of phosphomolybdic acid. The sulfur containing precursor mixture is subjected to a brief contact of from about 5 minutes to 60 minutes at a temperature ranging from about 300° F to 600° F to prepare the presulfided precursor concentrate. The use of elemental sulfur is described in detail in U.S. Patent No. 5,039,392 which is incorporated herein by reference.

The effluent of the presulfiding zone comprising the presulfided catalyst precursor concentrate and a gaseous phase including the unreacted sulfiding agent (for purpose of this discussion, H_2S) is passed by line 20 to separation zone 4 in which the gaseous phase comprising the H_2S and any remaining water is separated from the presulfided catalyst precursor concentrate. The gaseous phase is removed via line 22. The catalyst precursor concentrate can be fed via lines 24 and 46 as a separate stream to the reactor. This stream is maintained at a temperature up to, but not including the threshold temperature for catalyst formation. Figure 3 illustrates this. Direct injection of presulfided concentrate is therefore possible (without loss of activity) when the inlet line temperature is held below about 315° C, for example in the range of about 100° C to 315° C, preferably in the range of about 285-315° C. The threshold temperature of catalyst formation is approximately 315° C. Insulated nozzles are required. Furthermore, catalyst precursor injection should be at a point of severe mixing or turbulence.

Alternately, all or part of the concentrate may be passed through line 26 to be blended with the reactor chargestock of line 28. In this alternative, the inlet line temperature at the point where the concentrate mixes with process feed should not exceed about 315° C. Regardless of the option chosen, it is essential that the temperature of the presulfided precursor concentrate be maintained below about 315° C until such point that the precursor concentrate can be blended, in more or less instantaneous fashion (i.e., at a point of high turbulence) with process feed or with reactor liquid. Maintenance of concentrate temperature below about 315° C ensures that formation of catalyst solids does not occur (Figure 3), thus avoiding loss of activity that occurs when concentrates that contain above 0.7 wt.% Mo are converted to catalyst concentrates (i.e., the presulfided-preformed concentrates of Figure 2).

Line 28 carries a hydrocarbonaceous chargestock which may have the same boiling point range as the hydrocarbonaceous oil of line 10. It may alternately be a single hydrocarbon or a mixture of hydrocarbons having the same boiling point range as the hydrocarbonaceous oil of line 10, or a different boiling point range from the hydrocarbonaceous oil of line 10. The hydrocarbonaceous chargestock may be a hydrocarbonaceous oil or coal in a hydrocarbon diluent. Suitable hydrocarbonaceous oil chargestocks include crude oils; mixtures of hydrocarbons boiling above 220° C, preferably above 340° C, for example, gas oils, vacuum residua, atmospheric residua, once-through coker bottoms, and asphalt. The hydrocarbonaceous oil chargestock may be derived from any source, such as petroleum, shale oil, tar sand oil, oils derived from coal liquefaction processes, including coal liquefaction bottoms, and mixtures thereof. Preferably, the hydrocarbonaceous oils have at least 10 wt.% materials boiling above 565° C. More preferably, the hydrocarbonaceous oils have a Conradson carbon content ranging from about 5 to about 50 wt.%. Coal may be added to any of these oils. Alternatively, slurries of coal in a hydrocarbon diluent may be used as chargestock to convert the coal (i.e., coal liquefaction). The diluent may be a single type of hydrocarbon or a mixture of hydrocarbons and may be a light hydrocarbon or a heavy hydrocarbon, as described in U.S. Patent No. 4,094,765, column 1, lines 54 to column 2, line 43, the teachings of which are hereby incorporated by reference.

When at least a portion of the presulfided catalyst precursor concentrate is introduced into the chargestock, the concentrate disperses in the chargestock. If the chargestock comprises coal in a diluent, the presulfided precursor concentrate is added to the diluent before, after or simultaneously with the addition of coal to the diluent. A hydrogen-containing gas is introduced via line 30 into line 28. The mixture of hydrocarbonaceous chargestock and presulfided catalyst precursor concentrate and hydrogen is passed into slurry hydroconversion zone 6.

The presulfided catalyst precursor concentrate is added to the hydrocarbonaceous chargestock in an amount sufficient to provide from about 10 to about 1000 wppm molybdenum, preferably 50 to 300 wppm molybdenum, calculated as elemental molybdenum, based on the total hydroconversion zone chargestock, i.e., presulfided precursor concentrate plus hydrocarbonaceous chargestock.

Catalyst effectiveness is reduced when precursor concentrates containing more than about 0.7 wt.% Mo are converted to catalyst concentrates prior to injection into the hydroconversion zone (see Figure 2). Therefore, it is preferred that the direct injection of presulfided concentrate into the hydroconversion zone, or into chargestock prior to the reactor, be so configured that the injection line and/or nozzle be operated at a temperature below that at which the precursor concentrate is converted to the corresponding catalyst concentrate, i.e., the temperature at which catalyst particles are formed.

