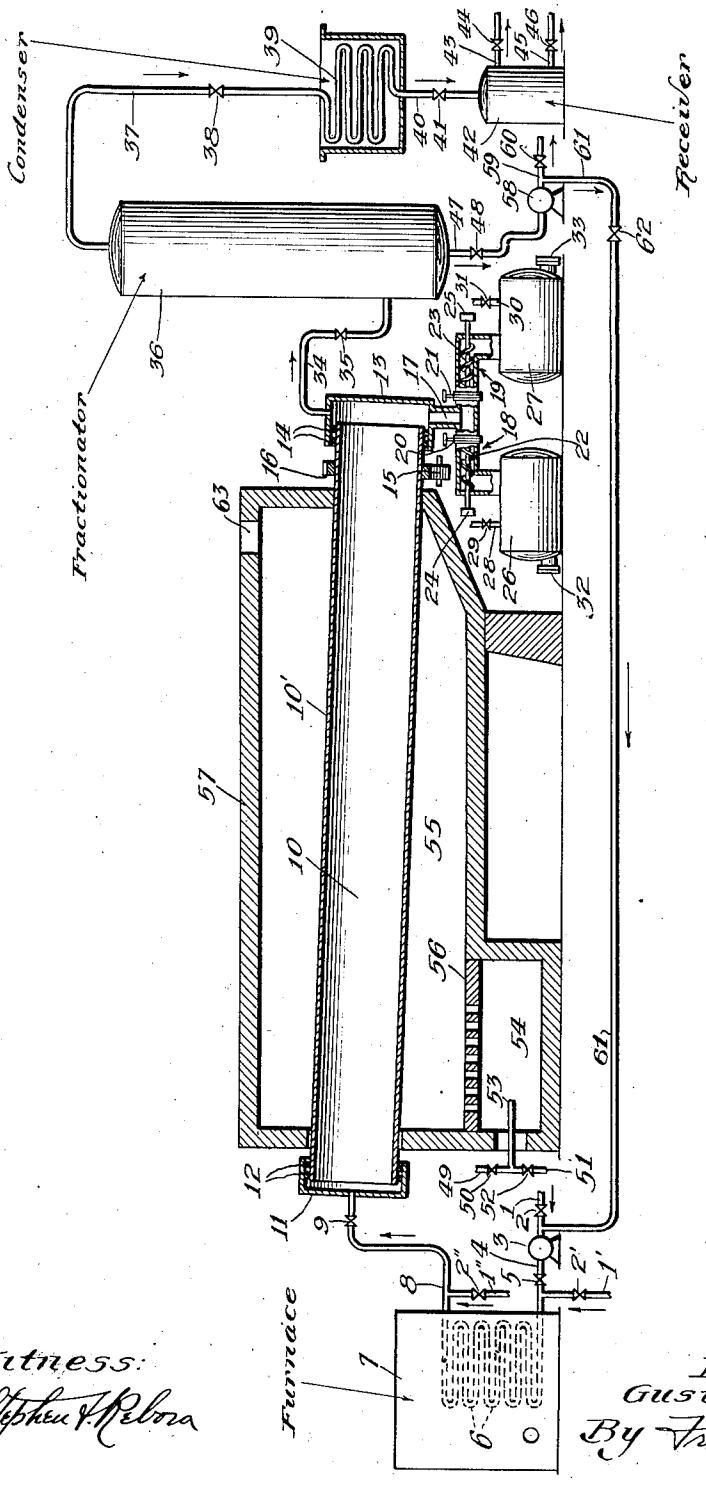
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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This invention relates to the treatment of hydrocarbons and refers more particularly to the treatment of solid carbonaceous bituminous materials such as coals and the heavier portions of petroleum, shale oils, tars, etc. to produce therefrom products of a more valuable nature.

More specifically the invention contemplates the provision of a process whereby mixtures of liquid hydrocarbons and solid carbonaceous or bituminous materials may be economically treated at sufficiently elevated temperatures and pressures to convert the mixture into substantial amounts of low-boiling hydrocarbons and gases on the one hand and readily utilizable coke on the other. The method of operation disclosed permits of substantially continuous operation.

In the present practice when heavy liquid hydrocarbon mixtures or solid carbonaceous materials are subjected to heat treatment and/or cracked to produce coke, the processes are intermittent because of the necessity for frequent removal of accumulations of coke in the apparatus and it is among the aims and objects of the present invention to disclose a method of operation and apparatus therefor which will permit of substantially continuous operation upon bituminous and hydrocarbon materials or mixtures of the same, such as coal-oil mixtures to produce on the one hand marketable coke and on the other hand satisfactory yields and good quality of liquid and gaseous products. Further improvements and advantages over processes at present in use in the art of cracking mixtures of coal and oil will become apparent from the detailed description.

