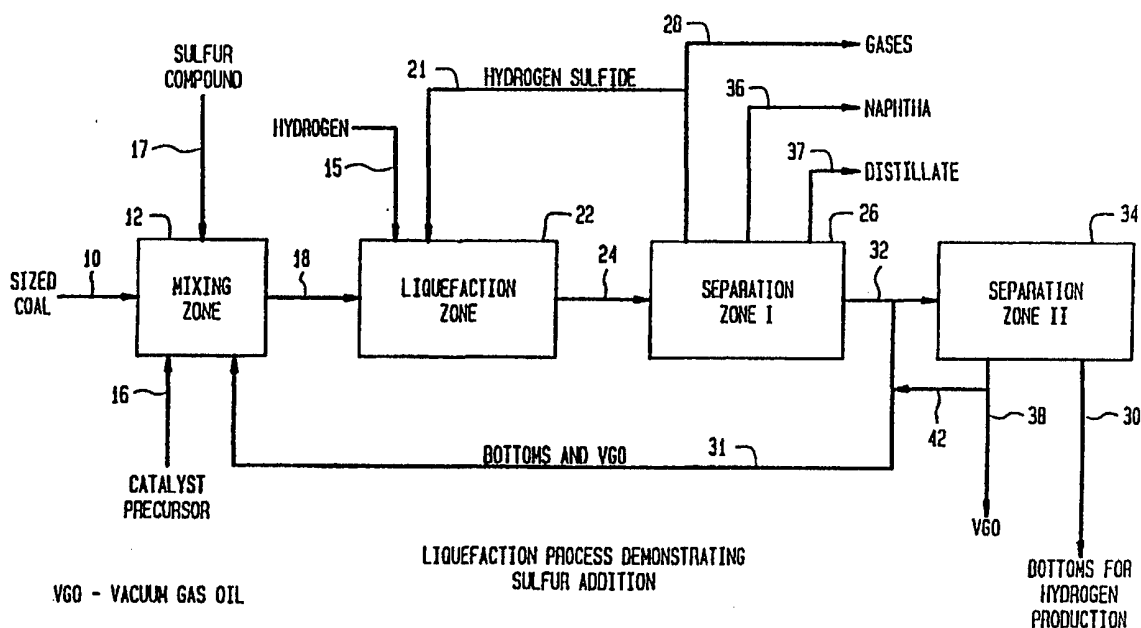




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US93/09998 <b>(22) International Filing Date:</b> 18 November 1993 (18.11.93) <b>(71) Applicant:</b> EXXON RESEARCH AND ENGINEERING COMPANY [US/US]; 180 Park Avenue, P.O. Box 390, Florham Park, NJ 07932-0390 (US). <b>(72) Inventors:</b> LeVINESS, Steven, C.; 1850 Cloverdale Avenue, Baton Rouge, LA 70808 (US). HSIA, Stephen, J.; 12524 Newcastle Avenue, Baton Rouge, LA 70816 (US). WEN, Michael, Y.; 2050 Oakcliff Drive, Baton Rouge, LA 70810 (US). DAVIS, Stephen, M.; 15739 Chickamauga Drive, Baton Rouge, LA 70817 (US). CULROSS, Claude, C.; 16027 Chantilly Avenue, Baton Rouge, LA 70817 (US). MAA, Peter, S.; 1521 Wood Chase Boulevard, Baton Rouge, LA 70809 (US). BILLIMORIA, Rustom, M.; 1147 Masterson Drive, Baton Rouge, LA 70810 (US). <b>(74) Agents:</b> JORDAN, Richard, D. et al.; Exxon Research and Engineering Company, P. O. Box 390, Florham Park, NJ 07932-0390 (US).		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> <i>With international search report.</i>

**(54) Title:** LIQUEFACTION PROCESS**(57) Abstract**

The present invention relates to a catalytic coal liquefaction process. A mixture of coal, a sulfur compound and a catalyst precursor is formed. The mixture is formed by adding coal through line (10) into mixing zone (12), a catalyst precursor is added to the mixing zone (12) through line (16), and a sulfur compound is added to the mixing zone (12) through line (17). The mixture from the mixing zone (12) is passed through line (18) to the liquefaction zone (22).

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LIQUEFACTION PROCESSFIELD OF THE INVENTION

This invention relates to a catalytic process for converting a solid carbonaceous material, such as coal, to a liquid product.

5 BACKGROUND OF THE INVENTION

Hydroconversion of coal to coal liquids in a hydrogen donor solvent process (liquefaction employing hydrogen) is well known. In such a process, a slurry of coal in a hydrogen donor solvent is reacted in the presence of molecular hydrogen at elevated temperature and pressure. See, 10 for example, U.S. Patent No. 3,645,885, the teachings of which are hereby incorporated by reference. The hydrogen donor solvent which becomes hydrogen depleted during the coal liquefaction reaction, in the prior art processes, is generally subjected to an independent hydrogenation step prior to its being recycled to the Hydroconversion Zone.

15 It is also known to convert coal to liquid products by hydrogenation of coal which has been impregnated with an oil-soluble metal naphthenate or by hydrogenation of coal in a liquid medium such as an oil having a boiling range of 250°C (482°F) to 325°C (617°F) containing an oil-soluble metal naphthenate, as shown in Bureau of Mines Bulletin No. 622, 20 published 1965, entitled "Hydrogenation of Coal in Batch Autoclave", pages 24 to 28. Concentrations as low as 0.01% metal naphthenate catalysts, calculated as the metal, were found to be effective for the conversion of coal. U.S. Patent Nos. 3,532,617 and 3,502,564 also disclose the use of metal naphthenates in coal hydroconversion.

25 U.S. Patent No. 3,920,536 discloses a process for the liquefaction of sub-bituminous coal in a hydrogen donor solvent in the presence of molecular hydrogen, carbon monoxide, water, and an alkali metal or ammonium heptamolybdate in an amount ranging from 0.5 to 10 percent by

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weight of the coal.

U.S. Patent No. 4,485,008 discloses a process for hydroconverting coal in a hydrogen donor solvent to liquid hydrocarbon products in the presence of a catalyst prepared in situ from a small amount of metals added  
5 to the mixture of coal and solvent as oil soluble metal compounds. Recycled solids concentrate can also be present in this invention, although it is not critical.

In prior art liquefaction processes, those processes in which coal is liquefied in the absence of added catalyst and in the presence of a  
10 solvent or diluent have been favored over catalytic processes even though the non-catalytic processes do not result in complete conversion of available carbon to either a liquid or gaseous product. One reason for this preference is the relatively high cost of the catalyst and the cost associated with its recovery and return to the liquefaction zone. In either case, the catalytic  
15 processes of the prior art have not, on a continuous basis, approached quantitative conversion of the available carbon and have not been economically attractive when compared to the thermal conversion processes. Since quantitative conversion of available carbon is most desirable, however, the need for an improved catalytic process is readily apparent.

It is well known in the liquefaction art that molybdenum sulfide catalyst must be present in a highly dispersed form in order to function effectively as a catalyst. The preferred process conditions needed to provide a catalytic material with optimum activity have not been clearly defined, at least for process applications using low cost catalyst precursors  
25 such as phosphomolybdic acid. With high sulfur coals such as Illinois, it has been found that effective catalysts can be formed in situ during liquefaction by simply adding phosphomolybdic acid to fresh coal/solvent/bottoms slurry mixtures. Similar behavior has been noted during catalytic conversion of residuum.

