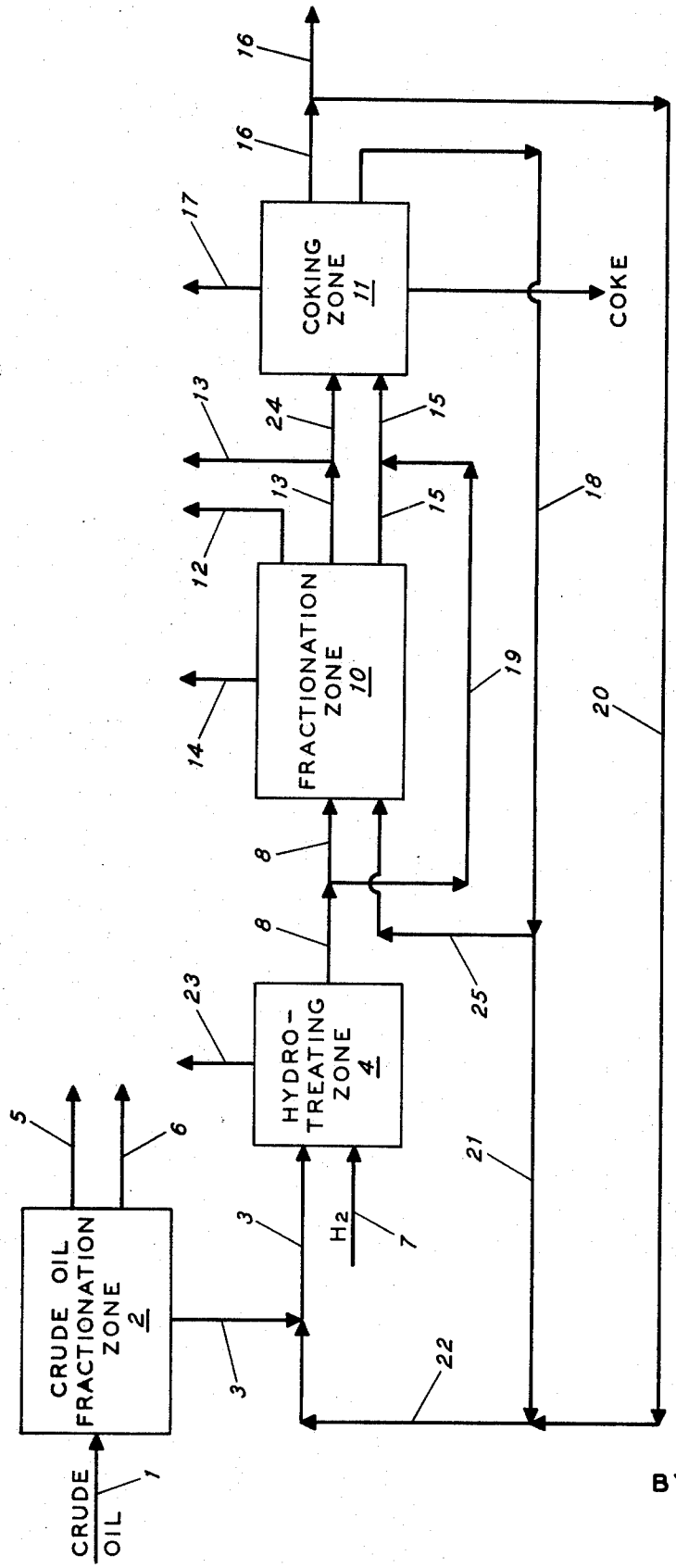
Aug. 15, 1972 R. R. ROSELIUS 3,684,688

HEAVY OIL CONVERSION

Filed Jan. 21, 1971



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United States Patent Office 3,684,688
Patented Aug. 15, 1972

3,684,688

HEAVY OIL CONVERSION

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Filed Jan. 21, 1971, Ser. No. 108,378
Int. Cl. C10b 55/00; C10g 23/02; B01d 11/82
U.S. Cl. 208—50 10 Claims

ABSTRACT OF THE DISCLOSURE

A process for obtaining increased normally liquid hydrocarbon yields from coking a hydrocarbon feed containing at least three parts per million metals which process comprises: (a) contacting the feed, at elevated temperature and pressure and in the presence of added hydrogen, with a hydrotreating catalyst comprising Group VI and Group VIII metals and an inorganic refractory base, and having at least 50 percent of its pore volume from pores 100 angstroms or larger in pore diameter to obtain a hydrotreated feedstock, and (b) coking at least a portion of the hydrotreated feedstock at a temperature between 700° F. and 1100° F. to obtain solid coke and vaporized normally liquid hydrocarbons. Preferred hydrotreating catalysts for use in the process are obtained by expanding the catalyst during catalyst production by adding a high molecular weight detergent to the catalyst hydrogel before the hydrogel is dried and calcined. Also, it is preferred to use a common fractionation zone for both the hydrotreating step and the coking step and to eliminate vacuum distillation ahead of the hydrotreating step.

BACKGROUND OF THE INVENTION

The present invention relates to coking, particularly coking of metals-contaminated hydrocarbon feedstocks. The present invention also relates to the combination of hydrotreating and coking and fractionation facilities.

Various types of coking processes are known, including delayed coking, moving bed coking and fluidized coking. Furnace type coking units are called "delayed cokers" because they heat the residuum or other hydrocarbon feedstock to coking temperatures so rapidly that little reaction occurs while the charge is in the furnace. Effluent from the furnace discharges at about 850° F. to 1000° F. into a large "coke drum," where it remains until it either cracks and passes off as vapor or condenses into coke. Coke drums operate at pressures in the range of 10 to 150 p.s.i.g. Because the reaction is endothermic, vapors leave the coke drum at about 800 to 850° F. When a coke drum is filled, the furnace effluent is diverted to another drum, and the coke is removed from the first one.