In one specific embodiment the invention comprises heating mixtures of coal and oil in a coil, discharging the heated products into an enlarged vaporizing and/or reaction zone consisting of an elongated rotating retort, fractionating the vapors from the reaction zone to produce overhead fractions which are cooled, condensed and collected and insufficiently converted reflux condensates which are either removed from the system or returned to the heating zone for further treatment and continuously discharging solid carbonaceous residues from the reaction zone. Simultaneously gases of an oxidizing character may be introduced into the retort to promote oxidation reactions or hydrogen or carbon monoxide may be introduced to promote reducing reactions or hydrogenations.

To enable a clear understanding of an operation characteristic of the process of the invention, the attached diagrammatic drawing is provided which shows in essential detail a side elevation in partial section of an arrangement of equipment which may be employed.

Referring to the drawing, proportioned mixtures of finely divided coal and oil may be introduced to the process through a line 1 controlled by a valve 2 leading to a pump 3 which discharges through a line 4 controlled by a valve 5 into a tubular heating element 6 disposed to receive heat from a furnace 7. The liquid component of the mixture may be hydrocarbons from any source such as those obtained in the various refining operations conducted upon petroleum oils, for example, a residuum produced by the topping of crudes to remove gasoline fractions, or analogous fractions produced in the cracking or non-cracking distillation of coals, shales, asphalts, etc. The solid components of the blend or mixture are preferably finely divided coals, which have been ground to a degree of fineness necessary for making a homogeneous semi-stable suspension in the oils which can be handled as a liquid under proper temperature conditions, and with precautions for preventing settling. The suspension may be maintained in a substantially uniform condition by mechanical agitating devices or stabilizing substances used in maintaining colloidal suspensions may be added. Prior to the admission of the coal-oil mixtures to the heating element they may receive increments of reflux condensates from line 81 leading from subsequent fractionating devices as will be later more fully described. Selected gas mixtures may also be introduced from a line 1' controlled by valve 2' to effect the reactions of conversion and these gases may be either of an oxidizing or reducing character depending upon the products desired from the process. Steam may also be employed alone or in conjunction with the oxidizing or reducing gases, to produce gas-making reactions in case the manufacture of relatively large amounts of fuel gas is a particular object. Similarly gas mixtures may be introduced for particular purposes after the heating element from a line 1'' controlled by a valve 2''. The heated products from the element 6 which may be of the common type of continuous tubular construction may pass through a line 8 controlled by a valve 9 into an enlarged vaporizing or reaction zone 10. The line 8 may be of a design free from sharp turns or bends to prevent accumulations of solid material along the path of flow and similarly return headers employed in the construction of heating element 6 may be of the so-called stream-line type to prevent similar difficulty.

Reaction zone 10 is preferably formed of a

rotating cylindrical shell 10' adapted to rotate in fixed heads 11 and 13. Means are indicated in trunnion 15 driven by power means not shown and gear 16 fixed on shell 10' for rotating the shell at controllable rates of speed. To prevent leakage when operations are conducted under superatmospheric pressures, multiple packing rings indicated by 12 and 14 are provided, and in addition to such devices special oil sealed pressure rings and the like may be employed. There may also be present means for continuously transferring solid accumulations of coke toward the lower or discharge end of the reaction chamber such as, for example, a fixed internal shaft supported at either end on the two stationary heads 11 and 13, the shaft in turn supporting curved blades or hobs which work the material toward the discharge end during the rotation of the shell and insure the continuous removal of such deposits. Since other means such as loose steel balls, chains, etc. may be employed in a similar manner and since such means do not constitute an essential part of the present invention, no particular means has been indicated in the drawing.

The reaction zone may be exteriorly heated by hot combustion gases produced in a combustion zone 54, which forms a part of a furnace setting 57 having a perforated arch 56 between combustion zone and the heating zone 55 to prevent the direct impingement of combustion gases upon the reaction chamber and a proper outlet 63 for the exit of combustion gases to a suitable stack not shown. Fuel may be supplied to a burner 53 from a line 51 controlled by a valve 52 and gases such as steam or air for atomizing the fuel may be admitted from a line 49 controlled by a valve 50.