In catalytic liquefaction processes such as that of U.S. Patent No. 4,077,867, the solvent employed is usually the vacuum gas oil (VGO)

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products stream, which boils mostly at 343°C (650°F) or above. The VGO stream has been called "solvent" because the stream is believed to help coal dissolution. The VGO stream can be recycled from the separation step after liquefaction or can be added from alternate sources. The VGO stream is also  
5 believed to be more efficient in hydrogen mass transfer than heavier solutions, such as the bottoms of the coal liquefactions process since it has a lower viscosity than these streams. Furthermore, the donor hydrogen in VGO is believed to also enhance coal conversion. Overall, it was almost universally agreed that higher VGO-to-coal ratios improve coal conversion and  
10 increase liquid yields of smaller molecules boiling below 538°C (1000°F). Solvent to coal ratios were generally maintained at 1:1. If coal liquefaction bottoms were present in addition to VGO, the ratio of bottoms to coal was also generally maintained at 1:1.

#### SUMMARY OF THE INVENTION

15 In order to overcome the problems inherent in the art, the present invention provides for a process for the liquefaction of a solid carbonaceous material, which comprises forming a mixture of solid carbonaceous material, a catalyst or a catalyst precursor and a hydrogen donor solvent, said catalyst or catalyst precursor being comprised of a  
20 thermally decomposable compound of Groups IIB, IVB, VB, VIB, VIIB and VIII of the Periodic Table of the Elements; introducing a sulfur containing hydrogen transfer agent into said mixture, wherein the mixture is maintained at a temperature of 200-400°F and a pressure of 0-100 psig for effective promotion of hydrogen transfer; introducing the mixture into a liquefaction zone under  
25 liquefaction conditions, wherein at least a portion of the solid carbonaceous material is converted in the presence of hydrogen to a liquid product.

In preferred embodiments, the invention also provides that the solid carbonaceous material is selected from the group consisting of bituminous coal, sub-bituminous coal, lignite and mixtures thereof. It is  
30 preferable that the solvent comprises at least 10 wt.% of bottoms material which boils at a temperature above 538°C (1000°F), and the solvent is

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preferably selected from a petrochemical, coal derived solvent, or a hydrogen donor solvent. When a coal derived solvent is used, it is preferred that coal derived solvent has a boiling range from about 343°C (650°F) to about 538°C (1000°F).

- 5           In other preferred embodiments, the catalyst precursor is a heteropolyacid, most preferably a phosphomolybdic acid or is a compound selected from the group consisting of dioxo-bis-(n-dibutyldithiocarbamate)MoO<sub>2</sub> and Mo<sub>2</sub>O<sub>2</sub>(μ-S)<sub>2</sub>(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub> where R is n-butyl.

- 10           It is also preferred that the sulfuring containing hydrogen transfer agent be selected from the group consisting of elemental sulfur, H<sub>2</sub>S or sulfur containing hydrocarbons, and that the agent be mixed at a concentration of 0.1 to 5.0 wt.%.

#### BRIEF DESCRIPTION OF THE DRAWINGS

- 15           Figure 1 demonstrates the relationship between the level of conversion (liquefaction) of low sulfur coal and the wt.% of added sulfur or H<sub>2</sub>S.

Figure 2 is a schematic flow diagram of a process within the scope of the present invention. The elements of the process are referenced numerically in the Detailed Description of the Invention.

#### 20 DETAILED DESCRIPTION OF INVENTION

- 25           The present invention relates to an improved process for liquefying coal and similar solid carbonaceous materials wherein total carbon conversion in the coal or solid carbonaceous material is increased by effecting the liquefaction of at least a portion of the solid carbonaceous feed when a catalyst or catalyst precursor is combined with a sulfur containing hydrogen transfer agent, a bottoms recycle material or both.

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According to this invention, the addition of a separate sulfur containing component to coal, improves conversion. In general, carbon conversion and coal liquefaction are increased and gas production is decreased if a sulfur promoter is added in an effective range to the coal during the liquefaction process.

The instant invention also concerns a catalytic liquefaction process for coals in which a sulfur containing hydrogen transfer agent is fed in at least one stage together with a slurry of fresh coal, solvent and a partially liquefied solid carbonaceous material, referred to hereinafter as "recycle bottoms" or "bottoms recycle." The bottoms material is preferably added as a recycle stream from a separating zone, and can contain VGO or other solvents. The bottoms material can, however, be introduced from an outside source if desired. Liquefaction can be accomplished in a single stage or in a plurality of stages, preferably with the catalyst being present in all stages. The bottoms material can be introduced in all stages or in fewer stages.

According to one aspect of the invention, when the ratio of coal liquefaction bottoms to coal is increased to 1.5 to 1, coal conversion as well as liquid yields of products of boiling point below 538°C (1000°F) is increased. These increases appear to be independent of catalyst concentration employed or the residence time of bottoms in the reactor. It is apparent that bottoms recycle material is an effective solvent for coal, a fact that has been previously overlooked.

The process of this invention includes a liquefaction zone which is maintained at a temperature ranging from about 343° to 538°C (650° to 1000°F), preferably from about 416° to 482°C (780° to 900°F), more preferably from about 421° to 449°C (790° to 840°F), and a hydrogen partial pressure ranging from about  $3.5 \times 10^6$  Pa (500 psig) to about  $3.5 \times 10^7$  Pa (5000 psig), preferably from about  $6.9 \times 10^6$  Pa (1000 psig) to about  $2.1 \times 10^7$  Pa (3000 psig). The space velocity, defined as volumes of the mixture of coal and solvent and bottoms feedstock per hour per volume of reactor (V/Hr./V), can vary widely depending on the desired conversion level. Suitable space

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velocities can range broadly from about 0.1 to 10 volumes feed per hour per volume of reactor, preferably from about 0.25 to 6 V/Hr./V, more preferably from about 0.4 to 2 V/Hr./V.

Liquefaction can be accomplished either in a single stage or in a plurality of stages. When multiple liquefaction stages are employed, sulfur is added to a single stage or multiple stages. It is generally preferred to incorporate a major portion of the sulfur before conversion in the first liquefaction stage, however. The total nominal residence time (NRT) of all the stages will, generally, range from about 25 to about 250 minutes.

When a plurality of liquefaction zones is employed, part of the gaseous and lighter boiling liquid hydrocarbons can be separated between each stage. Generally, this separation includes all components having a boiling point from about 177°C (350°F) to about 343°C (650°F). Moreover, a portion of the remaining slurry can be recycled to the immediate previous stage as bottoms recycle. Further, at least a portion of the remaining product slurry can be further separated to yield a solvent fraction having an initial boiling point within the range from about 177°C (350°F) to about 218°C (425°F) and a final boiling point within the range from about 288°C (550°F) to about 371°C (700°F). All or a portion of this fraction can then be hydrogenated to produce a hydrogen-donor solvent which can be used in any one or all of the multiple liquefaction zones.

