

[54] **HYDROCONVERSION OF COAL-DERIVED OILS**

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[*] Notice: The portion of the term of this patent subsequent to Nov. 23, 1988, has been disclaimed.

[22] Filed: **Oct. 16, 1972**

[21] Appl. No.: **297,930**

[52] U.S. Cl. **208/59, 208/112, 208/251 H, 252/465, 252/477 R**

[51] Int. Cl. **C10g 13/02, C10g 13/18**

[58] **Field of Search** 208/59, 112

[56] **References Cited**
UNITED STATES PATENTS

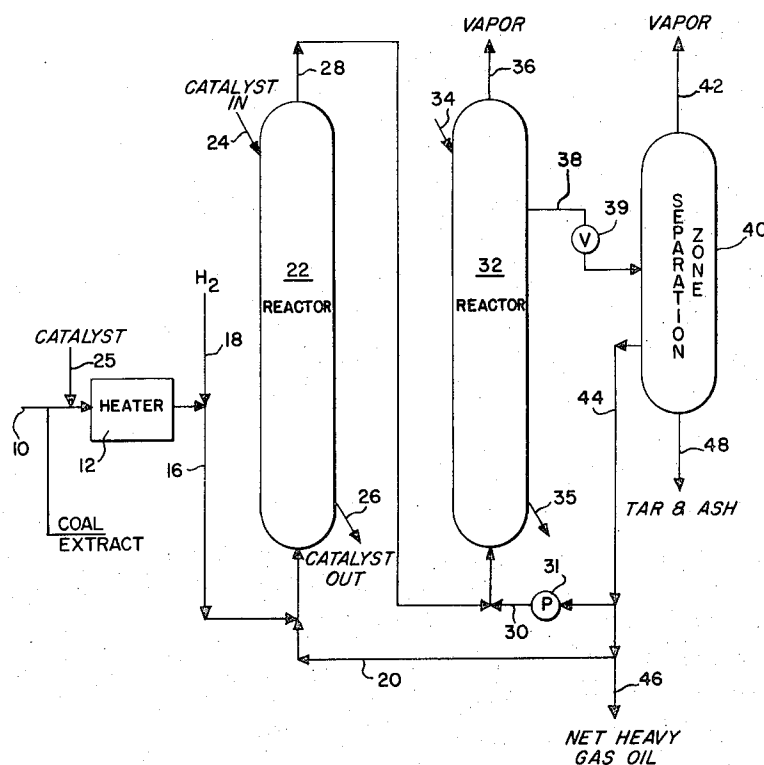
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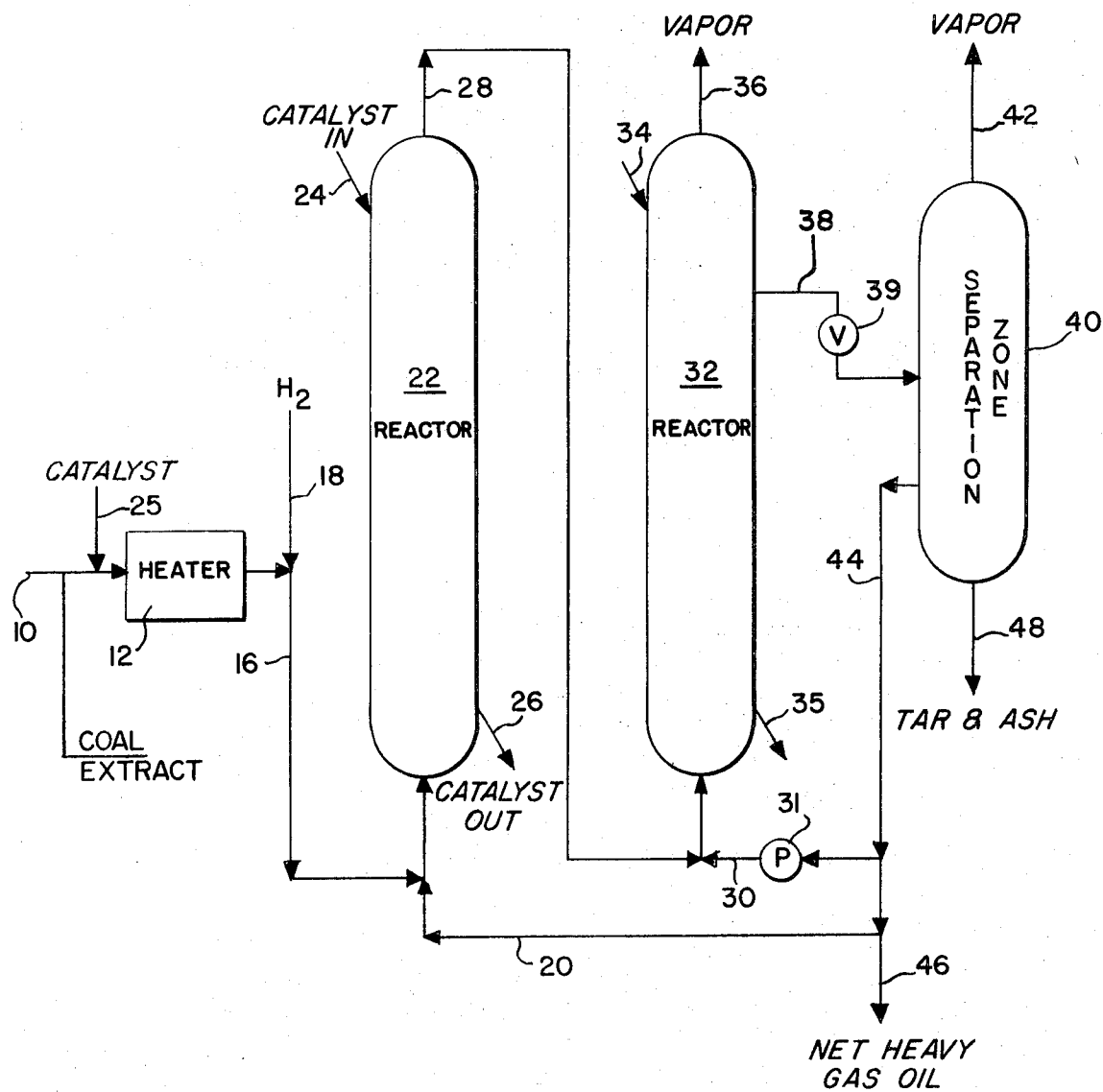
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[57] **ABSTRACT**

