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(12) **Patent:**

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(54) PROCESS FOR THE PREPARATION OF CARBON MONOXIDE AND HYDROGEN FROM HEAVY OILS

(54) PROCEDE POUR LA PREPARATION D'OXYDE DE CARBONE ET D'HYDROGENE A PARTIR D'HUILES LOURDES

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ABSTRACT:

CLAIMS: Show all claims

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This invention relates to a process for the production of carbon monoxide and hydrogen from heavy oils. Topped or reduced petroleum crudes, recycle stocks and sludges of petroleum refineries, coal tars, pitches, asphalts and heavy fractions from shale oil are examples of suitable heavy oils which may be converted to carbon monoxide and hydrogen in accordance with the present invention.

This invention involves subjecting a heavy oil in the presence of a fluidized particulate mass in a gasification zone to contact with an oxidizing gas comprising oxygen, preferably admixed with steam and/or carbon dioxide, under conditions suitable for conversion of combustible constituents of said oil into a gas comprising a substantial amount of carbon monoxide and hydrogen and compounds containing both carbon and hydrogen atoms in the same molecule, including gaseous hydrocarbons. The resulting gaseous products, including the above-mentioned compounds, are immediately subjected to reforming by reaction with an oxidizing gas in a controlled amount and at an elevated temperature to convert the hydrocarbons to carbon monoxide and hydrogen. The gasification of the heavy oil is conducted in a dense phase fluidized bed while the reforming of the hydrocarbon gases to carbon monoxide and hydrogen is conducted in an unpacked reaction zone in heat exchange relation with the fluidized particulate mass.

An important feature of the present invention is in the treating of the gaseous effluent from the gasification zone, which contains hydrocarbons in addition to carbon monoxide and hydrogen, in a reforming zone with oxygen to convert the constituents containing both hydrogen and carbon atoms in the same molecule into carbon monoxide and hydrogen. The process permits a wide latitude in the control of the composition of the resulting product gas to provide valuable synthesis gas, i.e., a mixture of carbon monoxide and hydrogen in the desired proportions for the synthesis of hydrocarbons and oxygenated hydrocarbons. By conducting the gasification of the heavy oil in heat exchange relation with the reforming of the gasification products, it is possible either to supply heat to the gasification zone from the reforming zone or to supply heat from the gasification zone to the reforming zone. If a product gas of high hydrogen-to-carbon monoxide ratio is desired, it is advantageous to supply heat to the gasification zone from the reforming zone. This permits gasification with a relatively large quantity of steam as compared with the amount of oxygen employed and permits conversion of a greater percentage of steam to hydrogen by the water gas reaction. On the other hand, if a product gas relatively rich in carbon monoxide is desired, it is advantageous to transfer heat from the fluidized bed gasification zone to the reforming zone. In this manner carbon dioxide may be reacted with the gaseous hydrocarbons in the reforming zone to increase the production of carbon monoxide relative to hydrogen.

By-product and waste hydrocarbons, oxygenated hydrocarbons or the like, for instance, methane-containing tail gas produced in the synthesis of hydrocarbons, may also be converted in the reforming zone to additional carbon monoxide and hydrogen.

When a heavy oil is fed directly into the gasification zone of the present invention, the hydrocarbon vapors and gases, which result from the vaporization and cracking of the oil in the gasification zone and which escape oxidation while in the gasification zone, are converted in the reforming zone directly into carbon monoxide and hydrogen. The reforming step is also advantageous from the standpoint of converting sulphur compounds, particularly organic sulphur compounds, from the heavy oil into a form more readily removable from the product synthesis gas.

The drawing is a more or less diagrammatic elevational view, partly in cross section, of apparatus suitable for carrying out the process of the present invention. In describing a specific modification of the present invention in detail in connection with the accompanying drawing, reference will be made to the treatment of a heavy oil wherein the oil is injected into a fluidized bed of coke particles in the gasification zone of the apparatus. The particles of the fluidized bed will usually pass through a 40-mesh screen and, preferably, at least about 40 per cent by weight of the particles will pass through a 100-mesh screen.