Among the moving bed coking processes which have been developed are contact coking in the U.S.A. and the Hoechst process in Germany. In both processes the product coke particles constitute the circulating heat carrier. However, in contact coking, heat is supplied by burning part of the coke in the preheater, whereas the Hoechst process employs indirect exchange with flue gas in tubes in the preheater. Also, mass lift is used in the contact process, gas lift in the Hoechst process. Moving bed coking processes are described in Petroleum Refiner, 34(10):139 (1955); and Petroleum Engineering, 26 (8):C-10 (1954).

Fluidized beds are also used in coking heavy oil feedstocks such as residuum feedstocks. As with moving beds, the product coke is circulated through a burner and a reactor, and high reaction temperatures are possible. Steam is used to fluidize the coke bed in the reactor.

Typical reactor conditions are 925° F., and 5 to 10 p.s.i.g. Because the coke particles grow during the operation, a portion of the circulating solids may be drawn off (in addition to the net coke production), ground, and returned to the unit as "seed coke." Sufficient seed coke is recycled to hold the circulating solids in the desired size range. The size of the circulating coke may also be controlled by the use of an elutriator. The net coke production is withdrawn from the elutriator as large particles, and the finer particles are recycled to the reactor.

Coking is generally applied to the conversion of feedstocks such as vacuum residuum to coke and suitable charge for a hydroconversion step such as hydrocracking and hydrodesulfurization or as a charge for catalytic cracking or catalytic reforming. For example, U.S. Pat. 2,727,853 describes a process for the upgrading of heavy oils wherein effluent from a delayed coking step is passed to catalytic polymerization and vapor phase hydrogenation with a portion of the hydrogenated material being passed to catalytic cracking. According to the process disclosed in U.S. Pat. 2,727,853, asphaltic material from a propane deasphalting step ahead of the delayed coking step is fed to the coking step. Effluent from the coking step can be fed in part to the propane deasphalting step with the deasphalted material from the propane deasphalting step being fed to catalytic cracking, U.S. Pat. 3,238,117 and U.S. Pat. 3,493,489 also disclose coking ahead of a hydroconversion step, particularly coking ahead of hydrocracking. U.S. Pat. 2,988,501 and U.S. Pat. 3,027,317 disclose coking ahead of hydrodesulfurization.

U.S. Pat. 2,871,182 discloses hydrodesulfurization ahead of coking. According to the U.S. Pat. 2,871,182 disclosure, any sulfactive catalyst such as cobalt and molybdenum oxides on alumina can be used for the desulfurization step ahead of coking. The metals content of the feed to the U.S. Pat. 2,871,182 process is not given.

SUMMARY OF THE INVENTION

According to the present invention, a process is provided for obtaining increased normally liquid hydrocarbon yields from coking a hydrocarbon feed containing at least three parts per million metals which process comprises: (a) contacting the feed, at elevated temperature and pressure and in the presence of added hydrogen, with a hydrotreating catalyst comprising Group VI and Group VIII metals and an inorganic refractory base, and having at least 50 percent of its pore volume from pores 100 angstroms or larger in pore diameter to obtain a hydrotreated feedstock, and (b) coking at least a portion of the hydrotreated feedstock at a temperature between 700° F. and 1100° F. to obtain solid coke and vaporized normally liquid hydrocarbons.

In the process of the present invention, I have found that unexpected yields of normally liquid hydrocarbons are obtained from the coking step when using certain expanded catalysts in the hydrotreating step preceding the coking step. The term "normally liquid" is used herein to mean hydrocarbons which exist in the liquid form at room temperature and pressure, i.e., about 70° F., and atmospheric pressure. The use of catalysts having relatively large pore sizes is particularly important in the process of the present invention as opposed to the use of general hydrotreating catalyst particles which usually have average pore sizes considerably below 100 angstroms in diameter. The pore size of the catalyst can be calculated by various methods, usually assuming the pores in the catalyst can be treated as approximately cylindrical. Pore size distribution can be obtained, for example, by capillary condensation methods as described, for example, by

E. P. Barrett, L. G. Joyner, and P. H. Halenda in the Journal of the American Chemical Society, vol. 73, p. 373 (1951). Larger pore sizes, usually in the range of 100 angstroms and larger, are frequently determined by a pressure porosimeter method described, for example, by H. L. Ritter and L. C. Drake in Industrial and Engineering Chemistry, vol. 17, p. 782 (1945).

Various methods can be used to obtain the hydrotreating catalyst of larger than average pore diameters for use in the hydrotreating step of the present invention. For example, commonly assigned application Ser. No. 774,203, filed Nov. 7, 1968, and now abandoned, discloses that optimum catalyst properties, including increased pore sizes may be obtained by adding titania, Alundum particles, or recycle catalyst fines to the catalyst during the process of forming a catalyst. Also, Ser. No. 778,332, filed Nov. 22, 1968, now U.S. Pat. 3,577,353, discloses a process for producing catalysts of increased pore size obtained by extracting the catalyst with an alcohol, such as methanol, during manufacture of the catalyst particles. The disclosures of the two aforesaid patent specifications are incorporated by reference into the present patent application.

Johnson and Mooi, in the Journal of Catalysis, 10, 342–354 (1968), discuss pore distribution in alumina catalysts. In their discussion, reference is made to treating alumina gels with methanol to exchange methanol for water in the alumina gels. The catalyst obtained upon drying and calcining had larger pore sizes than for those catalysts which were not treated with methanol to replace water prior to drying and calcining.