In an alternate embodiment employing a plurality of stages, part of the gaseous and lighter boiling liquid hydrocarbons can be separated between each stage. Generally, this separation includes all components having a boiling point from about 177°C (350°F) to about 343°C (650°F). Moreover, a portion of the remaining slurry can be recycled to the immediate previous stage as bottoms recycle. Further, at least a portion of the remaining product slurry can be further separated to yield a solvent or diluent fraction having an initial boiling point within the range from about 177°C (350°F) to about 218°C (425°F) and a final boiling point within a range from about 288°C (550°F) to about 371°C (700°F). All or a portion of this



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fraction can then be hydrogenated to produce a hydrogen-donor solvent which can be used in any one or all of the multiple liquefaction zones.

If a plurality of stages is used, a series of two or more liquefaction zones can be arranged in series and operated so that the temperature in each zone increases from the initial to the final zone. The effluent from each liquefaction zone is then passed to the next succeeding higher temperature zone in the series. Liquid hydrocarbonaceous products are recovered from the effluent withdrawn from the last zone. At each stage, the liquefaction effluent can be separated into a vaporous stream and a liquid stream, the liquid stream consisting of a low molecular weight liquid fraction and a high molecular weight liquid fraction. A sufficient amount of the low molecular weight liquid fraction is removed from the high molecular weight liquid fraction (comprising all mineral matter and all liquids boiling at or above 650°F including unconverted coal constituents) to form a heavy bottoms stream containing less than about 50 wt.% of the low molecular weight liquid fraction based on the weight of the high molecular weight liquid fraction. The heavy bottoms stream can be treated with additional vacuum gas oil (VGO) and hydrogen-containing gas in a second liquefaction zone. The product of the second liquefaction zone is separated into a vaporous fraction and a liquid fraction. Hydrogenated liquid products are recovered from the vaporous and liquid fractions. The high molecular weight constituents in the liquid fraction from the second liquefaction reactor can be further treated with recycled vacuum gas oil and hydrogen-containing gas in a third liquefaction zone.

As previously indicated, catalyst can be present in all stages and can be added as necessary to the slurry containing the solid carbonaceous material, sulfur containing hydrogen transfer agent, and recycled bottoms. The catalyst can be added in any stage in the form of catalyst or catalyst precursor. It is preferred that the sulfur containing hydrogen transfer agent be added before conversion in the first liquefaction stage.

In general, solid carbonaceous materials which are known to be susceptible to hydrogenation, cracking and liquefaction can be used in this

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invention. The method of the invention is particularly useful in the liquefaction of coal, coke, wood and similar solid carbonaceous materials containing a relatively high ratio of carbon to hydrogen. In general, coals known in the prior art including anthracite, bituminous coal, sub-bituminous coal, lignite, and mixtures thereof can be liquefied with the method of this invention.

The solid carbonaceous material used a feed is preferably ground to a finely divided state. The particular particle size or particle size range actually employed, however, is not critical to the invention, and essentially any particle size can be employed. It is preferred, however, that the solid carbonaceous material which is liquefied in accordance with the invention be ground to a particle size of less than 1/4 inch, more preferably to a particle size of less than about 8 mesh (NBS sieve size).

Solvents useful in this invention include any of the solvents or diluents known to be useful in the liquefaction of coal and similar solid carbonaceous materials. When a solvent having donatable hydrogen is used, any of the solvents or diluents known contain donatable hydrogen can be used. Preferred hydrogen-donor solvents contain at least 1.00 wt.% donatable hydrogen and include pure compounds as well as mixtures of such compounds in combination with components which will not donate hydrogen at liquefaction conditions. Compounds which will donate hydrogen during liquefaction are described, for example, in U.S. Patent No. 3,867,275. These include the dihydronaphthalenes, the  $C_{10}$ - $C_{12}$  tetra-hydronaphthalenes, the hexahydrofluorenes, the dihydro-, tetrahydro-, hexahydro- and octahydrophenanthrenes, the  $C_{12}$ - $C_{13}$  acenaphthenes, the tetrahydro-, hexahydro- and decahydropyrenes, the di-, tetra- and octahydroanthracenes, and other derivatives of partially saturated aromatic compounds. The donor hydrogen solvent can be prepared by subjecting a distillate stream from atmospheric distillation to a conventional hydrogenation reactor. Particularly effective mixed solvents include heavy gas oil fractions (often called vacuum gas oils, or VGO) with an initial boiling point of about 343°C (650°F) and a final boiling point of about 538°C (1000°F). This stream comprises aromatics, hydrogenated aromatics, naphthenic hydrocarbons, phenolic materials, and

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similar compounds. If a solvent is used which does not have donatable hydrogen, hydrogen can be added from another source.

The solvent and solid carbonaceous material are preferably mixed in a solvent-to-coal weight ratio ranging from about 0.8:1 to 4:1, more preferably from about 0.9:1 to 2:1, producing a slurry which preferably comprises from about 3 to 50 wt.%, more preferably from about 20 to about 40 wt.% solid carbonaceous material.

The "bottoms" of this invention comprises distilled fraction which boils above 538°C (1000°F). It can comprise solid residue which contains catalyst, as well as carbonaceous materials which can be useful as cracking stocks, lube base stocks, heavy fuel oil or asphalts. Bottoms can be used to generate hydrogen in a partial oxidation reactor.

It is also preferable that the ratio of bottoms material to solid carbonaceous material range from about 0.5:1 to about 5:1, more preferably from about 1:1 to about 3:1, and most preferably from about 1.5:1 to about 2:1.

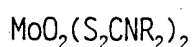
Catalysts known to exhibit hydrogenation activity for the liquefaction of coal can be used in the improved liquefaction process of this invention. Examples of such catalysts include the metals of Group IIB, IVB, VB, VIB, VIIB and VIII of the Periodic Table of the Elements, and mixtures thereof, in accordance with the table published by E. H. Sargent and Company, copyright 1962, Dyna Slide Company, that is, zinc, cadmium, mercury, tin, lead, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel. Generally, the catalyst or a precursor thereof is added to the slurry in a form which is readily dispersible or soluble in the solvent or diluent used during liquefaction. Preferred compounds (precursors) which are convertible to active catalysts under process conditions include (1) inorganic metal compounds such as halides, oxyhalides, hydrated oxides, heteropoly acids (e.g., phosphomolybdic acid, molybdosilicic acid); (2) metal salts of organic acids such as acyclic and alicyclic aliphatic carboxylic acids containing two or more carbon atoms

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(e.g., toluic acid); sulfonic acids (e.g., toluene-sulfonic acid); sulfinic acids; mercaptans, xanthic acid; phenols, di- and polyhydroxy aromatic compounds; (3) organometallic compounds such as metal chelates, e.g., with 1,3-diketones, ethylene diamine, ethylene diamine tetraacetic acid, 5 phthalocyanines, etc.; (4) metal salts of organic amines such as aliphatic amines, aromatic amines, and quaternary ammonium compounds.

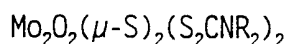
The preferred catalyst compounds or precursors are the oil soluble metal compounds containing a metal selected from the group consisting of molybdenum, vanadium and chromium. More preferably, the metal constituent 10 is selected from the group consisting of molybdenum and chromium. Most preferably, the metal constituent of an oil soluble metal compound is molybdenum.

