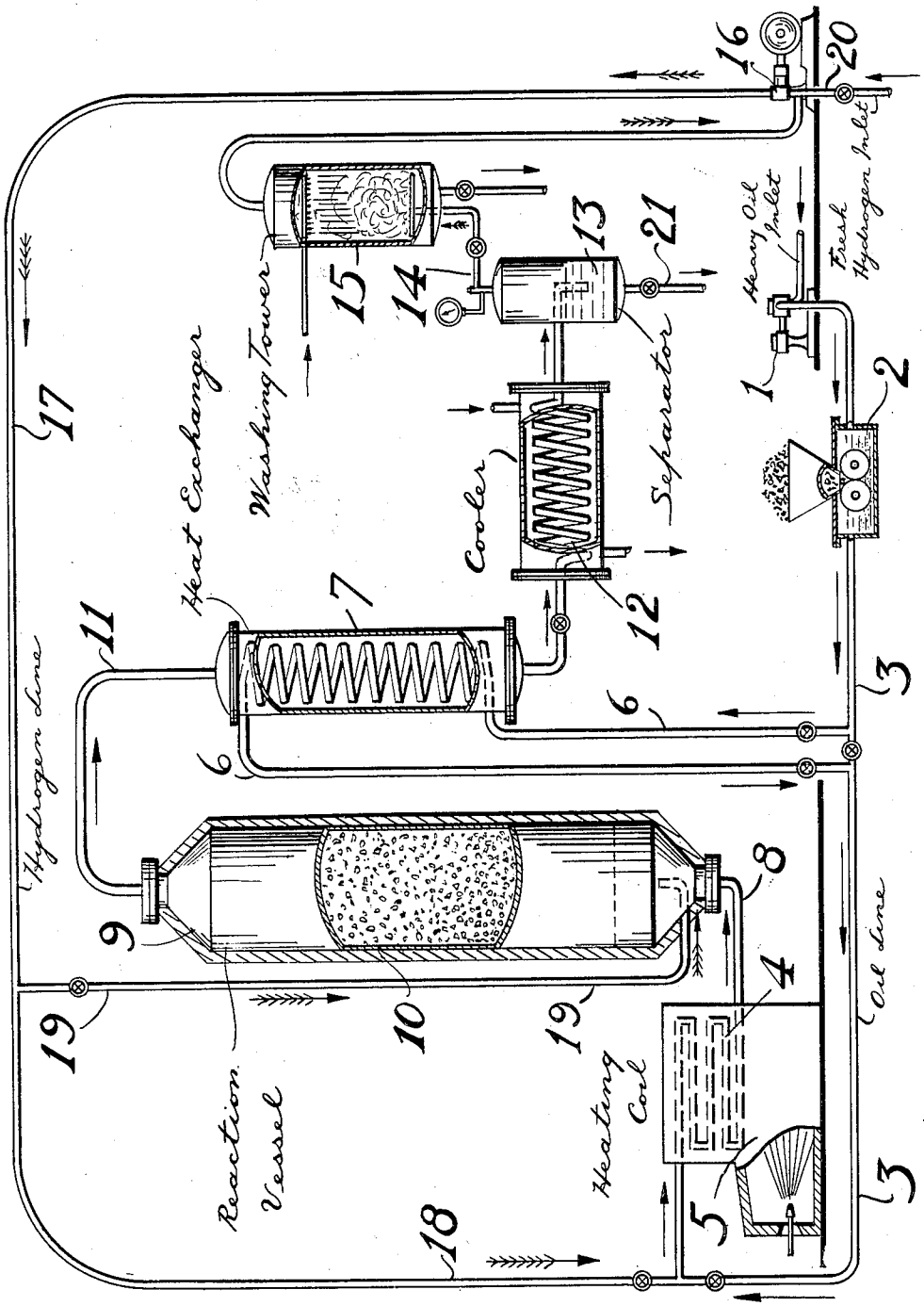
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IMPROVED METHOD FOR THE PRODUCTION OF HYDROCARBON OILS FROM SOLID CARBONACEOUS MATERIAL

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IMPROVED METHOD FOR THE PRODUCTION OF HYDROCARBON OILS FROM SOLID CARBONACEOUS MATERIAL

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8 Claims. (Cl. 196—53)

The present invention relates to an improved method for the production of hydrocarbon oils from solid carbonaceous material such as coal and more specifically comprises an improved process for producing hydrocarbon distillates of high quality from coal by the action of high pressure hydrogen at elevated temperatures. The present invention will be fully understood from the following description of the process.

The drawing is a diagrammatic representation in sectional elevation of an apparatus suitable for carrying out the present invention.