A particularly preferred method for producing catalysts with larger average pore diameters is described in commonly assigned application Ser. No. 3,239, the disclosure of which application is incorporated by reference into the present specification. The expanded (or increased pore size) catalyst production process described in Ser. No. 3,239 comprises (a) forming a hydrogel comprising at least one inorganic compound (which is typically converted to an oxide upon subsequent calcination), (b) adding a detergent to the hydrogel, and (c) carrying out at least part of the drying of the hydrogel after the detergent is added to the hydrogel.

Particular hydrotreating catalysts which can advantageously be expanded in accordance with the above process include composites comprising discrete substantially insoluble metal phosphate particles surrounded by a continuous phase matrix comprising at least one solid oxide and at least one hydrogenating component selected from Group VI–B metals, and compounds thereof, and Group VIII–B metals, and compounds thereof. Particularly preferred catalyst composites for production in expanded form for use in the process of the present invention are described in more detail in U.S. Pat. 3,493,517, the disclosure of which patent is incorporated by reference into the present specification. The hydrotreating catalysts to which U.S. Pat. 3,493,517 is directed are particularly preferred for use in the process of the present invention for reasons including the following reasons:

(1) the hydrotreating catalyst containing metal phosphates in a continuous phase matrix of other catalyst components as described in U.S. Pat. 3,493,517 can be readily expanded using methods such as the use of a high molecular weight detergent as described in Ser. No. 3,239;

(2) the metal phosphate particles in the catalyst to which U.S. Pat. 3,493,517 is directed appear to contribute both to larger pore sizes of the catalyst composite and to enhanced hydrotreating activity for the catalyst;

(3) in addition to the increased metals capacity for the expanded or relatively large pore-sized catalyst, the stability of the catalyst is relatively high in hydrotreating, particularly hydrodesulfurizing, metals-contaminated heavy feedstocks, such as residuum feedstocks, so that the catalyst can be kept on-stream at high activity ahead of the coking step of the present invention for relatively long periods of time.

In the process of the present invention, although it is particularly important to use a catalyst having relatively large pores, it is also preferred to use a relatively high hydrogenation activity catalyst, particularly a catalyst having a high activity for hydrodesulfurization and hydrodemetallation of heavy feedstocks. It is strongly preferred that the catalyst used in the process of the present invention have high activity for hydroconversion of asphaltenes and hydrogenation of aromatics.

In order to achieve a high activity for hydrotreating reactions such as hydrogenation, hydrodesulfurization, hydrodenitrification and hydrodemetallation, as opposed to only a high capacity for demetallation, it is usually preferred to use catalyst composites having a surface area of at least 100 square meters per gram of catalyst. Using the expansion methods as described in Ser. No. 3,239, average pore diameters of 100 angstroms and larger can be obtained while still producing catalyst particles having a surface area above 100 or 200 square meters per gram as, for example, 275 square meters per gram.

For the hydrotreating step of the process of the present invention, it is preferred to use a hydrotreating catalyst bed as described in U.S. Pat. 3,496,099 in order to reduce the rate of pressure drop build-up due to the deposition of metals, particularly iron, when hydrotreating the residuum feedstock ahead of the coking step. Thus, when using one or more fixed catalyst beds with the hydrotreating step of the present invention, it is preferred to pass the hydrocarbon feed together with hydrogen through a first or initial catalyst bed or layer having increasing hydrogenation catalytic activity along the normal direction of feed flow through the bed or layer. Other preferred methods for carrying out hydrotreating, particularly hydrodesulfurization simultaneously with hydrodemetallation of heavy feedstocks such as atmospheric residuum or vacuum residuum, are described in commonly assigned applications Ser. Nos. 2,096 and 2,097. The disclosures of U.S. Pat. 3,496,099 and Ser. Nos. 2,096 and 2,097, particularly those portions of the latter two applications relating to the porosity of the catalyst used for simultaneous hydrodesulfurization and hydrodemetallation, are incorporated by reference into the present specification.

The process of the present invention is applied to heavy oils or residuum feedstocks containing three parts per million metals present as soluble organometallic compounds, and usually 20–200 parts per million metals. The term "metals" is used herein (in reference to metals in the hydrocarbon feedstock to the hydrotreating step) to mean metals selected from the group consisting of iron, nickel, and vanadium. Other metals may also be present, such as sodium and calcium, but the term "metals" is not used in the present specification to include metals outside the iron, nickel, and vanadium group. Iron, nickel, and vanadium, which are frequently present in residuum feedstocks to a substantial extent, present a difficult problem in hydrotreating processes as the metals are usually in large part converted from the soluble organometallic form during the hydrotreating reactions to insoluble elemental and sulfided forms which plug up and otherwise foul the catalyst particles used in the hydrotreating step.

However, the preferred catalyst used in the hydrotreating step, particularly expanded hydrogel catalysts containing at least 200 $m.^2/g.$ of surface area but also containing a substantial amount of pores having a diameter of 100 angstroms or greater, operate to achieve high hydrogenation (and hydrodesulfurization) activity as well as high hydrodemetallation activity and capacity.

Thus, the process of the present invention is particularly advantageously applied to a residuum feedstock containing at least 0.5 weight percent sulfur present as organic sulfur compounds, and usually between about 1.0 and 7 weight percent sulfur in addition to a substantial quantity of metals contaminants. Also, the preferred ex-

panded catalysts, as indicated previously, operate in a surprising cooperative manner with the subsequent coking step to achieve considerably greater yields from the coking step than would be expected on the basis of the boiling range of the feed fed to the coking step.

