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DESTRUCTIVE DISTILLATION OF SOLID CARBONIZABLE MATERIAL

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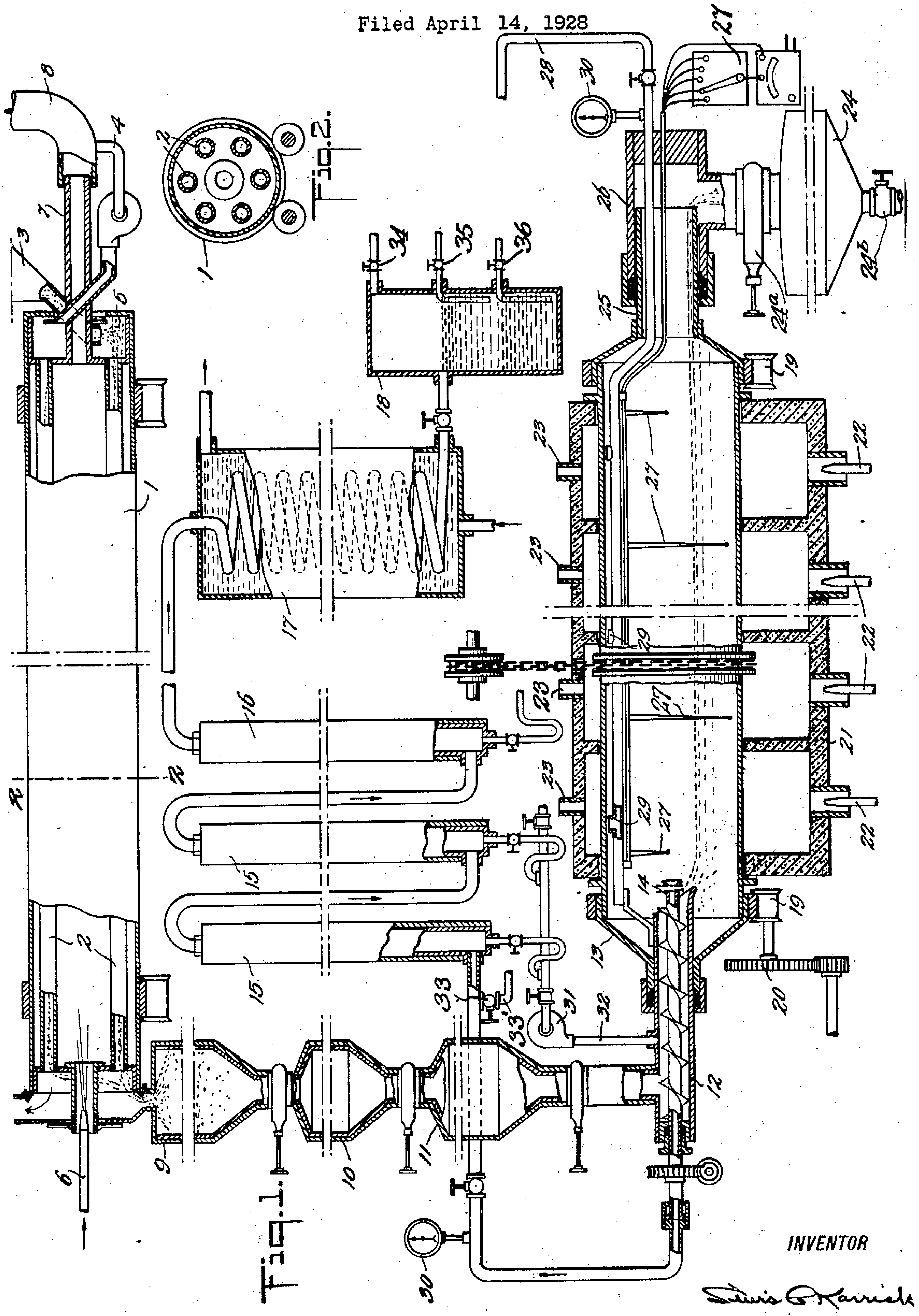

Fig. 1.