As illustrated in Figure 3, there is an apparent threshold temperature of about 315° C at which the presulfided precursor catalyst concentrate is converted to a catalyst concentrate. Thus, for direct injection of precursor concentrate into the reactor, the maximum temperature for the injection line and/or nozzle will be preferably held to a maximum of about 315° C, more preferably below 315° C and most preferably between 285° C-315° C. Once the presulfided precursor concentrate is injected into the reactor liquid in the reaction zone, there is concurrent formation of catalyst particles and dilution of catalyst particles in the reactor liquid, which condition results in retention of the maximum catalyst effectiveness.

Alternatively, presulfided precursor concentrates that contain more than about 0.7 wt.% Mo can be preblended with part or all of the chargestock prior to injection into the hydroconversion zone. Preferably, in this mode of operation, the mixing of presulfided precursor concentrate with chargestock results in a stream in which the presulfided precursor concentrate, expressed as concentration of Mo, is less than about 0.7 wt.% and more preferably below about 0.5 wt.%. Further, in this mode of operation, the temperature of the presulfided precursor concentrate will also be held below about 315° C.

Suitable hydroconversion operating conditions are summarized in Table 3.

TABLE I

Conditions	Broad Range	Preferred Range
Temperature, °C	425 to 510	435 to 470
H_2 Partial Pressure, psig	50 to 5000	100 to 2500

The hydroconversion zone effluent is removed by line 32 and passed to a gas-liquid separation zone 7 wherein the normally gaseous phase is separated from a normally liquid phase. The gaseous phase is removed from separation zone 7 via line 34. Alternatively, the gaseous phase,which comprises hydrogen, may be recycled via line 36, preferably after removal of undesired constituents to hydroconversion zone 6 via line 30. The normally liquid phase, which comprises the molybdenum-containing catalytic solids and a hydroconverted hydrocarbonaceous oil product is passed via line 38 to liquid-liquid separation zone 8 for fractionation by conventional means, including distillation into various fractions, such as light, medium, and heavy boiling heavy bottoms fractions. The light fraction is removed via line 40. The medium boiling fraction is removed via line 42 and collected for further use or processing. The heavy bottoms fraction is removed via line 44, and if desired, at least a portion of this bottoms fraction may be recycled to hydroconversion zone 6.

Furthermore, if desired, the catalytic solids may be separated from the hydroconverted oil product and the separated solids may be recycled to hydroconversion zone 6.

The following examples are presented to illustrate the invention.

EXAMPLES

Example 1 - Preparation of presulfided catalyst precursor concentrate that contains 0.44 wt.% Mo (preparation R-1839-CP)

This preparation was carried out in a standard Autoclave Engineer's 300 cc autoclave with Magnedrive stirrer. The concentrate was prepared in whole Cold Lake bitumen, which bitumen had an initial boiling point of about 232° C, 50 wt % of bottoms that had a boiling point greater than 524° C, and a Conradson Carbon content of 13.4 wt.%. Phosphomolybdic acid solutions were prepared from crystalline phosphomolybdic acid ($20\ MoO_3 . 2\ H_3PO_4 . 48\ H_2O$) supplied by Fisher Scientific.

The autoclave was charged with 90 g. of bitumen, flushed with nitrogen and heated to 80° C with stirring. At this point, 10 g. of a solution of phosphomolybdic acid in deionized water (4 wt.% Mo in solution) was injected into the autoclave and stirring was continued at 80° C for 10 minutes. At the end of this period a flow of nitrogen was started through the autoclave and the temperature was raised to 149° C and maintained at 149°C for 10 minutes to remove water. Sulfiding was then carried out by adding 50 psig hydrogen sulfide for a 30 minute stirred treatment at 149° C. The autoclave was subsequently vented, flushed with hydrogen and cooled to room temperature. There was recovered about 90 g. of presulfided catalyst precursor concentrate that contained 0.44 wt.% Mo.

Example 2 - Preparation of presulfided catalyst precursor concentrate that contains 0.5 Wt.% Mo (preparation R-2589-CP)

The procedure of Example 1 was repeated with the exceptions that whole Athabasca Bitumen was substituted for whole Cold Lake Bitumen and that 9 g. of a 5 wt % Mo solution was injected. This Athabasca Bitumen, comparable to the Cold Lake Bitumen, had an initial boiling point of about 260°C, contained 47 wt.% of components boiling above 525° C and 12.3 wt.% Conradson Carbon. Upon completion of the sulfiding step there was recovered 91 g. of presulfided catalyst precursor concentrate that contained 0.55 wt.% Mo.

Example 3 - Preparation of presulfided catalyst precursor concentrate that contains 1.0 Wt.% Mo (preparation R-2590-CP)

The procedure of Example 2 was followed, except that the concentration of phosphomolybdic acid in deionized water was increased such that the concentration of Mo in the solution was 6.0 wt.%, and the amount of solution injected into 90 g. of Athabasca Bitumen was increased to 15.0 g. There was recovered 92 g. of presulfided catalyst precursor concentrate that contained 0.98 wt.% Mo.

Example 4 - Preparation of presulfided catalyst precursor concentrate that contains 1.5 Wt.% Mo (preparation R-2596-CP)

The procedure of Example 2 was followed except that the concentration of phosphomolybdic acid in deionized water was increased such that the concentration of Mo in the solution was 7 wt.%, and the amount of solution injected into the Athabasca Bitumen was increased to 20.0 g. Also, H_2S pressure in the sulfiding step was increased to 100 psig. There was recovered 103 g. of presulfided catalyst precursor concentrate that contained 1.5 wt.% Mo.