A very important aspect of the preferred large-pore catalysts used in the hydrotreating step is their high capability to reduce the asphaltenes (normal-pentane insoluble constituents) of the residuum hydrocarbon feed to the hydrotreating step by at least 25 percent and, more preferably, about 40 percent or more as, for example, from an asphaltene weight percent of about 5 percent to an asphaltene weight percent of about 2.5 percent. Heavy oil effluent from the hydrotreating step of substantially reduced asphaltene content has been found to result in particularly high liquid yields from coking of the reduced asphaltene content heavy oil.

Preferably, the coking step utilizes a delayed coking process with a furnace outlet temperature of about 900 to 1100° F., and a coking temperature for the coking drum between about 700° and 900° F.

We have found that the hydrotreating step and the coking step of the present invention are advantageously integrated by feeding long residuum derived from a crude oil feedstock directly to the hydrotreating step without any vacuum distillation and with at least a portion of the hydrotreating step effluent being fed to the coker main fractionation column. The coker fractionation column thus receives effluent from the hydrotreating step as well as coker oil effluent from the coking step.

Particularly in the case of delayed coking, it is preferred to use vaporized normally liquid hydrocarbon effluent from the coke drum as a stripping medium in the coker fractionation column which receives the effluent from the hydrotreating step. In this manner, the coker fractionation column serves multiple purposes, operating in part as a replacement for the normal vacuum distillation column, and also as a main rough fractionation column for the effluent from the hydrotreating step, and as a fractionation column for the effluent from the coking step. Products from the coker fractionator or common fractionation column usually include a gaseous stream, a gasoline stream which can be further upgraded as, for example, by catalytic reforming, and a gas oil stream which can be further upgraded as, for example, by hydrotreating or by hydrocracking and/or catalytic cracking.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a process flow diagram schematically indicating a preferred embodiment of the process of the present invention.

DETAILED DESCRIPTION

Referring now in more detail to the drawing, a crude oil is fed to crude oil fractionation zone **2** via line **1**. In addition to crude oil, other hydrocarbon sources such as shale oils and oils derived from coal can be fed to fractionation zone **2**; crude oil represents a preferred and typical feedstock for the process of the present invention. Crude oil fractionation zone **2** can consist of various fractionation columns such as an atmospheric crude oil distillation column followed by a vacuum distillation column receiving reduced crude from the bottom of the atmospheric distillation column. However, in accordance with a preferred embodiment of the present invention, fractionation zone **2** consists basically of an atmospheric distillation column with the typical vacuum distillation column being omitted. A reduced crude or long residuum is withdrawn from the bottom of the atmospheric distillation column in zone **2**, via line **3**, and is fed to hydroconversion zone **4**. Lighter products including, for example, a naphtha product and a gas oil product are withdrawn via lines **5** and **6** from fractionation zone **2**.

Hydroconversion zone **4** must contain catalyst particles having relatively large pore diameters as this is a critical aspect of the process of the present invention. The hydroconversion zone can serve primarily to hydrodemetallate the long residuum feed to zone **4** by contacting the feed at elevated temperature and pressure and in the presence of hydrogen added via line **7** with a hydrotreating catalyst comprising Group VI and Group VIII metals and an inorganic refractory base. The hydrotreating catalyst preferably is used to accomplish at least some desulfurization of the residuum feedstock introduced via line **3** in addition to accomplishing the removal of 25–50 weight percent or more (e.g., up to 80 or 90 wt. percent) of the metals in the residuum feedstock. The catalyst used in the hydroconversion zone should have at least 50 percent of its pore volume from pores 100 angstroms or larger in pore diameter, or have an average pore diameter of about 100 angstroms.

For high metals content feedstocks, larger pore diameters are desired for the hydrotreating catalyst used in zone **4**. In many instances, it is advantageous to have a substantial amount of macropores in the catalyst used in zone **4**, macropores being defined herein as pores having a diameter greater than about 500 angstroms. When using the catalyst in zone **4** in one or more fixed catalyst beds, as opposed to fluidized or ebulated catalyst beds, it is particularly preferred to use the macroporous catalyst in the uppermost part of the fixed hydroconversion catalyst bed as described in more detail in the previously mentioned applications, Ser. Nos. 2,096 and 2,097.

Preferably, a large amount of the catalyst used in hydroconversion zone **4**, for example, 40 percent or more of the catalyst, is catalyst which has a high activity for both hydrodesulfurization (usually requiring a surface area of at least 100 $m.^2/g.$, and preferably at least 200 $m.^2/g.$) and hydrodemetallation, as well as having a relatively high capacity for demetallation. As indicated previously, preferably the catalyst has at least 50 percent of its pore volume from pores 100 angstroms or larger in pore diameter. For feedstocks to the hydrotreating step having a metals content greater than 20 parts per million, the high desulfurization activity, high demetallation activity and capacity catalyst preferably has at least 50 percent of its pore volume from pores 130 angstroms or larger in pore diameter. For residua feedstocks having 35 parts per million metals or more, the catalyst preferably has at least 50 percent of its pore volume from pores 150 angstroms or larger in pore diameter. I have found that in using expanded catalysts of high hydrodesulfurization activity, and high hydrodemetallation capacity, and activity, between 25 and 95 percent of the sulfur present as organic sulfur in the residuum feed to the hydrotreating step can be converted to H_2S, and then easily removed from the feed so that subsequent coking of the 900° F.+ or 1000° F.+ effluent fraction from hydrotreating can be coked to give a relatively low sulfur and low metals content coke and surprisingly high liquid hydrocarbon coking yields.