Fig. 2.

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DESTRUCTIVE DISTILLATION OF SOLID CARBONIZABLE MATERIAL

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5 Claims. (Cl. 202—16)

This invention relates to a process for the production of organic liquid products of controlled physical and chemical properties from coal and other solid carbonizable fuel materials.

The principal object of my invention is to produce directly from solid carbonizable fuel substances a crude liquid tar oil which is lighter than water.

A feature of the invention resides in continuously producing synthetic oil from solid carbonizable fuel materials and simultaneously extending the thermal decomposition of the oil so produced under controlled conditions to give an oil of lower density than water. This unusual property of the tar oil so produced obviates the necessity for subsequent dehydration by distillation as well as the necessity for subsequent cracking by auxiliary means.

The process also provides for the continuous disposal of the carbon formed in the thermal decomposition of tar oils by causing it to be intimately mixed with and deposited on the cell surfaces of the carbonaceous materials treated. This enables the process to utilize advantageously low grade coals and other carbonaceous materials of high carbon content for producing light oils without the necessity of interrupting the process to dispose of the carbon formed, or using run down stills.

The tar oils produced from coals by the many proposed forms of low-temperature carbonizing processes or by accepted assay methods, are of higher density than water due to the high molecular weights of the ingredients forming the tar oils and their high carbon-hydrogen elemental ratio. In general, the density of the tar oil formed is greater in inverse ratio to the amount of low temperature dissociation which is caused to take place. I have found that as the amount of low temperature decomposition of the oil forming bitumens is increased the density of the tar oils decreases and the carbon to hydrogen percentage-composition likewise decreases; this applies to the acid tars and the unsaturated hydrocarbons as well as to the neutral oils. However, if the tar oils are subjected to high temperature dissociations as they are formed much of the tar is lost by conversion to fixed gases while the density of the resulting tar is increased due principally to polymerization of a part of the tar oils which go to form the pitch residuum. I, therefore, apply conditions in my process which accomplish controlled low temperature pyrolysis of the primary bitumens and of the tar oils, thereby resulting in a minimum of conversion to fixed gases or to polymerized products and I reduce the carbon percentage in the oils simultaneously with a considerable reduction in their densities. I also apply conditions which catalyze these reactions as herein described.

In carrying out the invention, the materials to be treated are preferably finely crushed in order that all the substance may receive identical heat treatment, which would not be the case if lumps of considerable dimension were in process of heating for, or during, the same period of time. The process is well suited to destructive distillation of the granular or dust size coal delivered to power plants, or to fine sizes of oil shale. The process is also adapted to utilize accumulations of other low grade solid carbonizable fuel materials which are common at mines, power plants, coke or gas plants and the like. In the description of the process, the treatment of coal will be described, but it is understood that other carbonaceous materials may be treated similarly and like reactions will be obtained. I do not limit the treatment to any one carbonaceous substance, but have found that improved results are in many cases obtained by using mixtures of solid ingredients such as different grades of oil shales of varying richness and physical and chemical properties, or various types of coals of varying rank, coking index, or coals with mixtures of carbonaceous residue added.

In addition to the benefits obtained in the fluid products by using mixtures of solid ingredients in the reaction zones, I find that if certain of the liquid products are continuously mixed with the charged materials, a uniform and regulated destructive distillation or cracking takes place, and thereby any desired degree of modification of the fluids can be carried out. The process is primarily for carrying out the regulated thermal decomposition, or cracking, of the bitumen which forms the primary decomposition product in the heat treatment of oil shales and coals so as to produce liquid oil products of any desired gravity and volatility. Some of the primary products may be permitted to leave the cracking system with the highly volatile oils before the desired ultimate degree of dissociation has taken place. This procedure may be necessary for reasons of practicability in order to quickly remove and protect the light volatiles which form oils of the desired gravity before their excessive decomposition takes place. I therefore provide for the retention of the heavy or unfinished ingredients in the system and return them to the reaction chamber by controlled separating means and subject them to further destructive distillation.