It has previously been suggested that coals, lignites, semi-cokes and the like may be liquefied by the action of high pressure hydrogen at elevated temperatures and pressures. However, it is difficult to use a catalyst effectively in this operation, since if a pulverized catalyst is used, it is withdrawn from the reactor along with inert and unconverted materials which must be withdrawn from time to time in order to prevent their accumulation. On the other hand if a lump catalyst is used particles of ground carbonaceous materials tend to collect on the catalyst and close the pores. I have found that if coal or other carbonaceous material is reduced to a state showing fine subdivision preferably a colloidal condition, lump catalysts may be successfully used. The action proceeds at a much more rapid rate and can be carried to a substantially complete conversion of the carbon containing compounds to liquid materials. Heretofore when no catalyst was used the action was relatively slow and could not be carried to completion resulting in a considerable waste in the formation of excessive quantities of gaseous materials and difficultly hydrogenating residues in the incomplete conversion of the solid carbonaceous material to oils.

In the operation of my process coal or other carbonaceous material, such as lignites, solid bitumens, tar sands and the like, is reduced to a fine state of sub-division, for example passing a 100 or 200 mesh screen. Grinding is usually done in an oily vehicle and it is then preferably passed through any convenient type of colloid mill whereby the size of the solid material is further reduced to substantially colloidal dimensions so that the solid material is capable of remaining in suspension for relatively longer periods of time. The oil which is used as a suspending medium may consist of heavy reduced crudes, cracking coil or coke oven tars and the like. A heavy oil which was previously obtained by the hydrogenation of coal may be used advantageously. The colloidal or finely ground mixture as fed to the reaction drum may contain 20 to 50 percent of coal by weight depending on the density of the liquid medium and the degree of dispersion. The mixture, or rather suspension of oil and coal is then forced either continuously or at intervals into retort which may be operated at an elevated temperature and at a pressure in considerable excess of 20 atmospheres.

Hydrogen is continuously passed through the retort in excess and is preferably heated in a coil in admixture with the suspension on its way to the reactor. The hydrogen after passing through the retort is purified of gaseous hydrocarbons formed in the process and is then recycled back to the retort by means of a booster compressor. The purification may consist of any suitable means such as scrubbing with heavy oils. The hydrogen is ordinarily recycled in the ratio of about 15,000 to 30,000 or more cubic feet of hydrogen per barrel of coal and oil mixture fed to the retort. To compensate for the gas consumed in the hydrogenation of the material in the retort fresh hydrogen is continuously added to the gas recycle stream. The hydrogen consumed by the process amounts to about 3 to 8% of the weight of the suspension fed to the apparatus depending on the degree of hydrogenation desired.

The temperature of the reaction drum is ordinarily at 700 to 850° F. but it has been found that it is unnecessary to heat the oily suspension above 650° F. or thereabouts before charging into the retort. The use of a catalyst promotes the reaction rate to such an extent that sufficient heat of reaction is emitted to cause the material to be raised to and converted at the reaction temperature. Addition of heat to the reaction zone is thus unnecessary and it is likewise unnecessary to heat the mixture of oil and coal in the coil to temperatures which would cause agglomeration of the solid particles and consequent plugging. Runs may therefore be made for extremely long periods in this manner.

Catalysts may be packed in the reaction zone in lumps of 2 to 4 mesh or larger and generally comprise substances such as the oxides of chromium, tungsten and molybdenum, either alone or in admixture with each other or other materials such as zinc oxide, aluminum oxide, magnesium oxide and the like. These catalysts are characterized by a high resistance to the action of sulphur and are aptly termed sulphactive. The lump catalyst is admirably suited to the process since by its use it is possible to force the colloidal mixture of coal and oil through the reaction zone,

converting a large part of the coal to low boiling oils and at the same time remove ash or materials not capable of hydrogenation as a suspension in heavy oil without disturbing the catalyst. The passage of the recycle gas through the lumps affords sufficient mixing when the carbonaceous material is in a finely divided state, say above 100 mesh.

In the operation of this improved process it is possible to withdraw vapor and liquid in separate streams from the reaction zone. The gas which is sent through the reactor passes off with the vapor. The gas and vapor stream is cooled and sent to a separator where the gas is separated from the condensed liquid and passed to a purification system as mentioned. The condensed liquid may be drawn from the separator which may be maintained at the full pressure of the catalytic reactor as finished product. The liquid stream which is withdrawn from the reactor is cooled and may be distilled in order to separate the lighter fractions and treated to remove the ash and unconverted materials by filtration or otherwise. The heavy oil obtained may be advantageously used as the oil vehicle for the carbonaceous material fed to the apparatus. The liquid and vapor may be withdrawn together as one stream from the reactor, in which case the operation of cooling and separating the gas is the same as noted above, except that the total effluent liquid and solid materials are withdrawn from the gas separator.

In a complete conversion of coal to oil a yield of 25 to 35% by weight on the combustible matter of naphtha and kerosene is obtained, together with 30% of Diesel and middle oils and 30% of heavy oils similar to reduced petroleum crudes or bottoms. About 10% of the carbonaceous material is converted to gas. Products are much improved over ordinary coal hydrogenation since the reaction time is shortened and the hydrogenating conditions made more intense. Phenol and cresol-formation is greatly reduced and may be substantially eliminated.