Preferred compounds of the metal include the salts of acyclic (straight or branched chain) aliphatic carboxylic acids, salts of alicyclic 15 aliphatic carboxylic acids, heteropolyacids, hydrated oxides, carbonyls, phenolates and organo amine salts. Another preferred metal compound is a salt of an alicyclic aliphatic carboxylic acid such as the metal naphthenate. The most preferred types of metal compounds are the heteropoly acid, e.g., phosphomolybdic acid as well as oil soluble and/or highly dispersible 20 molybdenum complexes selected from:



where R is a  $\text{C}_1$  to  $\text{C}_{18}$  alkyl group, a  $\text{C}_5$  to  $\text{C}_8$  cycloalkyl group, a  $\text{C}_6$  to  $\text{C}_{18}$  alkyl substituted cycloalkyl group, or a  $\text{C}_6$  to  $\text{C}_{18}$  aromatic or alkyl substituted aromatic group;

25 or



where R is as indicated, or any related complex of molybdenum with dithiocarbamate, dithiophosphate, xanthates, or thioxanthate ligands.

In another preferred embodiment of the present invention, the 30 molybdenum complex is dioxo bis(n-dibutyldithiocarbamato)MoO<sub>2</sub>, also referred to as dioxoMoDTC.

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In still other preferred embodiments of the invention, the molybdenum complex is  $\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNR}_2)_2$  ( $\text{R} = \text{n-butyl}$ ).

When the oil-soluble metal compound or dispersible metal compound is added to the slurry of vacuum gas oil and bottoms in the mixing zone, it  
5 dissolves or disperses. Various methods known in the art can be used to convert the dissolved or dispersed metal compound in the coal-solvent slurry to an active catalyst.

The catalyst or catalyst precursor is preferably added to the slurry at a concentration within the range from about 20 to about 2000 ppm,  
10 based on active metal, by weight of dry coal feed, such that the catalyst concentration in the liquefaction vessel will be within the range from about 30 to about 6000 ppm based on total solids depending upon the amount of bottoms recycled during the liquefaction operation. When multiple stages are  
15 employed the catalyst concentration in any particular stage can vary due to different amounts of bottoms recycled to different stages but the catalyst concentration within any given stage or zone will be within the aforementioned range of from about 30 to about 6000 ppm, based on active metal components, by weight of total solids.

The sulfur containing hydrogen transfer agent used in this  
20 invention is preferably introduced in readily releasable forms. Non-limiting examples include  $\text{H}_2\text{S}$ , elemental sulfur, or sulfur containing compounds which readily transfer hydrogen to unsaturated hydrocarbon compounds. Use of elemental sulfur is generally preferred for low toxicity, low cost and ease of handling. Elemental sulfur, either as the sublimed powder or as a  
25 concentrated dispersion of sublimed powder, such as commercial flowers of sulfur, in heavy hydrocarbonaceous oil, is preferred. Allotropic forms of elemental sulfur, such as orthorhombic and monoclinic sulfur are also preferably for use herein. Elemental sulfur can also be introduced as molten sulfur or as sulfur vapor. The amount of sulfur containing hydrogen transfer  
30 agent added is such that the atomic ratio of sulfur to metal 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. Alternatively, the sulfur containing hydrogen transfer agent can

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be added at any point in the catalyst concentrate preparation procedure as long as it is not contacted with an aqueous solution prior to it being introduced into oil. For example, it can be added as a concentrate in a hydrocarbonaceous oil after the precursor concentrate has been dried. It can  
5 also be added during formation of the catalyst concentrate. If the elemental sulfur is added as a concentrate in oil, the amount of sulfur in the concentrate is such that it will meet the aforementioned requirements pertaining to atomic ratio of sulfur to metal. That is, the atomic ratio of sulfur to metal of the metal compound will remain 1/1 to 8/1.

10           The sulfur containing hydrogen transfer agent is preferably mixed with the solid carbonaceous feed prior to treatment in the liquefaction zone. Preferably, the mixing of the sulfur containing transfer agent with feed will be carried out at a temperature of about 200-400°F, more preferably from about 250-350°F, and a pressure of less than 100 psig, preferably between 0  
15 and 50 psig.

It should be noted that the sulfur containing hydrogen transfer agent used in this invention is effective regardless of the sulfur content of typical hydrocarbonaceous feeds. This is because sulfur in hydrocarbonaceous feeds are present as pyritic sulfur, sulfate sulfur and organic sulfur which  
20 do not effectively function as hydrogen transfer agents. Even though it is possible that some of the pyritic sulfur in the hydrocarbonaceous feed can decompose to ultimately form a H<sub>2</sub>S product, this product does not generally tend to form unless the feed is in a high temperature environment of at least 500°F. At this relatively high temperature, and under low pressures, the  
25 hydrogen transfer mechanism is not favorable to the overall liquefaction process.

The process of this invention can be advantageously applied using both presulfided and non-presulfided catalysts and catalyst precursors with or without continuous bottoms recycle. The preferred ranges of feed sulfur  
30 addition correspond to catalytic liquefaction operations with about 100 ppm fresh catalyst or catalyst precursor and about 400-700 ppm catalyst contained in bottoms recycle, based on the weight of dry coal.

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Figure 1 demonstrates that a sulfur containing hydrogen transfer agent, such as elemental sulfur or  $H_2S$ , is effective in enhancing conversion. In general, the sulfuring containing hydrogen transfer agent is especially effective from about 0.1 to 5.0 wt.%, preferably from about 0.2 to 4.0 wt.%,  
5 most preferably from about 0.5 to 1.5 wt.% sulfur, based on moisture free coal.

In a preferred embodiment as shown in Figure 2, sized solid carbonaceous material (line 10) is slurried with a solvent (such as vacuum gas oil) and bottoms (line 31) and combined with a suitable catalyst or  
10 catalyst precursor (line 16) in a mixing zone 12. Preferably, the ratio of solvent to coal (on a moisture-free basis) in the slurry is within a range of from about 0.8:1 to about 4:1 on a weight basis. Ratios in the higher portion of this range are preferred at higher bottoms recycle rates to facilitate transport of the slurry by pumping or similar means. Part of the  
15 solvent can be recycled from a separation zone II (34) through a line 42.

The sulfur containing hydrogen transfer agent is added to the mixing zone 12 through a line 17 and slurried with the carbonaceous material from line 10, the catalyst or catalyst precursor from line 16 and the bottoms and VGO from the recycle line 31. The contents of the mixing zone 12 are  
20 preferably mixed at 200-400°F, and the mixing zone 12 is most preferably open to atmospheric pressure. As the materials in mixing zone 12 are slurried, hydrogen transfer takes place, thereby promoting hydrogen transfer before the liquefaction reaction is initiated under high pressure conditions.

After the solid carbonaceous material has been slurried in the  
25 mixing zone 12, the slurry is transported to a liquefaction zone 22 via line 18 and the liquefaction process is initiated. In general, the liquefaction process (in liquefaction zone 22) results in the production of a gaseous product, a liquid product and a normally solid bottoms product. After liquefaction, the products are separated (in separation zone I (26) and in  
30 separation zone II (34)) into their respective phases using conventional techniques. Distillation at atmospheric pressure is preferably applied in separation zone I, and in separation zone II, vacuum distillation is

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preferably applied. The light gases, naphtha and distillate are separated from VGO and bottoms in separation zone I (lines 28, 36 and 37). Part of the VGO and bottoms are recycled to the mixing zone via line 31. A purge stream from separation zone I (line 32) is further separated in separation zone II to give VGO (line 38) and bottoms (line 30). The catalyst, in some form, is contained in the heavier product from separation zone I.