Example 5 - Preparation of presulfided and preformed catalyst concentrate that contains 0.44 Wt.% Mo (preparation R-1851-CP)

The procedure of Example 1 was followed through completion of the sulfiding step and removal of excess

H_2S. At this point the reactor was sealed and the temperature was increased to 371°C and held for a period of 20 minutes, which step resulted in conversion of the presulfided preformed catalyst concentrate to a sulfided catalyst concentrate. Upon cooling and venting the reactor there was obtained 90 g. of catalyst concentrate that contained 0.44 wt.% Mo.

When 30 g. of catalyst concentrate was diluted with 90 g. of toluene and filtered, there was recovered 0.84 g. (2.8 wt.%) of preformed catalyst solids.

Example 6 - Preparation of presulfided and preformed catalyst concentrate that contains 0.86 Wt.% Mo (preparation R-2511-CP)

The procedure of Example 5 was followed with the following exceptions; whole Athabasca Bitumen (see Example 2) was substituted for whole Cold Lake Bitumen, the concentration of phosphomolybdic acid in deionized water was increased such that the concentration of Mo in solution was 6 wt.%, the amount of solution injected was increased to 11.7 g. and H_2S pressure in the sulfiding step was increased from 50 to 100 psig.

Upon completion of the preforming step the reactor was vented while still at 371° C and then cooled to room temperature. Some light hydrocarbon liquid was removed from the reactor upon venting. There was recovered 88.2 g. of presulfided and preformed catalyst concentrate that contained 0.86 wt.% Mo. The concentration of toluene-insoluble, filterable catalyst solids was 6.1 wt.% in the concentrate.

Example 7 - Preparation of presulfided and preformed catalyst concentrate that contains 1.05 Wt.% Mo (preparation R-2510-CP)

The procedure of Example 6 was followed except that the amount of phosphomolybdic acid solution added to the 90 g. of bitumen was increased to 15 g. Upon completion of the preforming step there was recovered 86 g. of presulfided and preformed concentrate that contained 1.05 wt.% Mo. The concentration of toluene-insoluble, filterable catalyst solids in the concentrate was 6.9 wt.%.

Example 8 - Preparation of presulfided and preformed catalyst concentrate that contains 1.52 wt.% Mo (preparation R-2508-CP)

The procedure of Example 6 was followed except that the concentration of phosphomolybdic acid in deionized water was increased such that the concentration of Mo in solution was 7 wt.%, and the amount of solution injected was increased to 20.0 g. Upon completion of the preforming step there was recovered 88 g. of presulfided and preformed concentrate that contained 1.60 wt.% Mo. The concentration of toluene insoluble, filterable catalyst solids in the concentrate was not determined.

Example 9 - Test of presulfided precursor concentrate of Example 1 under hydroconversion conditions (Test no. R-1842)

A hydroconversion run was carried out with a Cold Lake Crude vacuum bottoms feed, which had an initial boiling point of about 490° C and which contained 94.8 wt.% of components boiling above 524° C and 23.4 wt.% Conradson Carbon.

To a 300 cc Autoclave Engineer's autoclave, equipped with Magnedrive stirrer, was charged 109.5 g. of Cold Lake vacuum bottoms, 5.00 g. of whole Cold Lake crude (see Example 1 for feed properties) and 5.50 g of the presulfided catalyst concentrate of Example 1. The amount of concentrate charged was sufficient to give a Mo concentration of 201 wppm in the total reactor charge, i.e., the combined weight of vacuum bottoms, whole Cold Lake crude and catalyst preparation. The autoclave was next flushed with hydrogen, sealed and stirred for 10 minutes at 93°C to mix the reactor contents.

Upon cooling to room temperature, the autoclave was charged with 1350 psig hydrogen. With stirring the autoclave was heated to 385° C and held at 385° C for 20 minutes. At this point, autoclave pressure was adjusted to 2100 psig, a flow of hydrogen was started through the autoclave to maintain an outlet gas rate of 0.36 liter/min. (as measured at room temperature and atmospheric pressure) and the temperature was increased to 443°C.

Upon completion of a three hour stirred contact at 443° C under 2100 psig with hydrogen flow of 0.36 l/min., the flow of hydrogen was stopped and the autoclave was cooled quickly to 93° C.

Gaseous products were vented form the autoclave at 93° C, scrubbed with dilute caustic solution to remove hydrogen sulfide, passed through a wet test meter to determine volume and then collected for analysis by mass spectrometry. Gaseous products that were collected during the flow-through portion of the run were also collected and analyzed. Some light liquid product, b.p. 16° C-316° C, swept from the autoclave during the flow-through period was collected in a cold, high-pressure knockout vessel that was attached to the autoclave gas exit line.

Liquid and solid products that remained in the autoclave were removed by washing with toluene, and the toluene wash was then filtered to recover solids, which solids comprise catalyst residues, demetallation products and toluene insoluble coke. After washing with toluene and drying under vacuum, the solids were weighed and analyzed for carbon content.