It is the purpose in the process to cause the thermal decomposition of the bitumens or primary liquid products to produce final distillates of the desired specific gravity by a series of heat treatments in the reaction chamber. In order that the distillation products will not be carried out prematurely from the reaction chamber in a vapor or suspended condition, I provide means for heating the materials under the proper pressures to elevate the vaporizing temperatures of the liquid bitumens to points where the desired cracking will largely be completed.

It is damaging to the quality of the oil products to permit the vapors to linger in the highly heated zones and especially in contact with iron retort walls, and I provide means for minimizing any harmful effects from such causes. I prefer to cause the vapors to move toward an exit in the direction of the feed end of the reaction chamber and into zones of lower wall temperature, and thereby flow counter to the general movement of the carbonaceous materials. The vapors may, however, be removed at either or at both ends if desired in producing special products. Furthermore, means are provided for introducing steam, oil, vapors, or gases at the discharge end, or into the distilling zone so as to protect the distillation products by chemical reaction or by dilution and with change of temperature while sweeping them from the chamber. I prefer also that the inner wall surface of the reaction chamber be copper or chromium plated to prevent formation of undesired compounds.

I have proved by my process that the highest quality oils from coals and oil shales are produced when the heating is very slow and with gradual rise of temperature. In order that the best rate and temperatures of heating may be applied to the reacting substances, the carbonaceous and volatile materials are each caused to move at controlled rates through the different heating zones while the zones are heated to different temperatures.

In applying the process conditions as stated above, I prefer to use a revolving retort of cylindrical form of standard pipe, its length being many times its diameter, for example: 3″×20′, 6″×40′, 12″×60′ or 20″×100′, in order that there will be very little conducted, convected, or radiated heat between the adjacent inside zones or between adjacent portions of the charge, through the retort walls or by the retort contents. The retort is set at a slight angle from the horizontal so that the materials treated will pass through by gravity during their uniform motion during rotation.

The cylinder is heated externally throughout part or all of its length by hot gases or other suitable means. The oven surrounding the cylinder is divided into zones so that different portions of the cylinder and contents are heated to different temperatures. In using a large cylinder there may be walls or constrictions (not specifically shown herein) extending different distances from the outer walls and serving as a means of damming the flow of materials and retaining it for a greater or less period in the zones according to the height of the walls. A slight modification in height of the constriction causes a relatively great difference in the depth of charge and its rate of progress through the zone. If the carbonaceous material is preheated, by separate means, close to its initial distillation temperature, it will not be necessary to use as many constrictions, or the entire chamber may serve as a single extended zone for carbonizing. The external heat will be regulated to increase the temperature of the material as it moves toward the outlet. However, if some of the partly cracked bitumen has escaped from the chamber and is returned to complete its thermal decomposition it may be desirable to use a constriction possibly at the second heating zone and thereby permit adequate cracking time near the feed end of the chamber. As a result the vapors will not come into contact with the more highly heated walls toward the exit end of the chamber.

Tar oils will crack and deposit a great deal of pitch carbon in distilling by ordinary methods to coke. Also, if the tar oil is first mixed with finely divided coal an increased amount of light liquid products may be formed. However, I have found that when the same initial tar oil is mixed with coke, particularly a highly adsorptive low temperature coke, and distilled preferably under pressure, a very much greater yield of valuable low boiling products is obtained. If the coke has ingredients adsorbed in its pores which react chemically with the tar oils the resulting product may be altered considerably. I have adsorbed metallic copper on the cell surfaces of the coke and found that it removed much of the sulphur from the tar oils. This treatment is also applicable to petroleum. I produced such a treated coke by activating the carbonaceous residue from the process by contacting with a current of superheated steam above 850° C. and immersing this coke immediately thereafter in a solution of copper chloride. Cobalt and chromium salts may also be used. I therefore prefer to charge continuously a quantity of the coke product, or other coke, either activated or unactivated, which may be treated or not as desired, into the retort with the coal in ample amount to absorb the incompletely cracked primary tar oil which is returned to the reaction chamber and thereby greatly increase the capacity and thoroughness of the thermal decompositions desired by use of this process.