A single stage liquefaction system can also be used. In the single stage system, the gaseous and lighter boiling liquid hydrocarbons are flashed overhead in separation zone I. A portion of the remaining slurry is recycled to the mixing zone (12) and the rest is further fractionated in a second separator (separation zone II, 34). A stream having an initial boiling point within the range from about 177°C (350°F) to about 218°C (425°F) and a final boiling point within the range from about 371°C (700°F) to about 427°C (800°F) is separated from the light hydrocarbons of lines 36 and 37. In an optional embodiment, at least a portion of this stream is subjected to hydrogenation and recycled to the mixing zone (12) to act as a hydrogen donor solvent. In separation zone II, the heavier products are separated into two streams. A stream having an initial boiling point within the range from about 288°C (550°F) to about 371°C (700°F) and a final boiling point within the range from 510°C (950°F) to about 593°C (1100°F) is withdrawn as a VGO product (line 38) from separation zone II and a portion is recycled via line 42. A second stream (line 30) having an initial boiling point within the range from about 510°C (950°F) to about 593°C (1100°F) is also withdrawn from separation zone II. This stream is used to produce hydrogen using a molten partial oxidation process or other conventional processes. It can be discarded if desired. Alternatively, the gaseous and lower boiling liquid hydrocarbon products can be flashed overhead in separation zone I and the entire remainder of the slurry subjected to further separation to obtain at least the three fractions, gases, naphtha and distillate, noted above. In this embodiment, at least a portion of the remainder of the slurry is recycled to the mixing zone (12).

When a portion of the slurry from separation zone I is recycled to the mixing zone (12), the load on separation zone II is reduced. As a



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result, the recycling of a portion of the entire slurry after the gaseous and lighter boiling liquid products are flashed overhead is preferred. When this is done, the recycled stream (line 31) has an initial boiling point within a range of from about 288°C (550°F) to about 427°C (800°F) and contains a  
5 portion of the unreacted solid carbonaceous material, a portion of the inert material contained in the solid carbonaceous material and a portion of the catalysts initially introduced.

After the liquefaction is completed the gaseous product from the liquefaction zone or zones can be upgraded to a pipeline gas or can be burned  
10 to provide energy for the liquefaction process. Alternatively, all or any portion of the gaseous product can be reformed to provide hydrogen for the liquefaction process through line 15. The H<sub>2</sub>S gas can be separated and recycled to the liquefaction zone 22 by line 21.

The liquid products can be fractionated into essentially any  
15 desired product distribution. A portion thereof can also be used directly as a fuel or upgraded using conventional techniques. Generally, a naphtha boiling range fraction will be recovered and the naphtha fraction will be further processed to yield a high-quality gasoline or similar fuel boiling in the naphtha range.

20 The following non-limiting examples are presented to illustrate the invention.

**Example 1.** A series of experimental runs was made using an Illinois #6 coal (Monterey mine) in a bench stirred autoclave unit with a volume of 380 cc. In each run, the particle size of the coal was -100 mesh.  
25 In each run, a slurry was prepared containing 39 wt.% coal and 1000 ppm of metal as molybdenum based on the weight of dry coal. The molybdenum was in the form of molybdenum dioxodithiocarbamate. Three sets of liquefaction conditions were carried out: 427°C (800°F)/150 minutes, 450°C (840°F)/60 minutes, and 427°C (800°F)/120 minutes. In each set of runs, 1 wt.% on a  
30 moisture-free basis of sulfur was added in one run, and no sulfur was added in the other run. The sulfur was added in the form of carbon disulfide. All

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the liquefaction reactions were carried out at  $1.6 \times 10^7$  Pa (2300 psig) constant pressure and were agitated at 1500 rpm to promote the hydrogen transfer from the gas phase to the liquid phase. Molecular hydrogen was initially added to the liquefaction reactor in an amount of 7 wt.% based on dry coal. The hydrogen was continuously added to the autoclave as it was consumed, the total hydrogen added being 9 wt.% based on dry coal. In each run, a solvent having an initial boiling point of 343°C (650°F) and a final boiling point of 538°C (1000°F), usually a vacuum gas oil stream, was used. The Monterey coal had the following analysis: Ash 9.67%, C 69.62%, H 4.81%, S 4.38%, N 1.30%, and O 10.22%. The (H/C) atomic ratio was 0.84. The coal conversion and C<sub>1</sub>-C<sub>4</sub> gas yield for each run is summarized in Table I.

TABLE I  
LIQUEFACTION PERFORMANCE  
WITH ADDED SULFUR AND MONTEREY COAL

15	Temperature, °C	427	427	450	450	427	427
	Temperature, °F	800	800	840	840	800	800
	Residence Time, minutes	150	150	60	60	120	120
	Sulfur Added, wt.% on Coal	1.0	0.0	1.0	0.0	1.0	0.0
	<u>Yields, wt.% DAF* coal</u>						
20	C <sub>1</sub> -C <sub>4</sub> gas	8.3	8.7	9.0	11.2	6.4	6.7
	C <sub>5</sub> -538°C (1000°F) liquids	55.0	51.6	53.8	48.3	53.0	49.1
	Conversion %	71.2	67.9	70.3	66.9	66.8	63.5
	δ Conversion	3.3	base	3.4	base	3.3	base

25 \*DAF = dry-ash-free

Table 1 shows that sulfur addition increased conversion and reduced the undesirable C<sub>1</sub>-C<sub>4</sub> gas yield.

Example 2. Three series of liquefaction studies were conducted in a pilot plant providing capabilities for continuous recycle of a 343°C (650°F)/538°C (1000°F) coal liquid solvent and 538°C+ (1000°F+) bottoms. The first series of studies was carried out using a western U.S. coal from the Wyodak mine in the Wyoming Powder River basin. The second and third series of studies were carried out using a Wyoming coal of similar petrographic

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composition from the Rawhide mine.

The pilot plant used in these investigations employed a nominal coal feed rate of 75 lb/day. An essentially constant reaction temperature of 427°C (800°F) or 450°C (840°F) was achieved using a series of tubular 1" reactors loaded in a sandbath. The pilot plant was equipped with mix tanks for thoroughly mixing solvent, coal, bottoms, catalyst precursor, and elemental sulfur before injection into the liquefaction reactors. To facilitate this injection, the mix tank and all associated transfer lines were heated to 107-149°C (225-300°F). In each series of studies, the nominal feed slurry contained about 34 wt.% solvent, 33 wt.% coal mixed with 100 ppm Mo catalyst precursor in the form of phosphomolybdic acid, and 33 wt.% bottoms.