Referring to the drawing, reference numeral 1 indicates a feed pump for forcing heavy oil into and through a combined grinding and mixing device 2 into which coal or other solid carbonaceous material is added and is reduced to a fine state of subdivision, for example passing 100 or 200 mesh or even to a state of colloidal fineness. It will be understood that a series of grinding devices may be used if desired. The suspension of coal in oil passes through a line 3 to a heating coil 4 arranged in a furnace setting 5. Hydrogen is introduced with the suspension. A part of the whole of the suspension may be directed by a line 6 through a heat exchanger 7 in order to obtain preheat. The suspension after passing through the coil 4 discharges by line 8 into a reaction vessel 9 which is adapted to withstand high temperatures and pressures required for reaction. The vessel is packed with a stationary catalyst of the type indicated above and designated by numeral 10. The catalyst is preferably in lump form as specified above and of sufficient size in proportion to the size of the suspended solids to allow free flow through the mass. It is preferably heaped into the reaction vessel without orderly arrangement and the solids, it will be understood, pass through the voids between the catalytic lumps. The material passes out of the reaction vessel by means of line 11 through the heat exchanger 7 and a cooler 12. It then is discharged into a separation zone 13 from which fixed gases are withdrawn by line 14. These gases are scrubbed for purification in a washing tower 15 to remove hydrocarbon constituents and hydrogen sulfide and the purified hydrogen may then be recompressed by a booster pump 16 and forced into a return line 17. This line feeds the heating coil 4 by means of branch 18 and a portion of the gas may be introduced directly into the reaction vessel by line 19. Fresh or make-up hydrogen is added by 20. The suspension is withdrawn from the separation drum 13 in a fluid liquid form by means of pipe 21 and it may be treated in any suitable method for removing unconverted coal and ash constituents. It may be distilled for example and the residue after removal of ash may be used for carrying additional quantities of fresh coal into the reaction zone.

This invention is not to be limited by any theory of the mechanism of the reactions nor to any specific example which may have been given for purpose of illustration, but only by the following claims in which I wish to claim all novelty inherent in this invention.

I claim:

1. Process for converting coal into valuable hydrocarbon oils which comprises reducing the coal to a state of substantially colloidal fineness, suspending the finely divided material in a heavy oil, and passing the suspension with hydrogen through a reaction zone packed with lumps of sulphactive catalyst of a size and arrangement adapted to provide voids permitting free flow of the suspended solids therethrough and maintained under pressure in excess of 20 atmospheres and at a temperature above 700° F.

2. Process for converting coal into valuable hydrocarbon oils which comprises reducing the coal to a state of division at least sufficiently fine to pass a 200 mesh screen, suspending the finely divided coal in a heavy hydrocarbon oil, passing the suspension together with hydrogen through a reaction zone packed with lumps of sulphactive catalyst of a size sufficient to be held by a 4 mesh screen and arranged to provide voids permitting free flow of the suspended solids therethrough and maintained under a pressure in excess of 20 atmospheres and at a temperature between 700 and 850° F.

3. Process according to claim 2 in which the suspension of finely divided coal in heavy oil is preheated to a temperature below the point at which agglomeration of the particles of coal occurs before passing the suspension through the reaction zone.

4. Process according to claim 2 in which the suspension of finely divided coal in oil is preheated to a temperature below about 650° F. and is then discharged into an unheated reaction zone packed with lumps of sulphactive catalyst wherein the temperature is raised to above about 700° F. solely by means of the exothermic heat of reaction.

5. Process according to claim 2 in which heavy oil is withdrawn from the reaction zone, the ash is separated therefrom and the remaining oil is returned with fresh finely divided coal to the reaction zone.

6. In a process for converting coal into valuable hydrocarbon oils by subjecting the coal to the action of hydrogen at high temperature and pressure while in the presence of a mass of catalytic material which promotes hydrogenation, the improvement which comprises reducing the coal to a size such that particles will pass at least through

a 100 mesh screen, suspending the finely divided particles in the heavy oil, and passing the suspension through a reaction zone packed with lumps of the catalytic material of a size sufficient to be retained by a 2 mesh screen and arranged to provide voids permitting free flow of the suspended solids therethrough.

7. Process according to claim 6 in which the coal is reduced to a state of substantially colloidal fineness.

8. In a process for converting coal into valuable hydrocarbon oils by the action of hydrogen at high pressure and temperature while in the presence of a mass of catalytic material which promotes hydrogenation, the improvement which comprises reducing the coal to a size such that the particles will pass at least through a 100 mesh screen, suspending the finely divided particles in the heavy oil, and passing the suspension through a reaction zone packed with lumps of the catalytic material of about 2 to 4 mesh size arranged to provide voids permitting free flow of the suspended solids therethrough.

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