With reference to the drawing, the apparatus comprises a closed pressure-resistant vessel having an outer shell 1. The vessel is divided into sections by partition 2. Preferably the outer shell of the vessel is covered with suitable insulating material, not illustrated in the drawing, to conserve heat within the vessel. The partition 2 divides the vessel to provide a gasification zone 5 within the vessel intermediate and spaced from each end of the vessel. The partition 2 is preferably in the form of a frusto-conical section with the small end of the frustum nearest the lower end of vessel 1. A conduit 4 extends through the lower end of the vessel and is connected with partition 2. This provides even distribution of gases from conduit 4 through the solid material maintained within the vessel in gasification zone 5.

The solid particles in the gasification zone are fluidized by gases flowing upwardly from conduit 4. The upper level 6 of the dense phase fluidized bed of particles is maintained somewhat below grille 3.

Grille 3 is provided with a multiplicity of openings 7 through which gases escape into the upper section 8 of the vessel. In the upper section 8, gaseous products from the gasification zone are admixed with an oxidizing gas stream introduced into the vessel through line 9. A plurality of vertical conduits 11 extending from grille 3 through partition 2 establish communication between upper end section 8 and section 12, the section of vessel 1 below partition 2. Reforming of the hydrocarbon constituents of the gas evolved in the gasification zone with the oxidizing gas takes place within sections 8 and 12 of the vessel and within conduits 11. Thus the gaseous reactants and reaction products within the reforming zone are in indirect heat exchange with the fluidized solids in the gasification zone 5.

The heavy oil is supplied through conduit 10 and sprayed from nozzle 15 into the fluidized coke mass in gasification zone 5.

Fresh solids, when desired, are introduced into the gasification zone 5 through conduit 13 while fouled or discard solids may be withdrawn from the gasification zone through line 14 at a rate determined by valve 16, to maintain the desired level 6 of the fluidized bed within the gasification zone.

Product gases from the reforming zone are withdrawn from section 12 through line 17. These gases consist essentially of hydrogen and carbon monoxide.

In operation, heavy oil is continuously supplied to the gasification zone through conduit 10 while oxygen with or without steam and/or carbon dioxide is introduced into the reaction zone through conduit 4. The oxidizing gases may be introduced as a mixture preheated to a temperature as high as about 1,000°F. Steam may be separately heated to higher temperatures. Sufficient oxygen is added to supply the amount of heat required to maintain a temperature within the gasification zone, preferably, in the range of about 1,600°F. to about 2,000°F.

The gasifier is preferably operated at superatmospheric pressure usually not exceeding about 50 atmospheres. A pressure in the range of about 20 to about 30 atmospheres is frequently desirable. The temperature in the reforming zone is maintained, preferably, in the range of about 2,000°F. to about 2,500°F. The temperature of the gasification zone may be regulated by control of the preheat of the oil and oxidizing gases fed thereto and the proportions of oxygen supplied to the gasifier through conduit 4 and the temperature within the reforming zone may be controlled similarly by the proportions of oxygen supplied through conduit 9.

While coke particles are often chosen to provide the fluidized bed in the gasification zone, other solid particles capable of withstanding the reaction conditions without disintegrating or agglomerating may be employed. For instance, sand, bauxite, alumina, magnesia, zircon and beryl are illustrative of solids which may provide the fluidized bed in the gasification zone. Whether combustible coke or an incombustible solid like bauxite forms the fluidized bed in the gasification zone, the fluidized solid particles have the function of presenting large surface areas to the heavy oil charged into the gasification zone. In this way, the highest boiling components and carbonaceous residue of the oil injected into the gasification zone are spread over the extensive surface of the solid particles, avoiding the build-up of massive carbon in the gasifier. Thus, the carbonaceous residue and substantially nonvolatile hydrocarbons deposited on the fluidized solid particles are continuously undergoing gasification by reaction with the oxidizing gas supplied to the gasification zone. The solids in the gasifier may gradually change in particle size; for instance, there may be an accumulation of salts and mineral constituents originally present in the heavy oil feed stock. For such a reason, discard solids may be withdrawn through conduit 14 and fresh make-up solids may be added through conduit 13 to maintain a well fluidized bed in the gasifier.

Part or all of the heavy oil and/or oxidizing gases supplied through conduits 4 and 9 may be advantageously passed in indirect heat exchange relationship with the hot product gases exiting from conduit 17 to preheat these reactants before introduction into the gasifier.