The conversion of coal-derived oils such as coal extract by ebullated bed reactor processing with hydrogen using a unique macroporous microspheroidal catalyst is accomplished to the extent of 80 percent or more conversion of the 975°F plus boiling range material to useful products having less than 975°F boiling range.

5 Claims, 1 Drawing Figure





HYDROCONVERSION OF COAL-DERIVED OILS

BACKGROUND OF THE INVENTION

In our previous U.S. Pat. No. 3,622,500, a disclosure is made of an ebullated-bed hydroconversion process based on the treatment of petroleum residua such as Canadian residuum, Middle East crude, Kuwait vacuum residuum and others. By the use of macroporous microspheroidal catalyst and preferred reaction conditions of temperature and pressure and space velocity, it was found that at least 50 percent conversion of the heavy petroleum material to lower boiling products could be effectively achieved.

The hydroconversion of the high boiling (975°F plus) fractions of the aromatic coal-derived oils such as coal extract, whether from gasification, extraction, or liquefaction, has involved another factor not previously recognized in petroleum residuum hydrogenation operations. Initial efforts to convert more than about 50 percent of this coal-derived material met with operational difficulties, such as reactor coking and plugging, bed instability, and short onstream times.

With coal extracts having a normally solid characteristic, it is necessary to heat them so that they are liquid at reactor operating conditions of temperature and pressure. Hydroconversion reactions are influenced by factors of temperature, pressure and space velocity within the reactor, and also by the composition of the initial feed material. Variables of pressure, temperature, space velocity and catalyst porosity were examined at length before discovering the successfully operable conditions and specific catalyst porosity needed for the hydroconversion of coal-derived oils in accordance to the present invention.