The yield of toluene insoluble coke was calculated as follows:

$$\text{Tol. Insol. Coke, Wt.\% on } 524{+}^\circ\text{C Feed} = \frac{\dfrac{\text{g. dry solids X wt frac carbon}}{0.85^*}}{\text{g. } 524{+}^\circ\text{C Feed}} \text{ X } 100$$

(* Empirical factor for converting g. carbon to g. coke)

Unconverted feed boiling at a temperature greater than 524° C (vacuum bottoms) was recovered from the toluene wash by distillation and the product was analyzed for Conradson carbon content.

The yield of toluene insoluble coke was 1.73 wt.% on feed boiling at a temperature greater than 524° C (i.e., 524+° C bottoms) and conversion of Conradson Carbon to non-coke products was 61%.

Example 10 - Test of presulfided precursor concentrate of Example 2 under hydroconversion conditions (test no. R-2592)

The hydroconversion test described in Example 9 was repeated with a reactor charge consisting of 109.5 g. of vacuum Cold Lake, 4.10 g. of whole Cold Lake Crude and 6.40 g. of the presulfided catalyst concentrate of Example 2. The concentration of Mo in the reactor charge was 266 wppm.

The yield of toluene insoluble solids from this test was 1.91 wt.% on 524+° C feed and conversion of Conradson Carbon to non-coke products was 67%.

Example 11 - Test of presulfided precursor concentrate of Example 3 under hydroconversion conditions (test no. R-2593)

The hydroconversion test described in Example 9 was repeated with a reactor charge consisting of 109.5 g. of vacuum Cold Lake bottoms, 7.23 g. of whole Cold Lake crude and 3.27 g. of the presulfided catalyst precursor concentrate of Example 3. The concentration of Mo in the reactor charge was 270 wppm.

The yield of toluene insoluble coke was 1.82 wt.% on 524+° C feed and conversion of Conradson Carbon to non-coke products was 66 %.

Example 12 - Test of presulfided precursor concentrate of Example 4 under hydroconversion conditions (test number R-2601)

The hydroconversion test described in Example 9 was repeated with a reactor charge consisting of 109.5 g. of vacuum Cold Lake bottoms, 8.36 g. of whole Cold Lake crude and 2.14 g. of the presulfided precursor concentrate of Example 4. The Mo concentration in the reactor charge was 267 wppm.

The yield of toluene insoluble coke was 1.81 wt.% on 524+° C feed, and Conradson carbon conversion to non-coke products was 65%.

Example 13 - Test of presulfided/preformed catalyst concentrate of Example 5 under hydroconversion conditions (test number R-1853)

The hydroconversion test described in Example 9 was repeated with a reactor charge that consisted of 109.5 g. of vacuum Cold Lake bottoms, 5.00 g. of whole Cold Lake crude and 5.50 g. of presulfided/preformed catalyst concentrate of Comparative Example 5. The Mo concentration in the reactor charge was 202 wppm.

The yield of toluene insoluble coke was 1.54 wt.% on 524+° C feed, and Conradson Carbon conversion to non-coke products was 67%.

Example 14 - Test of presulfided/preformed catalyst concentrate of Comparative Example 6 under hydroconversion conditions (test number R-2514)

The hydroconversion test described in Example 9 was repeated with a reactor charge that consisted of 109.5 g. of vacuum Cold Lake bottoms, 7.01 g. of whole Cold Lake crude and 3.49 g. of the presulfided/preformed catalyst concentrate of Comparative Example 6. The Mo concentration in the reactor charge was 250 wppm.

The yield of toluene insoluble coke was 2.11 wt.% on 524+° C feed and Conradson Carbon conversion to non-coke products was 65%.

Example 15 - Test of presulfided/preformed catalyst concentrate of Comparative Example 7 under hydroconversion conditions (test number R-2521)

The hydroconversion test described in Example 9 was repeated with a reactor charge that consisted of 109.5 g. of vacuum Cold Lake bottoms, 7.77 g. of whole Cold Lake crude and 2.73 g. of the presulfided/preformed catalyst concentrate of Comparative Example 7. The Mo concentration in the reactor charge was 238 wppm.

The yield of toluene insoluble coke was 2.43 wt.% on 524+° C feed and conversion of Conradson Carbon to non-coke products was 73%.

Example 16 - Test of presulfided/preformed catalyst concentrate of Comparative Example 8 under hydroconversion conditions (test number R-2517)

The hydroconversion test described in Example 9 was repeated with a reactor charge that consisted of 109.5 g. of vacuum Cold Lake bottoms, 8.62 g. of whole Cold Lake crude and 1.88 g. of the presulfided/preformed catalyst concentrate of comparative Example 8. The Mo concentration in the reactor charge was 251 wppm.

The yield of toluene insoluble coke was 4.92 wt.% on 524+° C feed and conversion of Conradson Carbon to non-coke products was 46%.