Preferred operating conditions for the hydrotreating step of the present invention include a temperature between 600° F. and 850° F., pressure between 500 and 5,000 p.s.i.g., a hydrogen rate between 100 and 10,000 standard cubic feet of hydrogen per barrel of feed, and a liquid hourly space velocity between about 0.1 and 10.0.

According to the preferred embodiment shown in the drawing, the effluent from hydrotreating zone **4** is passed via line **8** to fractionation zone **10**. Fractionation zone **10** is used to distill relatively light hydrocarbons including gasoline boiling range hydrocarbons and gas oil boiling range hydrocarbons from the hydrotreating zone effluent as well as from the effluent from coking zone **11**. The gasoline fraction is indicated as removed via line **12** and the gas oil fraction via line **13**. Light gases can be removed via line **14**. The gas oil fraction can be one or more cuts or hydrocarbon fractions such as light gas oil (400–600° F. boiling range), medium gas oil (500–800° F.), and heavy gas oil (650–1000° F.). The gas oil fractions with-

drawn via lines **12** and **13** are particularly attractive feedstocks to catalytic cracking and/or hydrotreating to produce gasoline and/or jet fuel. In the process of the present invention, streams **12** and **13** have a relatively high aniline point and low aromaticity, as is shown in more detail by Example I hereinbelow.

Fractionation zone **10**, according to the preferred embodiment, advantageously can serve to separate a heavy gas oil fraction which typically would be separated from vacuum residuum by a large and expensive vacuum distillation step applied to the reduced crude obtained from the atmospheric distillation column used in zone **2**.

Fractionation zone **10** can contain two or more distillation columns operating in series, but usually fractionation zone **10** basically consists of a large fractionation column with multiple cuts being removed from the column. The lower heavy cut from the fractionation zone can be a 1000° F.+ boiling range fraction for feed via line **15** to coking zone **11**.

The coking temperature usually is between about 700° F. and 1100° F. Coking in zone **11** can be, for example, fluid coking or delayed coking, although delayed coking is preferred.

Fluid coking is described in Petroleum Refiner, vol. 39, No. 5, May 1960, pages 157–160.

In delayed coking, the heavy hydrocarbon feed typically passes from the bottom of a fractionator column to a furnace wherein it is heated to a temperature sufficient for heavy oil cracking. The heated heavy oil is introduced to an insulated drum where the residence time is sufficient for coke to form and settle from the mixture. Suitable operating conditions for delayed coking in zone **11** include a furnace outlet temperature between about 850° F. and 950° F., a coke drum temperature between about 750° F. and 850° F., and a coke drum pressure between about 10 and 70 p.s.i.g.

When coke boils up to a predetermined level in one of the coke drums for a delayed coking unit, flow is diverted to another drum so that the furnace operation is continuous. Thus, the drums are operated in pairs with one on-stream while the other is being dumped. A full coke drum is removed from the process flow, steamed to strip light hydrocarbons from the coke, and cooled by water injection. Various means have been used to remove the coke from the coke drums with recent designs using high pressure (over 1000 p.s.i.g.) water jets to cut the coke from the drum.

According to that preferred embodiment of the process of the present invention wherein delayed coking is used in zone **11**, hot vapors from the coking drum are returned to fractionation zone **10** via line **18** and **25**. The hot vapors introduced via line **25** to zone **10** serve to aid in the stripping of the heavy material removed from hydrotreating zone **4** via line **8**. As indicated previously, gasoline boiling range hydrocarbons and gas oil boiling range hydrocarbons are removed from the fractionation zone via lines **14, 12** and **13**. Heavier material present primarily in the hydrotreating zone effluent, but also in the vapors removed via line **18** from coking zone **11**, are removed via line **15** from the common fractionation zone and fed to coking zone **11**. The hot vapors withdrawn from coking zone **11**, via line **18**, can be fed to hydrotreating zone **4** (usually after condensation and some fractionation) via lines **21, 22**, and **3** instead of feeding this portion of the coking zone effluent to fractionation zone **10**. Some fractionation facilities can form a portion of coking zone **11** so that product hydrocarbons are withdrawn via lines **17, 16**, and **18**. Thus, heavier gas oil hydrocarbons can be withdrawn via line **18**, medium boiling range hydrocarbons via line **16**, and then recycled, for example, to hydrotreating zone **4** via lines **20, 22**, and **3**, and light gaseous hydrocarbons via line **17**.

Gaseous hydrocarbons also are usually withdrawn from hydrotreating zone **4**, as is schematically indicated at line **23**.

EXAMPLES

Table 1a shows a liquid volume yield of C_5+ material of coking of 1000° F.+ residuum of 76.8%. Table 1b shows a C_5+ vol. percent yield of 86.4% from coking of hydrotreated 975° F.+ residuum. Thus, the yield from the hydrotreated residuum was about 10 percent greater than the yield from the non-hydrotreated residuum.

The hydrotreating catalyst used for hydrotreating the residuum ahead of the coking step was one in accordance with the process of the present invention, i.e., a hydrotreating catalyst having more than 50 percent of its pore volume in pores larger than 100 angstroms in diameter. Furthermore, the hydrotreating catalyst was a catalyst formed by a cogelation preparation plus the use of a procedure to obtain an "expanded" catalyst, i.e., a catalyst with increased average pore sizes, not merely increased porosity. In particular, the average pore diameter of the catalyst used was greater than 130 angstroms.