The solid carbonaceous residues produced in the reaction zone are preferably discharged through a line 17 of sufficient diameter to readily accommodate the size of the lumps, this line being integral with lower fixed head 13 and branching into lines 18 and 19 leading respectively to coke receivers 26 and 27 which are preferably maintained under process pressure while receiving coke. To enable the continuous discharge of coke under pressure, slide valves 20 and 21 are provided in lines 18 and 19 respectively, these valves being designed to hold whatever pressure may be employed in the reaction zone and enable the alternate use of the coke receivers, one being filled with coke while the other is being cleaned, the pressure having been released prior to cleaning. The controllable removal of coke to the receivers may be effected by such means as is indicated by the screw conveyors 22 and 23 in lines 18 and 19, rotated by power means 24 and 25 respectively. Receivers 26 and 27, which typify any arrangement of pressure coke receivers in parallel may be provided with vent lines 28 and 30 containing valves 29 and 31 respectively and also tight doors 32 and 33 which can be removed to permit access to the coke deposits.

Vapors from the reaction zone may pass through a line 34 controlled by a valve 35 and enter a fractionator 36 which typifies any arrangement of apparatus which may be employed to segregate vapors of desired boiling range from liquids amenable to further heat treatment and the gases and vapors may pass through a line 37 controlled by a valve 38 and be cooled by a condenser 39, the cooled products passing through a line 40 controlled by a valve 41 to a receiver 42. Such a receiver may be provided with a gas line 43 controlled by a valve 44 and a liquid withdrawal line 45 controlled by a valve 46 for the removal of process liquids. Heavy refluxes accumulating in the fractionator may pass through a line 47 controlled by a valve 48 to a pump 58 which discharges into a line 59 controlled by a valve 60. A branch line 61 leading from line 59 and containing interposed therein a valve 62 may lead back to line 1 on the suction side of feed pump 3 and permit the return of such liquids to the heating zone for further conversion, such portions as are not desired for further processing being withdrawn to suitable storage through valve 60 in line 59.

The reaction chamber has been indicated in the drawing as being at a relatively slight angle with the horizontal but it is within the scope of the invention to vary this angle when necessary to adapt the process to different types of coal-oil mixtures which may be employed in the decomposition reactions which are brought about. In the majority of cases the amount of coke deposited during the passage of materials through the rotating chamber will increase toward the discharge end and it may at times be only necessary to provide scraping devices in the lower portion of the shell. In some instances also such devices may not be necessary as, for example, when large amounts of low volatile coal are employed in the charging mixture.

It is characteristic of the process of the invention that means are provided for the continuous removal of coke deposits formed by the cracking of coke oil mixtures under elevated temperatures and pressures. It is not intended to confine the invention to the cracking or pyrolysis of such mixtures to produce mainly coke and motor fuel but it is intended to include the manufacture of major amounts of fuel gases by utilizing mixtures of steam and air in the heating and conversion zones and on the other hand to include the use of reducing or hydrogenating gases in the presence of catalytic materials to produce maximum or optimum yields of liquid products under hydrogenating conditions. The means shown for exteriorly heating the rotating shell of the reaction chamber enable the employment of temperatures higher than those produced in the initial heating zone if necessary to the objects desired. In the case of conversion under hydrogenating conditions, it may sometimes be necessary to cool the reaction zone instead of heating it since the classes of reactions mentioned are characteristically exothermic.

In the matter of temperatures and pressures, any temperature found suitable for the particular object in view, either gas manufacture, motor fuel production or hydrogenation, may be employed and correspondingly the pressures necessary for successful operation of these types of processes.

Catalytic reagents may be employed in the reaction zone, particularly in the case that the process is utilized for hydrogenation, examples of such catalytic materials being such metals and oxides of the same as nickel, cobalt, iron, vanadium, tungsten, molybdenum, etc. and their oxides and sulfides either alone or in combination.

As an example of an operation which may be conducted within the scope of the invention and the results obtainable therefrom, mention may be made of a case wherein a 40% suspension of finely divided coal in oil is treated. The oil may be a 24° A. P. I. gravity straight run residuum

produced by the topping of Mid-Continent crude oil and the coal may be of a bituminous character containing 30% volatile matter by analysis. The mixture may be processed using a temperature at the exit of the heating element of 875° F. and a pressure at this point and throughout the reaction chamber and succeeding equipment of substantially 200 lbs. per sq. in. The retort may be exteriorly heated to maintain a mean temperature of approximately 1050° F. therein.