The first series of liquefaction studies was carried out at  $1.4 \times 10^7$  Pa (2000 psig) and 427°C (800°F) with a nominal residence time (NRT) of 140 minutes. Hydrogen was added at a treat rate of 10 wt.% on fresh coal. In these studies sulfur was introduced by cofeeding H<sub>2</sub>S with hydrogen at rates corresponding to 1.0 or 1.7 wt.% H<sub>2</sub>S on coal. The operations were carried out for periods of 200 to 400 hours. Several detailed material balance periods were conducted at each condition after achieving steady state conversion and solvent and bottoms composition. A summary of overall coal conversions and product distributions from these operations is provided in Table IIa, which shows that liquefaction performance was substantially improved with the addition of H<sub>2</sub>S.

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TABLE IIa

LIQUEFACTION PERFORMANCE  
WITH ADDED H<sub>2</sub>S AND WYODAK COAL

Added H <sub>2</sub> S (wt.% on coal)		0	1.0	1.7
5	<u>Yields, wt.% DAF coal</u>			
	Conversion	75.9	82.0	80.6
	C <sub>1</sub> -C <sub>4</sub> Gas	12.7	11.2	12.7
	C <sub>5</sub> -538°C (1000°F) liquids	47.8	54.8	52.5
	CO+CO <sub>2</sub>	7.7	6.6	7.7
10	H <sub>2</sub> O	12.2	14.4	11.7
	H <sub>2</sub> Consumption	4.8	5.2	4.8

@ 427°C (800°F),  $1.4 \times 10^7$  Pa (2000 psig), 140 min NRT

The second series of studies was also carried out at  $1.4 \times 10^7$  Pa (2000 psig), 427°C (800°F), 120 minutes nominal residence time (NRT), and with hydrogen treatment rates of 10 to 12 wt.% on fresh coal. However, in these studies, powdered elemental sulfur was used in place of H<sub>2</sub>S. The sulfur was introduced by adding powdered elemental sulfur into the mix tank together with solvent, coal, bottoms and catalyst precursor. Three levels of added sulfur were investigated: 0.5, 1.0, and 3.0 wt.%. As indicated in Table IIb, the effect of added elemental sulfur was similar to that observed with H<sub>2</sub>S.

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TABLE IIb

LIQUEFACTION OF RAWHIDE COAL  
WITH ADDED ELEMENTAL SULFUR

Added Sulfur (wt.% on coal)		0	0.5	1.0	3.0
5	<u>Yields, wt.% DAF coal</u>				
	Conversion	73.7	75.9	81.6	48.2
	C <sub>1</sub> -C <sub>4</sub> Gas	12.3	12.0	10.8	11.4
	C <sub>5</sub> -538°C (1000°F) liquids	46.6	48.9	55.3	51.3
	CO+CO <sub>2</sub>	7.3	7.5	8.3	8.2
10	H <sub>2</sub> O	11.7	11.8	11.4	11.7
	H <sub>2</sub> -Consumption	4.9	4.9	5.0	5.1

@ 427°C (800°F),  $1.4 \times 10^7$  Pa (2000 psig), 120 min NRT

The third series of experiments was carried out at  $1.4 \times 10^7$  Pa (2000 psig), 450°C (840°F), 60 minutes residence time, and with hydrogen treatment rates of 8-10 wt.% on coal. In this case, elemental sulfur was again investigated as a liquefaction promoter. As indicated in Table IIc, elemental sulfur had a strong positive effect on performance under these conditions.

TABLE IIc

EFFECT OF ADDED SULFUR ON RAWHIDE COAL  
LIQUEFACTION AT 450°C (840°F)

Added Sulfur (wt.% on coal)		0	1.5
25	<u>Yields, wt.% DAF coal</u>		
	Conversion	76.2	79.9
	C <sub>1</sub> -C <sub>4</sub> Gas	14.3	13.0
	C <sub>5</sub> -538°C (1000°F) liquids	47.2	51.3
	CO+CO <sub>2</sub>	7.1	9.0
	H <sub>2</sub> O	12.0	10.8
30	H <sub>2</sub> Consumption	5.2	5.0

@ 450°C (840°F),  $1.4 \times 10^7$  Pa (2000 psig), 60 min NRT

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Example 3. A series of experiments was conducted in a 75 lb/day pilot plant in which the effectiveness of different ratios of a recycle solvent to coal to bottoms recycle material was determined. The solvent was a vacuum gas oil fraction and the coal was sub-bituminous (Rawhide mine). The experiments were carried out at a temperature of 429°C (805°F), a residence time of 120 minutes, and a pressure of  $1.72 \times 10^7$  Pa (2500 psig). As part of the reaction mixture, 9 wt.%  $H_2$ , 100 ppm Mo catalyst precursor in the form of phosphomolybdic acid and 1 wt.% of powdered elemental sulfur were added. The results are shown in Tables IIIa and IIIb.

TABLE IIIa

YIELD FOR CATALYTIC LIQUEFACTION  
OF WYOMING (RAWHIDE) COAL

Conditions: 429°C (805°F); 120 min. NRT\*; 2500 psig ( $1.72 \times 10^7$  Pa); 9 wt.%  $H_2$  treat; 100 ppm Mo catalyst precursor; 1 wt.% sulfur addition.

<u>Solvent-Coal-Bottoms Ratio</u>	<u>1:1:1</u>	<u>2:1:1</u>
<u>Yields, Wt.% DAF** Coal</u>		
$C_1 - C_4$	13.3	14.3
$C_5 - 538^\circ\text{C}$ (1000°F) liquid	55.6	51.0
Conversion (%)	83.8	80.1

\*NRT = Nominal Residence Time

\*\*DAF = Dry-Ash-Free

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TABLE IIb

YIELD FOR CATALYTIC LIQUEFACTION  
OF WYOMING (RAWHIDE) COAL

Conditions: 429°C (805°F); 120 min. NRT\*; 1.72 x 10<sup>7</sup> Pa (2500 psig); 9 wt.% H<sub>2</sub> treat; 100 ppm Mo catalyst precursor; 1 wt.% sulfur addition.

<u>Solvent-Coal-Bottoms Ratio</u>	<u>1:1:1</u>	<u>1:1:1.5</u>
<u>Yields, Wt.% DAF** Coal</u>		
C <sub>1</sub> - C <sub>4</sub>	13.3	14.2
C <sub>5</sub> - 538°C (1000°F) liquids	55.6	59.4
Conversion (%)	83.4	88.1

\*NRT = Nominal Residence Time

\*\*DAF = Dry-Ash-Free

**Example 4.** A series of experiments was conducted in a 75 lbs/day pilot plant in which the effectiveness of different ratios of a recycle solvent to coal to bottoms recycle material was determined. The solvent was a vacuum gas oil fraction and the coal was bituminous (Illinois). The conditions were 427°C (800°F), a residence time of 145 minutes, pressure of 1.38 x 10<sup>7</sup> Pa (2000 psig), 9 wt.% H<sub>2</sub> present, and a concentration of 100 ppm Mo catalyst precursor in the form of phosphomolybdic acid. No sulfur was added. The results are shown in Table IV.

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TABLE IV

YIELD FOR CATALYTIC LIQUEFACTION  
OF ILLINOIS (MONTEREY) COAL

Conditions: 427°C (800°F); 145 min. NRT\*; 1.38 x 10<sup>7</sup> Pa (2000 psig); 9 wt.% H<sub>2</sub> treat; 100 ppm Mo catalyst precursor; no sulfur addition.