By this process, a highly reactive and adsorptive low temperature coke product is produced, with any desired percentage of volatiles retained, a large yield of rich gas, and a large yield of tar oil which is mostly of the same volatility as ordinary petroleum tops.

In the drawing:

Fig. 1 is a diagrammatic illustration of apparatus embodying the process of the invention and is an elevation with parts largely in section; and

Fig. 2 is a cross-section taken on the line 2—2 of Fig. 1.

Referring to the drawing: Fig. 1 shows a rotary pretreater 1 heated internally with hot gases and containing a multiplicity of externally heated tubes 2 through which the coal passes in parallel flow with modified combustion gases; a coal charging spout 3; a hot gas connection 4 entering the coal feed compartment 5; a source of hot gas supply 6 for the pretreater, and a waste gas outlet 7 to the stack 8. The pretreater heats the coal to any desired temperature such as about 250° C. to 350° C., and, in the case of young bituminous or sub-bituminous coals, may drive off some of the initial volatiles consisting of oxides of carbon or, in treating badly fusing coals, an oxidizing pretreatment with stack gases may be applied to reduce the fusing tendency.

The treated coal discharges into a heat insulated feed hopper 9 from which it passes through bin 10 and into magazine 11 from which it passes into feed regulator 12 and into rotary reaction chamber 13, suitable valves being provided for controlling the process, as shown. One or the other of the valves above and below bin 10 must be closed at all times to maintain the desired pressure in the system; the top valve is opened momentarily only while filling bin 10 and is otherwise closed, the lower valve being opened always excepting while bin 10 is being filled. The valve below magazine 11 is only for emergency in case the valve at the top of the magazine fails to seal perfectly. The feed regulator 12 is provided with a variable worm drive and gas tight stuffing box, as shown. The pipe enclosing the worm feed passes through a revolving gas tight gland into the end of retort chamber 13. The worm feed has a hollow shaft 14 through which the escaping volatiles pass out of chamber 12 and to the fractionating condensers 15, 16, 17.

The condensers 15 are of the refluxing insulated type regulated by temperature control, similar to petroleum practice, to condense out and return that portion of the tar oil vapors which has not received sufficient thermal decomposition in the retort. Condensed heavy high-boiling oils are returned continuously to the chamber 13 through the feed regulator 12 with the advancing supply of fresh coal. Condenser 16 will be regulated to condense any fractions such as acid oils containing phenols or cresols desired for special purposes while condenser 17 is of the parallel flow type and will condense out the lightest naphtha. Separator 18 is provided for continuous separation of the oil and water while under pressure and simultaneous removal of the fixed gases. The valves 34, 35 and 36 on the outlets of the separator 18 are regulated to maintain the desired pressure in the entire system.