Example 17 - Preparation of presulfided/preformed catalyst concentrate using H_2S as sulfiding agent and preforming at 360°C (preparation R-2535-CP)

A presulfided/preformed catalyst concentrate was prepared according to the following procedure:

Step A - To an aqueous solution of 20 g. of phosphomolybdic acid (Climax Molybdenum Lot Number 1768-37) which contained 5.18 wt.% Mo and 0.17% P there was added 0.19 g. of phosphoric acid (85 wt.% H_3PO_4). A sample of 8.82 g. of the resultant modified solution was then injected into 90 g. of whole Athabasca Bitumen while stirring at 80° C in a standard 300 cc autoclave from Autoclave Engineers. Stirring was continued for 10 minutes after injection of the solution.

Step B - The autoclave was then heated with stirring to a temperature of 149° C and held for 10 minutes with nitrogen flow-through to remove water.

Step C - At this point the autoclave was charged with 100 psig H_2S and stirring was continued at 150° C for an additional period of 30 minutes.

Step D - Excess hydrogen sulfide was removed from the autoclave by venting he autoclave while still at 150° C and then sweeping with nitrogen.

Step E - With the autoclave free of excess H_2S and sealed, the temperature was increased to 360° C for a 30-minute stirred contact to form the catalyst, i.e., the catalyst concentrate.

Upon dilution of a 30 g. sample of the resultant concentrate with 150 g. of toluene and then filtering over a #2 Whatman paper, there was recovered 1.19 g of catalyst solids that contained 11.6 wt.% Mo. Thus, the concentration of catalyst solids in this catalyst concentrate, which was preformed at 360° C, was 3.96 wt.%.

Example 18 - Preparation of presulfided/preformed catalyst concentrate using H_2S as sulfiding agent and preforming at 331°C (preparation R-2567-CP)

The procedure of Example 17 was repeated except that the temperature used to preform the catalyst in Step E was 331° C.

The resultant catalyst concentrate contained 4.03 wt.% catalyst solids, which solids contained 11.3 wt.% Mo.

Example 19 - Preparation of presulfided/preformed catalyst concentrate using H_2S as sulfiding agent and preforming at 318°C (Preparation R-2744-CP)

The procedure of Example 17 was repeated except that the temperature used to preform the catalyst in Step E was 318° C.

The resultant catalyst concentrate was not completely formed and contained only 1.77 wt.% solids.

Example 20 - Preparation of presulfided/preformed catalyst concentrate using sulfur as sulfiding agent and preforming at 360° C (preparation R-2534-CP).

Preparation of presulfided/preformed catalyst concentrate using sulfur as sulfiding agent was carried out in a manner similar to that described in Example 17, except that Steps C and D (associated with use of H_2S were omitted.

Step A - The procedure of Example 17 was repeated except that a blend of 89.14 g. of whole Athabasca Bitumen with 0.86 g. of Flowers of sulfur was substituted for the 90 g. charge of whole Athabasca Bitumen.

Step B - The procedure described in Step B of Example 17 was repeated.

Step C - Upon completion of the drying step of Step B, the autoclave was sealed and then heated with stirring to a temperature of 360° C to sulfide and to form the catalyst. The time required for heating the autoclave from 149° C to 360° C was 20 minutes, which interval provided time for formation of the presulfided precursor.

The resultant presulfided/preformed catalyst concentrate contained 4.87 wt.% catalyst solids, which solids contained 9.34 wt.% Mo.

Example 21 - Preparation of presulfided/preformed catalyst concentrate using sulfur as sulfiding agent and preforming at 343°C (preparation R-2552-CP)

The procedure of Example 20 was repeated except that the preforming temperature used in Step C was 343° C.

The resultant presulfided/preformed catalyst concentrate contained 4.56 wt.% catalyst solids, which solids contained 10.0 wt.% Mo.

Example 22 - Preparation of presulfided/preformed catalyst concentrate using sulfur as sulfiding agent and preforming at 327°C (preparation R-2566-CP)

The procedure of Example 20 was repeated except that the preforming temperature used in Step C was 327° C.

The resultant presulfided/preformed catalyst concentrate contained 4.60 wt.% catalyst solids, which solids contained 9.9 wt.% Mo.

Example 23 - Preparation of presulfided/preformed catalyst concentrate using sulfur as sulfiding agent and preforming at 327°C (preparation R-2575-CP)

The procedure of Example 20 was repeated except that the preforming temperature of Step C was 315° C.

The resultant concentrate did not contain filterable solids.

Example 24 - Preparation of presulfided/preformed catalyst concentrate using sulfur as sulfiding agent and preforming at 300°C (preparation R-2557-CP)

The procedure of Example 20 was repeated except that the preforming step of Step C was 300° C.

The resultant concentrate did not contain filterable solids.