The catalyst used for the hydrotreating step in the above examples was prepared in accordance with the procedure described in U.S. Pat. 3,493,517 for the production of a hydrotreating catalyst comprising discrete metal phosphate particles in a continuous phase matrix of other catalyst components such as Group VI compounds including molybdenum or tungsten and Group VIII compounds including nickel or cobalt. Furthermore, the catalyst was expanded using a high molecular weight detergent according to the process described in Ser. No. 3,239 for obtaining catalysts with a substantial amount of large pores, but yet with a relatively high hydrodesulfurization and hydrodemetallation activity. The average size of the pores in the catalyst used in Example I above was about 170 angstroms.

Referring again more particularly to the series of tables for Example I, the question can be raised as to the comparability of the C_5 liquid yield from the non-hydrotreated 1000° F.+ fraction versus the hydrotreated 970° F.+ fraction in view of the fact that the 975° F.+ fraction included 25° F. of material boiling below the material in the 1000° F.+ fraction. That is, it is difficult to estimate how much of the 975° F. to 1000° F. portion would go to light gases and coke in the coking step and how much would go to the formation of C_5+ liquid.

Table 1c of Example I shows the yields for C_5+ liquid on the basis of whole crude. Column 1 in Table 1c shows a C_5+ liquid volume yield of 43.4% for hydrotreating followed by 975° F.+ coking in accordance with the present invention.

Table 1c, column 2, shows a C_5+ liquid yield of 38.3 for coking a 750° F.+ feedstock.

Column 3 of Table 1c shows a yield of 39.6% C_5+ liquid for coking a 1000° F.+ residuum *and adding* in the C_5+ liquid fraction, represented by the 750 to 1000° F. boiling range vacuum gas oil.

Column 1 of Table 1c is thus directly comparable to columns 2 and 3 as all three columns show the yield of C_5+ liquid material in the 750° F.+ fraction except that the processing was different for the respective columns, as indicated in the headings for the respective columns. It is seen that the C_5+ liquid yield is about 4 vol. percent higher on the basis of whole crude and about 10% higher on the basis of 750° F.+ fraction. This is a surprising and unexpected increase in C_5+ liquid yield which I have found is achieved in accordance with the process of the present invention.

It may also be noted in comparing column 2 to column 3 of Table 1c that the amount of C_5+ liquid produced from coking decreases when the boiling point of the material to the coking step is lower. In column 2 the C_5+ liquid is 38.3 vol. percent for the coking of 750° F.+ residuum. In column 3 the yield is 39.6 for the coking of 1000° F.+ residuum with the 750 to 1000° F. material added back in so that the C_5+ liquid yield is on the basis of 750° F.+ material has a net overall yield as a percent

of whole crude. Thus, it appears that when the feedstock to the coking step is of a lower boiling point more material goes to light gases and coke than when the coking feedstock is of a higher initial boiling point. This indicates that the improved results in C_5+ liquid yield obtained in accordance with the process of the present invention are not a result of the lower boiling point of the feedstock to the coking step. (The comparative examples used do not have exactly the same boiling point cut point because the examples were generated from experimental data which was obtained previous to my finding of the unexpected advantage obtained in accordance with the process of the present invention.)

The data in the second example, which is presented by Tables 2a and 2b, further supports the unexpected advantage achieved in accordance with the process of the present invention. Example 2 also demonstrates that the process of the present invention applies to a variety of heavy hydrocarbon feedstocks. The process of the present invention, as indicated earlier, is preferably applied to feedstocks containing asphaltenes, and usually also contain a substantial amount of organometallic compounds. In general, the feedstock will contain at least 50% by volume of material boiling above 600° F. The feedstock also will usually have at least 2 vol. percent asphaltenes, that is, heavy hydrocarbon material which is not soluble in pentane.

The data presented in Example I shows that a higher aniline point is achieved for the products from the cokng step using the process of the present invention than when material is coked without using the process of the present invention. In Table 1a the aniline point of the 450 to 650° F. gas oil is 125, whereas in Table 1b in accordance with the present invention it is 138. Also, the aniline point for the 650° F.+ material in Table 1a is 153, whereas the 650° F.+ maetrial for the coking of hydrotreated 975° F. residuum in Table 1b is 170. The higher aniline points indicate more aromaticity. The lower aromaticity feedstocks are better catalytic cracking feedstocks, and also are better feedstocks for hydrocracking to produce jet fuel or gasoline.

TABLE 1a, EXAMPLE I—ALASKAN NORTH SLOPE CRUDE

	Coking nonhydrotreated (straight run) residua [1]									
	Straight run residuum feed		Coking, 750° F. plus residuum				Coking, 1,000° F. plus residuum			
			Product				Product			
	750° F.	1,000°F.+	Yield	Coke	400–650° F.	650° F.+ gas oil	Yield	Coke	400–650° F.	650° F.+ gas oil
Yield to crude, vol. percent (wt. percent)	44.6	21.7		(8.08)	9.54	22.5		(6.84)	5.66	8.22
Gravity, °API	14.0	8.5			31.7	20.2			32.6	21.0
Sulfur, wt. percent	1.7	2.2		2.57	1.13	1.30		2.63	1.22	1.48
Nitrogen, p.p.m.	3,880	6,800		2,450	800	2,170		2,650	870	4,100
Conradson carbon, wt. percent	9.0	17.3								0.5
n-Pentane insolubles (asphaltenes), wt. percent	4.3	7.7								
Viscosity, cs./210° F	80	1,950								
Metals, p.p.m:										
Fe	2.5	5		15				18		
Ni	24	49		135				170		
V	38	80		220				280		
UOP "K"/aniline point, ° F		11.60/			/126	/165			/125	/153
Asphaltene cut:										
Wt. percent residuum		7.7								
Sulfur, wt. percent		3.0								
Metals, p.p.m.:										
Fe		52								
Ni		310								
V		450								
Ashpaltene-free cut:										
Wt. percent of residuum		92.3								
Sulfur, wt. percent		1.98								
Metals, p.p.m.:										
Fe		~1								
Ni		26								
V		50								
Coking yields:										
Coke, wt. percent			16.6				27.8			
C_4—gas, wt. percent			5.7				7.7			
C_5+liquid, wt. percent			77.7				64.5			
C_5+liquid, vol. percent			86.0				76.8			
400–650° F., vol. percent			21.4				26.1			
650° F. plus gas oil, vol. percent			50.4				37.9			

[1] Temperature, 760–890° F., pressure, 15 p.s.i.a.