The rotary reaction chamber 13 rests on rollers 19 at each end, and at intermediate points, which are operated by a suitable variable speed drive 20. Instead of using rollers at the intermediate points, it may be advisable to support the cylinder at these points by means of endless chains passing under the cylinder and over sheaves mounted on a drive shaft above the cylinder, openings being provided through the roof of the enclosure surrounding the cylinder to permit the chain to pass into and out of the enclosure. If desired chain sheaves (not shown) may be mounted on the cylinder for use with the chains as a supporting means. These chain sheaves are preferably provided with spokes of sufficient length to permit free movement of the heating gases between them as the gases move longitudinally along the cylinder, and the length of the spokes resulting in the chain groove of the sheave wheel running in an annular recess in the brick work of the oven enclosure thereby preventing direct contact between the chain and the hot gases. Around the reaction chamber 13 is a long oven 21 divided into separate heating zones with individual heat sources 22 and chimneys 23. If desired, a part of the rotary cylinder 13 may extend beyond the ovens and serve as a partial cooler for the coke while giving up its heat to preheat air for use in combustion. I prefer, however, to cool the coke after it is deposited in the receiving bin 24 by means of coils (not shown) through which air is passed. It will be noted that both methods apply indirect cooling and thereby do not provide for removal of the contained heat of the coke by circulation of gases through the coke as is applied in dry quenching methods; the recovered heat is, however, reused in my method for the heating of the coal. The material passing into the bin 24 is a dry granulated coke. This coke when activated, as above described, in cylinder 13 or by external means, may be immersed in a solution of copper chloride and then returned to the chamber 13 with the advancing supply of fresh coal in an amount sufficient to absorb the condensed heavy high-boiling oils and to desulphurize the oil. Coke from any other source may also be treated and admitted to the system in this manner.

At the outlet of destructive distillation chamber 13 is an extension 25 passing into fitting 26 provided with a gas-tight stuffing box. At the lower outlet of fitting 26 is the pressure bin 24 with top and bottom valves 24*a* and 24*b* respectively, the top one remaining opened and the bottom one closed at all times while the bin is filling. After filling, the valves are reversed momentarily while the charge of coke is dropped out. At the end of fitting 26 is a plug with openings into which connections are made for the thermocouple installation 27, and for pipe 28.

Pipe 28 is provided for introducing fluids such as steam, oil, vapors, or gases into the revolving destructive distillation chamber. The pipe is provided with side openings 29 at intervals along its length so that it can be made to communicate with the chamber at any point from end to end. The volatile products may if preferred be conducted from the destructive distillation chamber 13 through any of the side openings in the pipe 28 and thence to the condensers 15 by way of a pipe 33′ and valve 33 instead of removing them through the feed regulator 12, as described above. Saturated steam may be released at any point intermediate the end of the chamber 13 to cool and scavenge the tar oil vapors and gases. Also, by introducing superheated steam at these intermediate points the carbonaceous residue may be activated to produce the highly adsorptive coke desirable to increase the yield of valuable low boiling products, as described above. Gases or oil vapors either produced from the process or from other sources may be introduced and permitted to crack simultaneously with the bitumens so as to affect advantageously their resulting compositions. Also, oxidizing gases may be introduced into the chamber 13 so as to reduce the tendency for the coal to fuse and stick together. When the pipe 28 serves as an exit for part or all of the volatiles from the carbonaceous materials receiving treatment it is connected to the pipe 33′ and valve 33 at the inlet of condensers 15. Pressure gages 30 are shown on the pipes leading into and out of the reaction chamber by which any desired pressure is governed. A pump 31 is provided at the outlet from condensers 15 for forcing the condensate back into the reaction chamber via pipe 32 and feed regulator 12.

In treating some oil yielding substances I prefer to return the under-cracked bitumens to the reaction chamber by pipe 28 which will then be connected to pump 31, and thereby the cracking of these bitumens takes place in contact with and catalyzed by the adsorptive coke made in the process.

I have found that the process operates advantageously under pressures above atmospheric for the reason that, first—it reduces the amount of undecomposed bitumens carried out of the reaction chamber suspended in the oil vapors and gases, by reducing the quantity of volatiles produced to a smaller volume which thereby retards the rate at which they flow from the pores of the carbonaceous substances; second, the vaporizing temperature of the primary bitumens is increased so that greater dissociation takes place; third, the boiling points of the bitumens subjected to further decomposition are raised to temperatures that will accomplish the dissociation to a degree required in the desired oil product. I have found that a pressure of sixty pounds gage and a temperature of 750° F. at the "cold" end of the reaction chamber and 950° F. in the "hot" zone is suited for producing a tar oil from coal with the same volatility as "tops" from shale oil or petroleum and which is considerably lighter than water. This oil from my process carries no water in suspension and is readily separated from water by decantation. One oil sample from Utah coal contained approximately 20 per cent of tar acids of the same volatility as phenol and cresol. The acid free oil contained about 35% of distillate which was easily refined into a sweet, gum-free antiknock motor fuel of excellent color. The residue consisted of neutral oils similar to gas oil and light lubricants, and sludge.