<u>Solvent-Coal-Bottoms Ratio</u>	<u>1:1:1</u>	<u>1:1:1.5</u>
<u>Yields, Wt.% DAF** Coal</u>		
C <sub>1</sub> - C <sub>4</sub>	13.5	12.8
C <sub>5</sub> - 538°C (1000°F) liquids	55.2	57.6
Conversion (%)	77.0	79.8

\*NRT = Nominal Residence Time

\*\*DAF = Dry-Ash-Free

**Example 5.** A series of experiments was conducted in a stirred autoclave in which the effectiveness of different ratios of recycle solvent to coal was determined. The solvent was a vacuum gas oil derived from a sub-bituminous coal pilot plant run and the bottoms was the material boiling at temperature above 538°C (1000°F) derived from the same pilot plant run, and the coal was sub-bituminous (Rawhide mine). In all experiments, the bottoms to coal ratio was maintained at 1:1, while the solvent to coal ratio was varied from 0 to 2. The conditions in the liquefaction zone were a temperature of 427°C (800°F), a residence time of 120 minutes, hydrogen pressure of 1.6 x 10<sup>7</sup> Pa (2300 psig), 9 wt.% hydrogen present, a concentration of 1500 ppm Mo in the form of molybdenum dioxodithiocarbamate liquefaction based on the weight of coal and 1 wt.% of added sulfur as CS<sub>2</sub>. The results are shown in Table V.



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TABLE V

AUTOCCLAVE YIELD FOR CATALYTIC LIQUEFACTION OF SUB-BITUMINOUS  
WYOMING COAL SHOWING SOLVENT TO COAL EFFECT

<u>Solvent/Coal</u>	0	0.25	0.50	0.75	1.0	1.5	2.0
<u>Yields. Wt.% DAF* Coal</u>							
C <sub>1</sub> -C <sub>4</sub>	16.7	8.8	8.2	8.5	8.2	9.7	9.4
C <sub>5</sub> -538°C (1000°F) Liquids	25.0	56.6	53.9	60.1	60.0	51.8	45.2
Conversion (%)	54.8	74.2	74.7	78.1	80.0	71.3	64.1

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\*DAF = Dry-Ash-Free

**Example 6.** A series of experiments was conducted in a stirred autoclave in which the effectiveness of different ratios of recycle bottoms to coal was determined at a constant coal to solvent ratio. The solvent was a vacuum gas oil derived from a sub-bituminous coal pilot plant run, the bottoms was the material boiling above 538°C (1000°F) derived from the same pilot plant run, and the coal was sub-bituminous (Rawhide mine). In all experiments, the solvent to coal ratio was maintained at 1:1, while the bottoms to coal ratio was varied from 0 to 2. The conditions in the liquefaction zone were a temperature of 427°C (800°F), a residence time of 120 minutes, total pressure of  $1.6 \times 10^7$  Pa (2300 psig), 9 wt.% hydrogen present, a concentration of 1500 ppm Mo in the form of molybdenum dioxodithiocarbamate based on the weight of coal and 1 wt.% of added sulfur as CS<sub>2</sub>. The liquefaction results are shown in Table VI.

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TABLE VIAUTOCLAVE YIELD FOR CATALYTIC LIQUEFACTION OF  
WYOMING COAL SHOWING BOTTOMS TO COAL EFFECT

<u>Bottoms/Coal</u>	0	1	2
<u>Yields. Wt.% DAF* Coal</u>			
C <sub>1</sub> -C <sub>4</sub>	6.8	8.2	9.9
C <sub>5</sub> -538°C (1000°F) Liquids	52.4	60.0	63.1
Conversion (%)	69.8	80.0	82.9

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\*DAF = Dry-Ash-Free

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WHAT IS CLAIMED IS:

1. A process for the liquefaction of a solid carbonaceous material, comprising:
  - a. forming a mixture of solid carbonaceous material, a catalyst or a catalyst precursor and a hydrogen donor solvent, said catalyst or catalyst precursor being comprised of a thermally decomposable compound of Groups IIB, IVB, VB, VIB, VIIB and VIII of the Periodic Table of the Elements;
  - b. introducing a sulfur containing hydrogen transfer agent into said mixture, wherein the mixture is maintained at a temperature of 200-400°F and a pressure of 0-100 psig for effective promotion of hydrogen transfer;
  - c. introducing the mixture into a liquefaction zone under liquefaction conditions, wherein at least a portion of the solid carbonaceous material is converted in the presence of hydrogen to a liquid product.
2. The process of claim 1, wherein the solid carbonaceous material is selected from the group consisting of bituminous coal, sub-bituminous coal, lignite and mixtures thereof.
3. The process of claim 1, wherein the solvent comprises at least 10 wt.% of bottoms material which boils at a temperature above 538°C (1000°F).
4. The process of claim 1, wherein the solvent is selected from a petrochemical, coal derived solvent, or a hydrogen donor solvent.
5. The process of claim 4, wherein the solvent is a coal derived solvent has a boiling range from about 343°C (650°F) to about 538°C (1000°F).
6. The process of claim 1, wherein the catalyst precursor comprises a heteropolyacid.

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7. The process of claim 6, wherein the heteropolyacid is phosphomolybdic acid.

8. The process of claim 1, wherein the catalyst precursor comprises a compound selected from the group consisting of dioxo-bis-(n-dibutyldithiocarbamato)MoO<sub>2</sub> and Mo<sub>2</sub>O<sub>2</sub>(μ-S)<sub>2</sub>(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub> where R is n-butyl.

9. The process of claim 1, wherein the sulfuring containing hydrogen transfer agent is selected from the group consisting of elemental sulfur, H<sub>2</sub>S or sulfur containing hydrocarbons.

10. The process of claim 1, wherein the sulfur containing hydrogen transfer agent in the mixture has a concentration of 0.1 to 5.0 wt.%.