TABLE 1b, EXAMPLE I—ALASKAN NORTH SLOPE CRUDE

	Coking hydrotreated residua [1]									
	Straight run residuum feed			hydrotreating 750° F+ residuum [2]			Coking hydrotreated 975° F. plus residuum			
				Product			Product			
	750° F.+	975° F.– fraction	975° F.+ fraction	Yield	C_5–800° F.	800–975° F.	975° F.+	Yield	Coke	400–650° F.	650° F.+ gas oil
Yield to crude, vol. percent (wt. percent)	44.6	20.5	24.1		7.5	16.7	22.2		(4.15)	5.95	9.50
Gravity, ° API	14.0	20.2	8.6		35.0	24.0	14.7			34.3	22.8
Sulfur, wt. percent	1.7	1.2	2.2		0.08	0.13	0.53		1.2	0.19	0.37
Nitrogen, p.p.m.	3,880	1,920	6,000		700	1,400	3,390		1,900	780	2,860
Conradson carbon, wt. percent	9.0	0.2	17.1				9.2				0.4
n-Pentane insolubles (asphaltenes), wt. percent			7.2				2.8				
Viscosity, cs./210° F	80	55	1,800			10	215				
Metals, p.p.m.:											
Fe	2.5		5				3				
Ni	24		43			0.08	10		60		
V	38		75			0.02	10		60		
UOP "K"/aniline point, ° F		/173	11.60/		/150	/190	11.83/			/138	/170
Asphaltene cut:											
Wt. percent of residuum			7.5				2.8				
Sulfur, wt. percent			3.0				4.8				
Metals, p.p.m.:											
Fe			50								
Ni			280				315				
V			400				360				

TABLE 1b, EXAMPLE I—Continued

	Straight run residuum feed			Coking hydrotreated residua [1] hydrotreating 750° F+ residuum [2]				Coking hydrotreated 975° F. plus residuum			
					Product				Product		
	750° F.+	975° F.− fraction	975° F.+ fraction	Yield	C_5− 800° F.	800− 975° F.	975° F.+	Yield	Coke	400− 650° F.	650° F.+ gas oil
Asphaltene-free cut:											
Wt. percent of residuum			92.5				97.2				
Sulfur, wt. percent			1.98				0.48				
Metals, p.p.m.:											
Fe			~1								
Ni			25				5				
V			45				4				
Coking yields:											
Coke, wt. percent								17.2			
C_4—gas, wt. percent								6.4			
C_5+liquid, wt. percent								76.4			
C_5+liquid, vol. percent								86.4			
400–650° F. vol. percent								26.8			
650° F+gas oil, vol. percent								42.8			
Hydrotreating yields:											
H_2 cons., s.c.f./b				600							
C_5–750° F., vol. percent				12.6							
750–975° F., vol. percent				41.6							
975° F.+, vol. percent				49.8							
975° F.+, wt. percent				49.5							

[1] Temperature, 760–800° F.; pressure, 15 p.s.i.a.
[2] Temperature, 750° F.; 0.6 LHSV; pressure, 2,400 p.s.i.g.; 2,000 s.c.f./b. H_2, rec.

TABLE 1c, EXAMPLE I—SUMMARY OF YIELDS

Net overall yield as percent of crude	Hydrotreating 750° F.+ residuum and coking hydrotreated 975° F.+ product	Coking 750° F.+ straight run residuum	Coking 1,000° F.+ straight run residuum and adding 750–1,000° F. vacuum gas oil
Coke, wt. percent	4.15	8.08	6.84
Total C_5+ liquid, vol. percent	43.4	38.3	39.6
C_5–400° F., vol. percent	4.7	6.3	2.8
400–650° F., vol. percent	7.6	9.5	5.7
650° F.+ gas oil, vol. percent	31.1	22.5	31.1

Although various embodiments of the invention have been described, it is to be understood that they are meant to be illustrative only and not limiting. Certain features may be changed without departing from the spirit or scope of the present invention. It is apparent that the present invention has broad application to a combination process involving asphaltene hydroconversion followed by coking wherein a catalyst of relatively large pore sizes is used in the hydrotreating step. Accordingly, the invention is not to be construed as limited to the specific embodiments or examples discussed but only as defined in the appended claims or substantial equivalents of the claims.