SUMMARY OF THE INVENTION

The present invention comprises a method for hydroconversion of coal-derived oils, such as normally solid coal extract, in an upflow ebullated bed reaction zone and utilizing a particulate macroporous microspheroidal catalyst having an approximate size range of 40 to 325 mesh (U.S. Sieve Series) and a specific porosity range. It was found necessary for the catalyst to have a pore volume of 0.20–0.40 cc/gram in pores larger than 250 Angstrom effective diameter, and only 0.10–0.30 cc/gram pore volume in pores smaller than 250 Angstrom. This particular porosity range provides a desirably higher density catalyst material which is easier to retain in the ebullated bed reactor during operations, and permits a greater catalyst weight inventory in a reactor of a given size and shape for a given range of reactor fluid velocities.

This invention has been found useful for processing coal-derived oils such as coal extracts derived by the solvent extraction of finely divided coal. No operating difficulties were encountered with feeds having 1.8 wt percent ash, and, it is anticipated that the ebullated-bed reactor could handle extract materials containing much higher levels of ash without difficulty.

The hydroconversion process of this invention may be performed at ebullated bed reactor general conditions comprising temperatures of 750°–950°F, hydrogen partial pressures of 2,000–3,500 psi, liquid-hourly space velocity of 0.15–0.45 V_f/V_r (volume of feed per hour per volume of reactor) and a hydrogen circulation rate of 3,000–10,000 SCF/bbl liquid feed. While

one stage of reaction may be used, multiple stage reactors are usually preferred because they permit achieving higher levels of conversion of the coal extract.

DESCRIPTION OF THE DRAWING

The drawing is a schematic view of a preferred two stage embodiment of the ebullated bed hydrogenation process for hydroconversion of coal-derived oils.

DESCRIPTION OF PREFERRED EMBODIMENT

In the drawing, a coal extract feed at 10, which usually is in liquid form resulting from immediately preceding processing steps (not shown), is heated in heater 12 to near reactor temperature. The resulting warm liquid charge stock at 16 is suitably pumped to reactor pressure together with hydrogen-containing gas at 18 and then passed to ebullated bed reactor 22. If desired, the heavy gas oil may be recycled at 20 to accomplish further conversion in the same reactor as the coal extract. Microspheroidal catalyst may be introduced directly into the reactor 22 through line 24, or alternatively into the feed line 10 through line 25 as desired.

In the reactor 22, the preheated coal extract feed, hydrogen and recycle gas oil are contacted with the catalyst. The upflow velocity of the gas and liquid prevailing in the reaction zone is controlled so as to expand the catalyst bed to a desired degree and maintain it in an ebullated state, substantially as described in the U.S. Reissue Pat. No. 25,770 to Johanson. When using such microspheroidal type catalyst, internal recycle of reactor liquids is usually not needed to maintain suitable ebullated conditions of the catalyst within the reaction zone. Used catalyst may be removed from the reactor through line 26 as necessary to limit the effective poisoning of the catalyst and thus maintaining a desired level of activity.

The total effluent removed at 28 from the first stage reactor 22 is fed to the bottom of the second stage reactor 32 also containing a catalyst. Heavy gas oil may be injected at 30 to react in the second stage reactor. Microspheroidal catalyst may be introduced directly into reactor 32 through line 34 and removed at line 35 as necessary. Vaporliquid separation is accomplished in the upper end of the second stage reactor 32 above the ebullated catalyst bed, with the vapor portion removed overhead at 36 and the liquid removed at 38. The vapors at 36 are customarily treated to recover hydrogen for recycle to the first stage reactor, and to recover light liquid hydrocarbons.