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EFFECTS OF SULFUR ADDITION  
TO RAWHIDE AND WYODAK COAL

SIMILAR EFFECTS ARE DEMONSTRATED  
FOR RAWHIDE AND WYODAK COAL ON SULFUR ADDITION

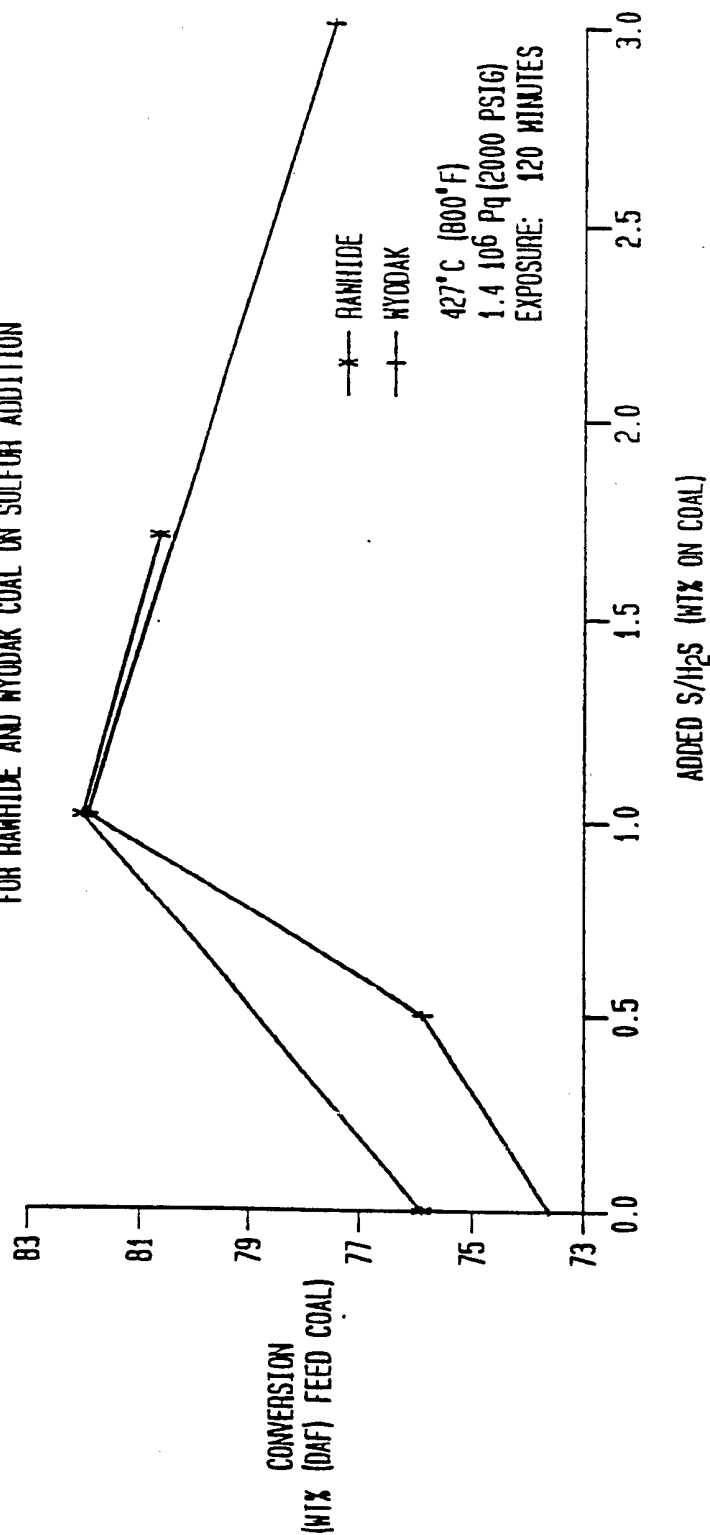
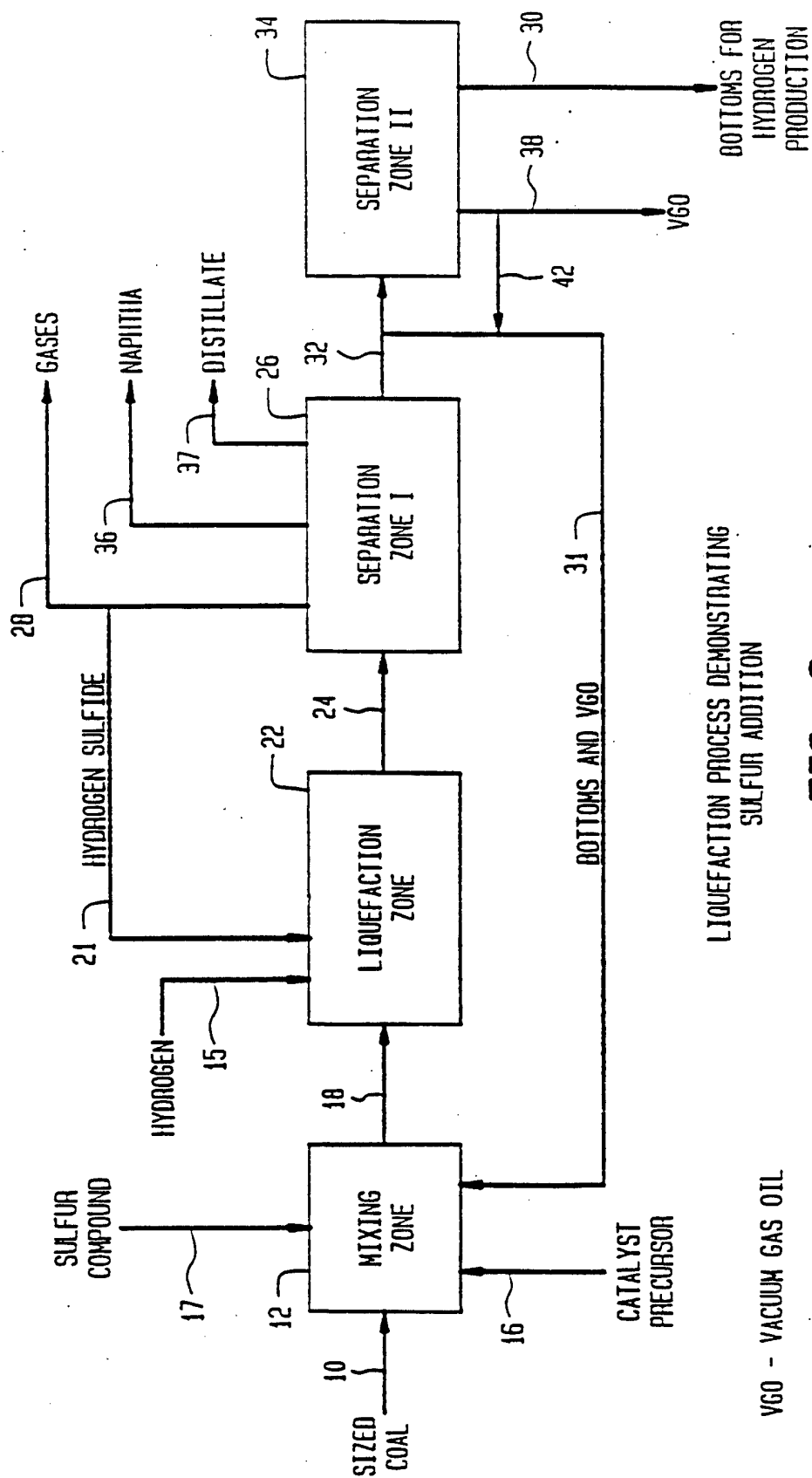


FIG. 1

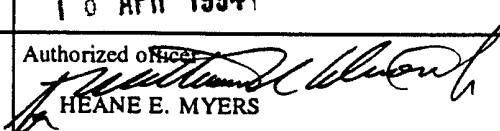


LIQUEFACTION PROCESS DEMONSTRATING  
SULFUR ADDITION

**FIG. 2**

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/09998

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(5) : C10G 1/06 US CL : 208/419, 420, 421, 422, 423 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 208/419, 420, 421, 422, 423 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,077,867 (Aldridge et al) 07 March 1978, col.1 line 61 to col. 2 line 29.	1-10
X	US, A, 5,064,527 (Singhal et al.) 12 November 1991, col. 2, line 3 to line 41.	1-10
X	US, A, 4,251,346 (Dry et al.) 17 February 1981, col. 5 line 52 to col.6, line 31.	1-10
X	US, A, 4,196,072 (Aldridge et al) 01 April 1980, col. 7, line 41 to line 65.	1-10
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 05 APRIL 1994		Date of mailing of the international search report 18 APR 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer  HEANE E. MYERS Telephone No. (703) 308-3323