Claims

1. A process for converting a hydrocarbonaceous chargestock to lower boiling products at hydroconversion conditions and in the presence of hydrogen, which process comprises:
   (a) forming a mixture of hydrocarbonaceous oil comprising constituents boiling above about 565°C with

a water-soluble or oil-soluble molybdenum compound in an amount to provide from about 0.2 to 5 weight percent molybdenum, calculated as elemental molybdenum, based on said hydrocarbonaceous oil, to produce catalyst precursor concentrate;

(b) drying said catalyst precursor concentrate if an aqueous solution was used to introduce a water-soluble molybdenum compound, to remove said water and produce a substantially water-free catalyst precursor concentrate;

(c) contacting said catalyst precursor concentrate with a sulfiding agent sulfide at a temperature from about 10°C up to, but not including catalyst formation temperatures, and a hydrogen sulfide partial pressure ranging from about 14.7 psia (101.36 kPa) to about 100 psia (689.5 kPa) to produce a presulfided catalyst precursor concentrate;

(d) separating any unreacted sulfiding agent from the presulfided catalyst precursor concentrate;

(e) introducing the presulfided catalyst precursor concentrate and the hydrocarbonaceous chargestock into a hydroconversion zone; and

(f) converting the hydrocarbonaceous chargestock to lower boiling products by subjecting said chargestock and presulfided catalyst precursor concentrate to hydroconversion conditions wherein the hydroconversion conditions include temperatures from about 425°C to 510°C, and a hydrogen partial (gauge) pressure of from about 50 to 5000 psig (0.345 to 34.475 MPa).

2. The process of claim 1 wherein the molybdenum compound is selected from polyacids and heteropolyacids.

3. The process of claim 1 or claim 2 wherein the molybdenum compound is a phosphomolybdic acid in aqueous solution.

4. The process of any one of claims 1 to 3 wherein the hydrocarbonaceous oil of step (a) is an atmospheric distillation residuum.

5. The process of any one of claims 1 to 4 wherein the sulfiding agent is selected from hydrogen sulfide and elemental sulfur.

6. The process of claim 5 wherein the sulfiding agent is elemental sulfur and is used in a ratio of elemental sulfur to molybdenum of from about 1:1 to 8:1.

7. The process of claim 6 wherein the ratio of elemental sulfur to molybdenum is from about 1:1 to 5:1.

8. The process of any one of claims 1 to 7 wherein the presulfided catalyst precursor concentrate is fed into the hydrocarbonaceous chargestock prior to its introduction into the hydroconversion zone.