As a result of this processing there may be produced from a barrel of material charged 22 gals. of a hydrocarbon mixture of the approximately boiling point range of commercial motor fuel, 150 lbs. of coke of 5–10% volatile matter and 1400 cu. ft. of gas having a specific gravity referred to air of 0.6 and a heating value of 900 B. t. u. per cu. ft. The gasoline, owing principally to its content of aromatic hydrocarbons produced in the cracking of the coal, may have a high antiknock value equivalent of 50 to 60% benzol. Owing to the return of the reflux from the fractionating column to the heating element the process may be so conducted that no other liquids other than the motor fuel are produced. In addition, owing to the means provided for the continuous removal of coke, such an operation may be conducted over a period of from one to two weeks without shut-down.

When introducing approximately 8% of hydrogen by weight of coal and oil mixture undergoing treatment in the proportions shown in the aforementioned example employing a mixture of 24° A. P. I. gravity straight run residuum and bituminous coal and under conditions of treatment cited, namely, 875° F. transfer temperature and a retort temperature of approximately 950° F. and approximately 300 pounds pressure in the reaction zones, treatment being conducted in the presence of a catalyst comprising approximately 1% of cobalt oxide, a yield of approximately 24 gallons of a hydrocarbon mixture of motor fuel boiling point range, 125 pounds of coke of low volatile matter and 1500 cubic feet of gas with an approximate heating value of 1000 B. t. u. per cubic foot for each barrel of the oil and coal mixture charged may be produced. The sulphur content of the distillate may also be reduced considerably by this treatment.

When introducing approximately 12% of air into the retort wherein the coal and oil mixture are undergoing treatment employing a transfer temperature of approximately 800° F. and a temperature within the retort of approximately 1050° F. maintaining substantially atmospheric pressure on the retort and the succeeding elements of the system and a pressure upon the heating element of approximately 200 pounds per square inch, the yield of material boiling within motor fuel boiling range may be approximately 23 gals. per barrel of material charged making in addition to the motor fuel product approximately 130 pounds of coke of low volatile matter and approximately 1500 cubic feet of gas having a heating value of approximately 850 B. t. u. per cubic foot. The gasoline may contain substantial percentages of oxidation products which increase the antiknock value over that of the product produced when air is not introduced into the retort of approximately 8 points in octane value or approximately 15 points in benzol value.

The foregoing description and example have served to indicate that the process of the invention is broad in scope and applicable to a wide variety of charging mixes and consequently the description and examples are not to be construed in a limiting sense but as illustrative merely.

I claim as my invention:

1. A process for recovering hydrocarbon liquids of motor fuel like character from hydrocarbon containing solids and liquids comprising mixing with a relatively heavy hydrocarbon liquid suitable proportions of a finely comminuted hydrocarbon containing solid to form a free flowing fluid mixture, subjecting the resultant mixture to a cracking temperature while flowing in a stream through a heating zone, discharging the heated mixture into an elongated rotary coking zone, introducing hydrogen to the mixture in the coking zone, maintaining the mixture in the presence of the hydrogen at a conversion temperature for the requisite time period to complete conversion, distilling the mixture to coke in the coking zone, subjecting vapors evolved from the mixture to reflux condensation and returning the resulting reflux for further treatment to the heating zone, condensing the vapors escaping reflux condensation and collecting the resulting distillate.

2. A process for recovering hydrocarbon liquids of motor fuel like character from hydrocarbon containing solids and liquids comprising mixing with a relatively heavy hydrocarbon liquid suitable proportions of a finely comminuted hydrocarbon containing solid to form a free flowing fluid mixture, heating the resultant mixture to cracking temperature while flowing in a restricted stream through a heating zone, discharging the heated mixture into an enlarged rotating hydrogenating zone, introducing hydrogen to the mixture in said rotating zone, maintaining the mixture in the presence of the hydrogen under hydrogenating conditions of temperature and pressure for a sufficient time to effect substantial conversion thereof into lower boiling products, subjecting vapors evolved from the mixture to fractionation and returning resultant reflux condensate to the heating zone, and finally condensing and collecting the fractionated vapors.

3. A process for recovering hydrocarbon liquids of motor fuel like character from hydrocarbon containing solids and liquids comprising mixing with a relatively heavy hydrocarbon liquid suitable proportions of a finely comminuted hydrocarbon containing solid to from a free flowing fluid mixture, heating the resultant mixture to cracking temperature while flowing in a restricted stream through a heating zone, discharging the heated mixture into an enlarged rotating hydrogenating zone, introducing hydrogen to the mixture in said rotating zone, maintaining the mixture in the presence of the hydrogen under hydrogenating conditions of temperature and pressure for a sufficient time to effect substantial conversion thereof into lower boiling products, and recovering lower boiling products thus produced.

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