The liquid product withdrawn at 38 from the second stage reactor 32 is reduced in pressure at valve 39 and passed into separation zone 40. The vapor portion is removed therefrom at 42 for further processing to recover hydrogen and light hydrocarbons. A portion of the heavy gas oil liquid stream 44 may be recycled through line 20 to the first stage reactor 22, and a smaller portion may be recycled through line 30 to the second stage reactor 32. The net liquid stream portion at 46 is withdrawn from separator 40 as one of the final products from the process. Heavy liquid product boiling above 975°F and ash are removed from separation zone 40 through line 48.

Coal extract feed materials which are useful in this invention, are specified in Table I.

TABLE I

COAL EXTRACT CHARACTERISTICS		
	Broad Range	Narrow Range
Gravity, °API	-15 to -24	-18 to -24
Analysis:		
Carbon, W %	84-90	84-90
Hydrogen, W %	5-8	5.5-7.0
Nitrogen, W %	0.5-2.5	0.6-1.5
Oxygen, W %	0.5-5.0	1.5-4.0
Sulfur, W %	0.1-5	1-4
Ash, W %	0.1-3.0	1.5-2.5
Tetrahydrofuran Insolubles, W %	5-16	10-15
Benzene Insolubles, W %	40-60	42-55
Distillation, V %		
IBP-975°F	5-50	10-30
975°F+	50-95	70-90
Specific Gravity, cc/gm	1.15-1.35	1.2-1.3

The narrow range material is usually somewhat easier to process and is the preferred feed.

For this invention, the reactor operating conditions should be maintained substantially the same in both first and second stage reactors. The general useful range and preferred reactor operating conditions found useful for this invention are specified in Table II below:

TABLE II

REACTOR OPERATING CONDITIONS		
	Useful Range	Preferred
Temperature, °F	750-950	800-900
Partial Pressure of Hydrogen, psi	2000-3500	2500-3000
Space Velocity, $V_p/hr/V_r$	0.15-0.45	0.20-0.40
Hydrogen Rate, SCF/Bbl feed	3000-10,000	5000-8000
Catalyst Replacement Rate, Lb/Bbl feed	0.1-0.3	0.12-0.20

Conversion achieved, defined as converting material boiling above 975°F to material boiling below 975°F, is 60-98 percent for the useful range operating conditions and 80-95 percent for the preferred range conditions.

The characteristics of the macroporous microspheroidal catalyst material used in processing the coal extract were found to be critical, in that the catalyst should not only have particle sizes within a relatively narrow range but also have specific porosity distribution ranges as described hereinafter. The catalyst particles should be within a relatively narrow size range to permit achieving uniform expansion and random motion of the catalyst bed under the controlled upflow liquid and gas flow conditions, as is known in the art. The required catalyst material characteristics are further specified in Table III below.

TABLE III

CHARACTERISTICS OF CATALYST		
Chemical Analysis	Broad Range	Preferred
MoO ₃ , W %	11-16	12-15
CoO, W %	2.5-4.0	3.0-3.5
Surface Area, M ² /gm	220-290	240-260
Apparent Bulk Density, gm/cc (Compacted)	0.7-0.8	0.72-0.78
Catalyst Size Range, U.S. Sieve Series Mesh	40-325	50-200
Min. Percent Catalyst Within 50-200 Mesh Range	75	85
Min. Percent Catalyst Within 50-140 Mesh Range	50	70
Pore Volumes, cc/gm		
Pores Larger Than 250 Å Dia.	0.20-0.40	0.25-0.35
Pores Smaller than 250 Å Dia.	0.10-0.30	0.15-0.20
Total Pore Volume	0.30-0.70	0.40-0.55

The catalyst pore volumes required for this invention may be determined by the Mercury Porosimeter Test performed at 60,000 psi. maximum pressure, which is a well known method. Other well known hydrogenation catalysts such as nickel-molybdenum on alumina and nickel-cobalt molybdenum on alumina for example, could be used for this invention as long as they had the proper pore size distribution.

EXAMPLE

A coal extract feed material having gravity of -19.1°API and as specified in Table IV hereinafter was processed in a two-stage bench-scale reactor unit utilizing macroporous microspheroidal catalyst under ebullated bed conditions in accordance with this invention.