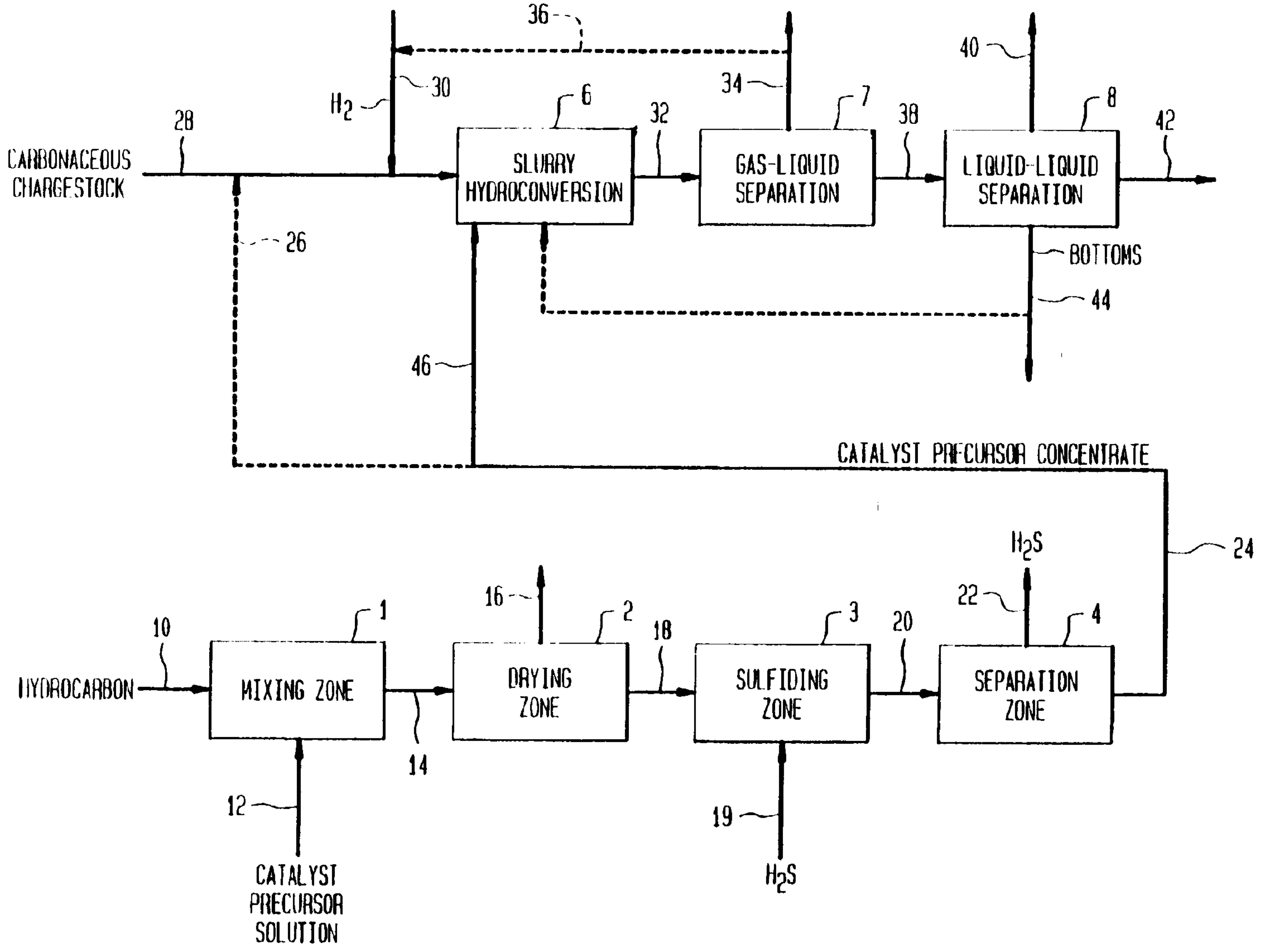


FIG. 1

CARBONACEOUS CHARGESTOCK
28
26
H2
30
36
6
SLURRY HYDROCONVERSION
32
34
7
GAS-LIQUID SEPARATION
38
40
8
LIQUID-LIQUID SEPARATION
42
BOTTOMS
44
46
CATALYST PRECURSOR CONCENTRATE
24
HYDROCARBON
10
1
MIXING ZONE
12
CATALYST PRECURSOR SOLUTION
14
16
2
DRYING ZONE
18
3
SULFIDING ZONE
19
H2S
20
22
H2S
4
SEPARATION ZONE

FIG. 2

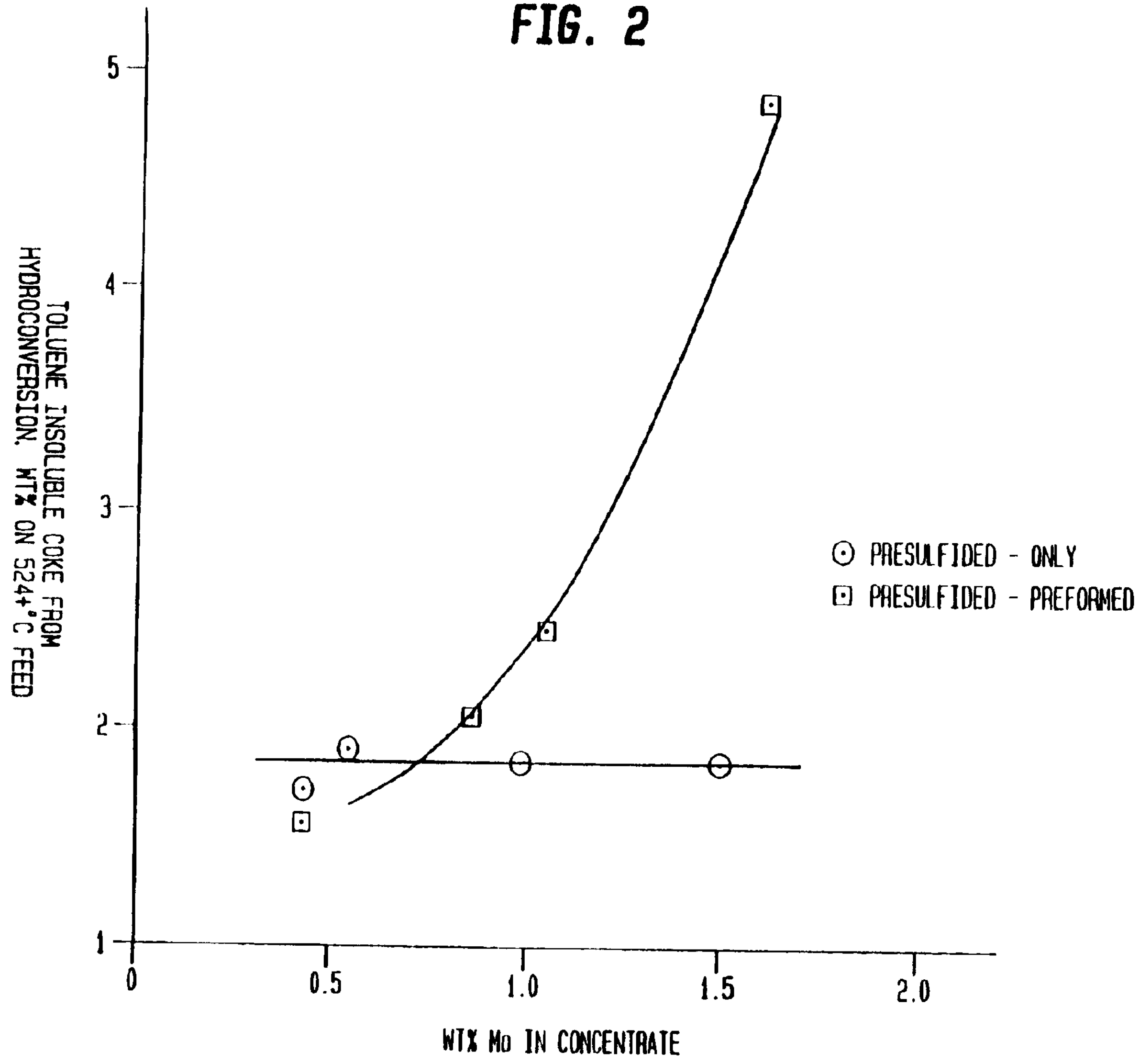
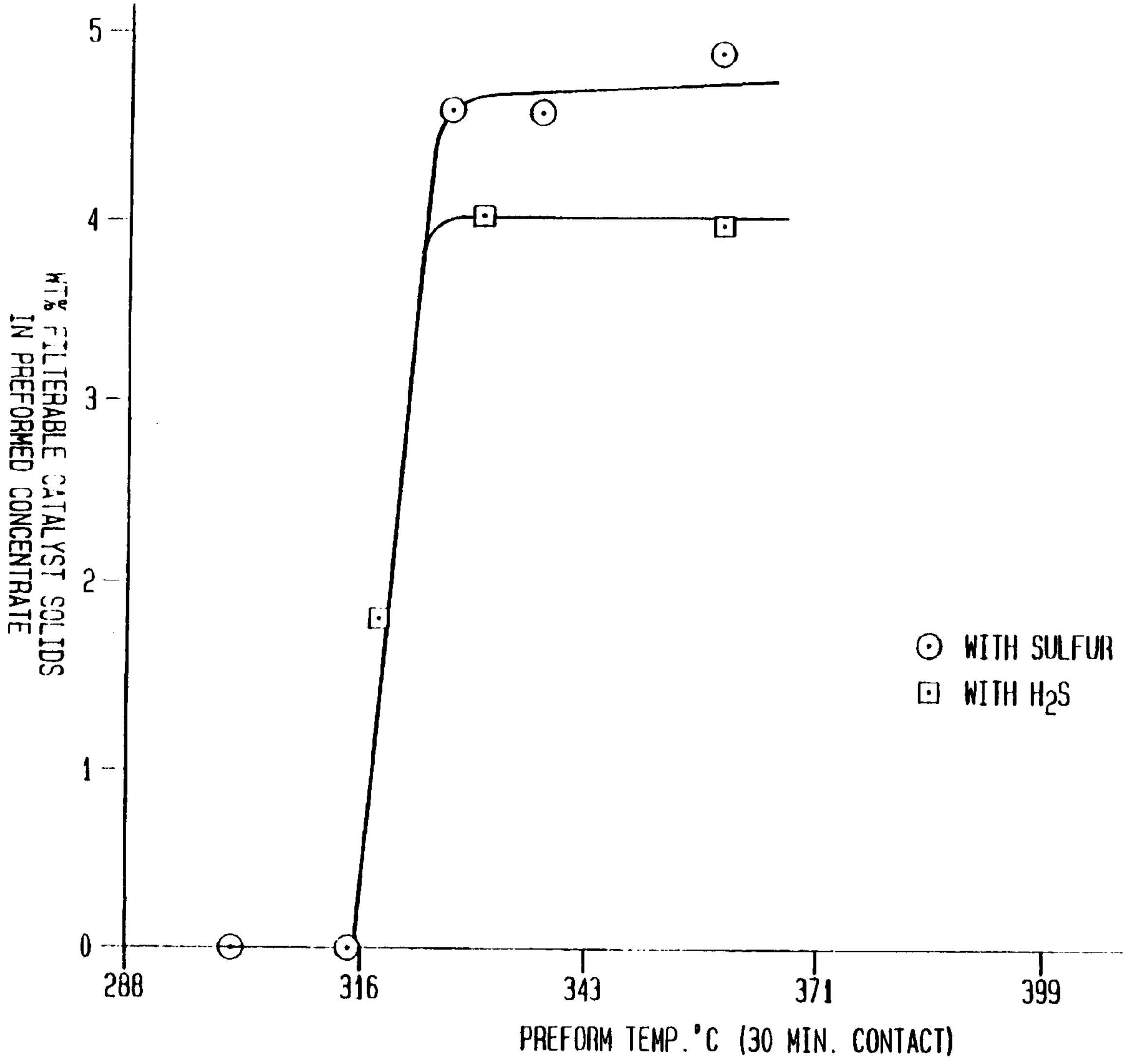