High-purity oxygen used in the process of this invention is generally the product of air liquefaction and rectification, containing at least about 90 per cent by volume of oxygen, preferably at least about 95 per cent by volume of oxygen. It is frequently advisable to supply the gasification zone with a mixture of steam and high-purity oxygen in which the steam-to-oxygen molar ratio is in the range of about 2:1 to 5:1. On the other hand, only high-purity oxygen is frequently introduced into the reforming zone by way of conduit 9.

Since the mixture of hydrogen and carbon monoxide which is produced by the process of this invention is often required for utilization in a plant producing synthetic gasoline by the reaction of hydrogen and carbon monoxide in the presence of an iron catalyst or the like at elevated pressures of the order of 20 atmospheres and higher, it becomes desirable to generate the hydrogen and carbon monoxide mixture by the process of this invention at such elevated pressures in order to avoid the difficulties and expense of compressing the product gas from this process prior to its introduction into the catalytic synthesis reactor. In this connection it is well to note that the operation of the gasification zone in the process of this invention at elevated pressures of the order of 20 atmospheres and higher generally tends to effect hydrogenation and methane-forming reactions with the result that the presence of hydrocarbons in the gases emerging from the fluidized bed in the gasification zone is increased. Accordingly, the present invention is particularly valuable in converting the hydrocarbons present in the gaseous stream leaving the gasification zone to additional carbon monoxide and hydrogen when the gasification is being conducted at elevated pressures to supply a synthesis gas comprising essentially hydrogen and carbon monoxide to a synthesis reactor operated at elevated pressures.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for the production of carbon monoxide and hydrogen from a heavy oil, the improvement which comprises subjecting said oil to the action of an oxidizing gas comprising oxygen and steam in a dense phase fluidized bed of solid particles in a gasification zone maintained at a temperature in the range of 1600 to 2000°F., discharging from said gasification zone gaseous products comprising carbon monoxide and hydrogen together with compounds containing both carbon and hydrogen atoms in the same molecule including gaseous hydrocarbons, and admixing oxidizing gas comprising uncombined oxygen with said gaseous products from the gasification zone in a reforming zone maintained at a temperature in the range of 2,000 to 2,500°F. wherein said compounds are converted into carbon monoxide and hydrogen while passing the reacting gaseous mixture therein in indirect heat exchange relationship with the fluidized particles in said gasification zone to supply heat to said gasification zone.

2. A process according to Claim 1 wherein said oxidizing gas supplied to the gasification zone consists essentially of steam and high-purity oxygen with a steam-to-oxygen molar ratio in the range of about 2:1 to 5:1.

3. In a process for the production of carbon monoxide and hydrogen from a heavy oil, the improvement which comprises subjecting said oil to the action of an oxidizing gas comprising oxygen and steam in a dense phase fluidized bed of solid particles in a gasification zone maintained at

a temperature in the range of 1600 to 2000°F., discharging from said gasification zone gaseous products comprising carbon monoxide and hydrogen together with hydrocarbons, and passing said gaseous products in admixture with an oxidizing gas through a reforming zone extending through said dense phase fluidized bed in said gasification zone and in indirect heat exchange relationship with said dense phase fluidized bed and maintained at a temperature in the range of about 2,000°F. to about 2,500°F., thereby effecting conversion of said hydrocarbons into carbon monoxide and hydrogen.