TABLE 2a, EXAMPLE II—ARABIAN LIGHT CRUDE

	Coking nonhydrotreated residuum				Coking hydrotreated residuum							
	Straight-run atmospheric (~685° F.+) residuum, feed to coking	Coking [1]			Straight-run atmospheric (~665° F+) residuum, feed to hydrotreating	Hydrotreating [2]			Coking 650° F.-hydrotreated residuum [1]			
		Product				Product			Product			
		Yield	Coke	C_5+ liquid		Yield	C_5+ liquid	650° F.+	Yield	Coke	C_5+ liquid	650° F.+
Yield to crude, vol. percent (wt. percent)	39 (43.9)		(7.94)	32.5 (32.7)	40.5 (45.2)		41.4 (44.1)	33.8 (36.5)		(4.38)	3.5 (30.8)	16.6 (16.5)
Gravity, °API	16			33.6	17.3			18.5				27.6
Sulfur, wt. percent	3.1		5.8		3.0		0.44	0.6		1.9		0.39
Conradson carbon, wt. percent	8.2				7.6			5.0				
Metals, p.p.m., Ni/V	10/29				9/27					35/80		
Coking yields:												
Coke, wt. percent		18.1							12.0			
C_5+liquid, wt. percent		74.6							84.2			
C_5+liquid, vol. percent		83.5							93.3			
C_4—gas, wt. percent		7.3							3.8			
Hydrotreating yields:												
C_5+, vol. percent						102.1						
C_5+, wt. percent						97.5						
350–650° F., vol. percent						17.4						
650° F+, vol. percent						83.5						
650° F.+, wt. percent						80.8						
								(Feed to coking—→)				

[1] 750–900° F. temperature; 15 p.s.i.a. pressure.
[2] 715° F. temperature; 0.75 LHSV; 1,700 p.s.i.g. pressure.

TABLE 2b, EXAMPLE II—SUMMARY OF YIELDS
(Arabian Light Crude)

Basis: 40.5 vol. percent residuum yield from crude

Net overall yields as percent of crude	Coking residuum (39 vol. percent of crude) and adding 665–685° F. gas oil (1.5 vol. percent of crude)	Hydrotreating 40.5 vol. percent residuum and coking 650° F.+ portion of hydrotreated product
Coke, wt percent	7.94	4.38
C_5 + liquid, wt. percent	34.0	38.4
C_5 + liquid, vol. percent	34.1	39.1

What is claimed is:

1. A process for obtaining increased normally liquid hydrocarbon yields from coking a hydrocarbon feed containing at least 3 parts per million metals which process comprises:

(a) contacting the feed, at elevated temperature and pressure and in the presence of added hydrogen, with a hydrotreating catalyst comprising Group VI and Group VIII metals and an inorganic refractory base and having at least 50 percent of its pore volume from pores 100 angstroms or larger in pore diameter to obtain a hydrotreated feedstock, and

(b) coking at least a portion of the hydrotreated feedstock at a temperature between 700° F. and 1100° F. to obtain solid coke and vaporized normally liquid hydrocarbons.

2. A process in accordance with claim **1** wherein at least 50 percent of the pore volume of the hydrotreating catalyst is from pores 130 angstroms or larger in pore diameter, and wherein the hydrocarbon feed contains at least 20 parts per million metals.

3. A process in accordance with claim **1** wherein the hydrotreating catalyst is produced so as to have larger average pore diameters by a process which comprises:

(a) forming a hydrogel comprising at least one inorganic compound,

(b) adding a detergent to the hydrogel, and

(c) carrying out at least part of the drying of the hydrogel after the detergent is added to the hydrogel.

4. A process in accordance with claim **1** wherein the hydrocarbon feed contains organic sulfur compounds, and between 25 and 95 weight percent of the sulfur present as organic sulfur compounds is converted to hydrogen sulfide during the hydrotreating of the feedstock.

5. A process in accordance with claim **4** wherein the hydrotreating catalyst has a surface area of at least 200 $m.^2/g.$ of catalyst.

6. A process in accordance with claim **1** wherein at least a portion of the hydrotreated feedstock is subjected to delayed coking at a coke drum temperature between about 750° F. and 950° F.

7. A process in accordance with claim **1** wherein the hydrotreating catalyst comprises

(a) a carrier comprising at least one component selected from silica and alumina, and at least one hydrogenating component selected from Group VI metals and compounds thereof, and Group VIII metals and compounds thereof, and

(b) discrete, substantially insoluble metal phosphate particles

(1) dispersed in said carrier,

(2) consisting essentially of at least one metal phosphate selected from phosphates of zirconium, titanium, tin, thorium, cerium and hafnium,

(3) containing substantially the entire phosphorus content of said catalyst, and

(4) containing phosphorus in an amount of 3 to 15 weight percent of the total catalyst, expressed as P_2O_5.

8. A process for obtaining increased normally liquid hydrocarbon yields from delayed coking of a hydrocarbon residuum feed containing at least 35 parts per million metals present as soluble organometallic compounds in the hydrocarbon feed which comprises:

(a) contacting the feed at a temperature between 600° F. and 850° F., and a pressure between 500 and 5,000 p.s.i.g., and in the presence of 100–10,000 standard cubic feet of hydrogen per barrel of feed with a hydrotreating catalyst comprising Group VI and Group VIII metals, and an inorganic refractory base with said catalyst having at least 50 percent of its pore volume from pores 150 angstroms or larger in pore diameter to obtain a hydrotreated feedstock, and

(b) subjecting the hydrotreated feedstock to delayed coking at a coke drum temperature between about 700° F. and 900° F. to obtain solid coke and vaporized normally liquid hydrocarbons.

9. A process in accordance with claim **1** wherein the hydrocarbon feed to the hydrotreating step is a long residua feed obtained without vacuum distillation of a crude oil, and wherein the hydrotreated feedstock is fed to a coker fractionator wherein hydrocarbon components are stripped and fractionated from the hydrotreated feedstock before the hydrotreated feedstock is fed to the coker, and wherein at least a portion of the vaporized normally liquid hydrocarbons from the coking step are fed to the coker fractionator

10. A process in accordance with claim **9** wherein vaporized normally liquid hydrocarbons from the coking step are used to aid in stripping and fractionating hydrocarbons boiling below 900° F. from the hydrotreated feedstock in the coker fractionator.

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U.S. Cl. X.R.

208—89, 216, 251 H; 252—437