TOLUENE INSOLUBLE COKE FROM HYDROCONVERSION. WT% ON 524+°C FEED
1
2
3
4
5
0
0.5
1.0
1.5
2.0
WT% Mo IN CONCENTRATE
⊙ PRESULFIDED - ONLY
⊡ PRESULFIDED - PREFORMED

FIG. 3


WT% FILTERABLE CATALYST SOLIDS
IN PREFORMED CONCENTRATE
0
1
2
3
4
5
288
316
343
371
399
PREFORM TEMP.°C (30 MIN. CONTACT)
⊙ WITH SULFUR
⊡ WITH H2S

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 92311502.6

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US - A - 5 039 392 (BEARDEN et al.) * Totality * --	1-8	C 10 G 47/02 C 10 G 47/06
X	EP - A - 0 243 143 (EXXON RESEARCH AND ENGINEERING COMPANY) * Totality * --	1-8	
D,X	US - A - 4 740 295 (BEARDEN et al.) * Claims * --	1-8	
D,X	US - A - 4 740 489 (BEARDEN et al.) * Claims * --	1-8	
D,X	US - A - 5 053 376 (BEARDEN et al.) * Claims * --	1-8	
P,X	US - A - 5 108 581 (ALDRIDGE et al.) * Claims * ----	1-8	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 10 G B 01 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	28-01-1993	BECK

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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