4. A process as defined in Claim 3 wherein said solid particles are coke particles.

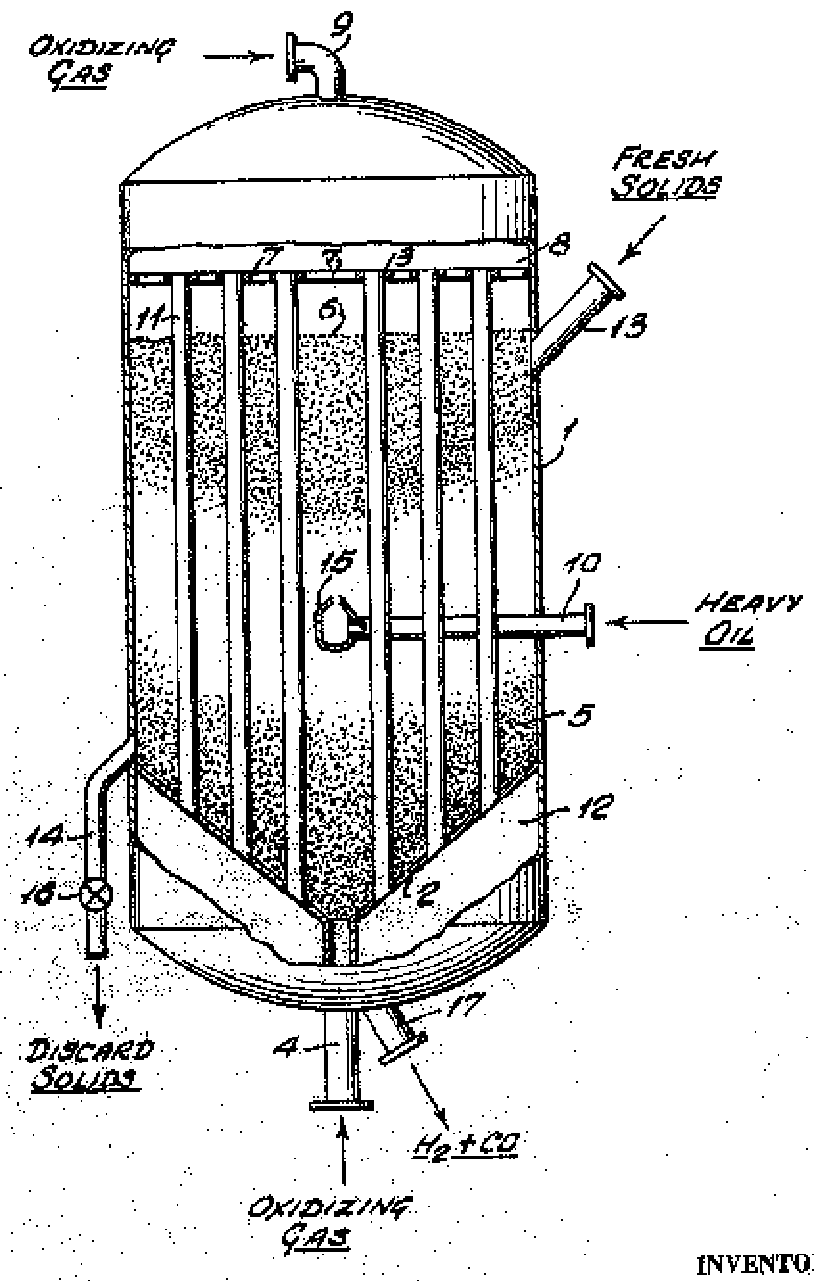
5. A process as defined in Claim 3 wherein said oxidizing gas supplied to said gasification zone is a mixture of high-purity oxygen and steam.

6. In a process for the production of carbon monoxide and hydrogen from a heavy oil, the improvement which comprises subjecting said oil to the action of a mixture of steam and high-purity oxygen in a dense phase fluidized bed of solid particles in a gasification zone maintained at a temperature in the range of about 1,600°F. to about 2,000°F., withdrawing the resulting gaseous products comprising hydrocarbons from said fluidized bed in said gasification zone, passing said products in admixture with high-purity oxygen into a reforming zone maintained at a temperature in the range of about 2,000°F. to about 2,500°F. in indirect heat exchange relationship with said fluidized bed in said gasification zone, thereby effecting conversion of said hydrocarbons

into carbon monoxide and hydrogen, and discharging the resulting mixture of carbon monoxide and hydrogen from said reforming zone.

7. A process as defined in Claim 6 wherein the gasification and reforming zones are maintained at a pressure of at least 20 atmospheres.

8. In a process for the production of carbon monoxide and hydrogen from a heavy oil, the improvement which comprises subjecting said oil to the action of an oxidizing gas comprising free oxygen and steam in a dense phase fluidized bed of solid particles in a gasification zone maintained at a temperature in the range of 1600 to 2000°F., injecting oxidizing gas comprising free oxygen into the gaseous products comprising compounds containing both carbon and hydrogen atoms in the same molecule upon discharge from said fluidized bed and flowing the resulting gaseous mixture as a plurality of parallel streams downwardly in indirect heat exchange relationship with said fluidized bed while maintaining said streams at a temperature in the range of 2000°F. to 2500°F. thereby converting said compounds into carbon monoxide and hydrogen.



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