TABLE IV

Analysis	
Carbon, W %	86.4
Sulfur, W %	2.2
Hydrogen, W %	6.1
Nitrogen, W %	0.9
Oxygen, W % (by difference)	2.6
Ash, W %	1.8
Benzene Insolubles, W %	50.6
Tetrahydrofuran Insolubles, W %	11.3
Distillation, V %	
IBP - 825°F	19.3
825 - 975°F	7.7
975°F+	73.0
Specific Gravity, cc/gm	1.27
The reactor operating conditions used in this experiment were:	
Temperature, °F	825
Hydrogen Partial Pressure, psi	2750
Hourly Space Velocity, $V_p/hr/V_r$	0.22
Hydrogen Feed Rate, SCF/Bbl	6000-7000
Catalyst Replacement Rate, lb/Bbl	0.15

A microspheroidal catalyst comprising cobalt molybdenum on alumina and having a particle size range of 50-200 mesh was mixed with the coal extract feed material and introduced into the bottom end of a pilot plant ebullated bed reactor unit. The feed material was processed for over 345 hours without noticeable operational difficulties. Specific characteristics of the catalyst material used are listed below:

TABLE V

Chemical Analysis:	
MoO ₃ , W %	14.0
CoO, W %	3.1
Total Surface Area, M ² /gm	257
Apparent Bulk Density (Compacted), cc/gm	0.76
Catalyst Size Range	50-200 Mesh*
Percent within 50-200 Mesh Range	96
Percent within 50-140 Mesh Range	70
Pore Volume, cc/gm:	
In Pores Larger than 250 A	0.32
In Pores Smaller than 250 A	0.18
Total Pore Volume	0.50

*U.S. Sieve Series

Between 83-94 percent hydroconversion of the feed material to lower boiling liquids was achieved without incurring noticeable operating difficulties.

Coal extract is defined as the liquid or liquefiable portion of material derived from coal as by solvent extraction, hydrogenation, or condensation of the gases from the pyrolytic treatment of coal.

While we have shown and described a preferred form of embodiment of our invention, we are aware that modifications can be made thereto and we therefore desire a broad interpretation of the invention within the scope and spirit of the description herein and of the claims appended hereinafter.

We claim:

1. A method for hydroconversion of coal-derived oil having in the order of more than 50 weight percent boiling above 975°F and at least 0.1 weight percent ash

to convert in excess of sixty percent of that boiling above 975°F to a fraction boiling below 975°F, wherein the oil is heated and passed upflow through a reaction zone under a hydrogen partial pressure of 2,000 to 3,500 psi and at a temperature of 750°-950°F and containing a particulate catalyst, the upflow velocity being such as to place the catalyst in random motion in the liquid in the reaction zone, the improvement which comprises:

- a. using a particulate microspheroidal catalyst having a relatively close particle size in the range of 40-325 mesh, at least 75 percent of which is in the 50-200 mesh (USS) size; and
 - b. selecting the catalyst from the hydrogenation group including cobalt molybdate on alumina, nickel molybdate on alumina, and mixtures thereof, and having a total pore volume of 0.30 to 0.70 cc/gm, of which 0.20 to 0.40 cc/gm is in pores larger than 250 Angstroms effective diameter and 0.10 to 0.30 cc/gm is in pores smaller than 250 Angstroms.
2. The method of claim 1, wherein multiple staged reactors are used to achieve at least 80 percent conversion of the coal-derived feed material.
3. The method of claim 1, wherein the coal-derived oil feed material is diluted with a gas oil boiling range material made in the process.
4. The method of claim 1, wherein the coal-derived oil is a coal extract having an ash content of 1.5-2.5 weight percent.
5. The method for the hydroconversion of coal extract according to claim 4, wherein the microspheroidal catalyst has a total pore volume of 0.40-0.55 cc/gm, of which 0.25-0.35 cc/gm is in pores larger than 250 Angstrom diameter and 0.15-0.20 cc/gm is in pores smaller than 250 Angstrom diameter, and the catalyst bulk density is 0.7-0.8 gm/cc.

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