By this invention, a continuous process is provided by which the desired light products are continuously produced, and the coke continuously discharged. The coke may be caused by regulating the degree of pretreating, and rate of heating, to agglomerate and roll together into large cylindrical chunks.

I do not restrict myself to the treatment of coal in the claims except where specifically stated, as many features of this invention are applicable to the treatment of petroleum and synthetic oils.

What I claim is:

1. A continuous process for producing hydrocarbon oil lighter than water from solid carbonizable material, which comprises passing a mixture of solid carbonizable material and a highly adsorbtive material containing adsorbed copper in a path of continuous direction at a substantially uniform rate while excluded from the atmosphere and maintained under a pressure materially above atmospheric, rolling the particles of mixed material continuously during its aforesaid passage, heating said mixed material to progressively increasing temperatures in progressive stages of its travel effective to produce controlled pyrolysis, withdrawing the vaporized distillation products in a direction counter to the general movement of the mixed material through zones of successively decreasing temperatures, and returning incompletely decomposed liquid distillation products to the heating zone with additional carbonizable substance to effect their further conversion.

2. A continuous process for producing hydrocarbon oil lighter than water from solid carbonizable material, which comprises passing a mixture of solid carbonizable material and a highly adsorptive material containing adsorbed copper through a cylindrical reaction chamber of relatively great length and small diameter in a path of continuous direction at a substantially uniform rate while excluded from the atmosphere and maintained under a pressure materially above atmospheric, rolling the particles of mixed material continuously during its aforesaid passage, heating said mixed material to progressively increasing temperatures in progressive stages of its travel effective to produce controlled pyrolysis, withdrawing the vaporized distillation products in a direction counter to the general movement of the mixed material through zones of successively decreasing temperatures, and returning incompletely decomposed liquid distillation products to the heating zones with additional carbonizable substance to effect their further conversion.

3. A process as defined in claim 2 which further returns the incompletely decomposed liquid distillation products into the charging end of said cylindrical reaction chamber for further treatment, and for continuously discharging the solid residue from said chamber without varying the pressure therein.

4. A continuous process for producing hydrocarbon oils lighter than water from solid carbonizable material, which comprises preheating the carbonizable material at atmospheric pressure to reduce the fusing properties of the material, continuously delivering the preheated carbonizable material to a retort while constantly effecting a seal between the preheated zone and the retort zone, said delivery of the preheated material into the retort zone being forcibly effected and the treatment in the retort zone being in successive stages of different temperatures, continuously withdrawing vaporized distillation products from the retort zone, separating the fractions of the vapors withdrawn from the retort zone, continuously returning a heavy high-boiling oil to the retort zone for further treatment, and continuously removing the solid residual coke from the retort zone while effecting a sealing of the discharge therefrom during the removal of the solid residue.

5. A system for producing oil lighter than water from a solid carbonizable material comprising a preheating chamber, a retort, communicating means therebetween, said preheating chamber being adapted to effect an initial pyrolysis of the carbonizable material at atmospheric pressure to reduce the fusing properties of the material, means for effecting a continuous delivery of the preheated carbonizable material to the charging end of the retort while constantly providing a seal between the preheating chamber and the retort, means for forcibly feeding the material into the retort, said retort being of an elongated character and provided with means for heating successive portions thereof to different temperatures, means for continuously withdrawing vaporized distillation products from the retort at a point adjacent the charging or discharging end thereof, means for separating fractions of the vapors withdrawn from the retort, means for continuously returning heavy high-boiling oils for release at several points within the retort for further treatment, and means for continuously removing the solid residue from the retort while effecting a sealing of the outlet end of the retort during the removing of the solid residue.

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