Sept. 24, 1935. A. OBERLE 2,015,085

METHOD OF THERMOLIZING CARBONIZABLE MATERIALS

Filed May 14, 1930 2 Sheets-Sheet 1

FIG. 1.

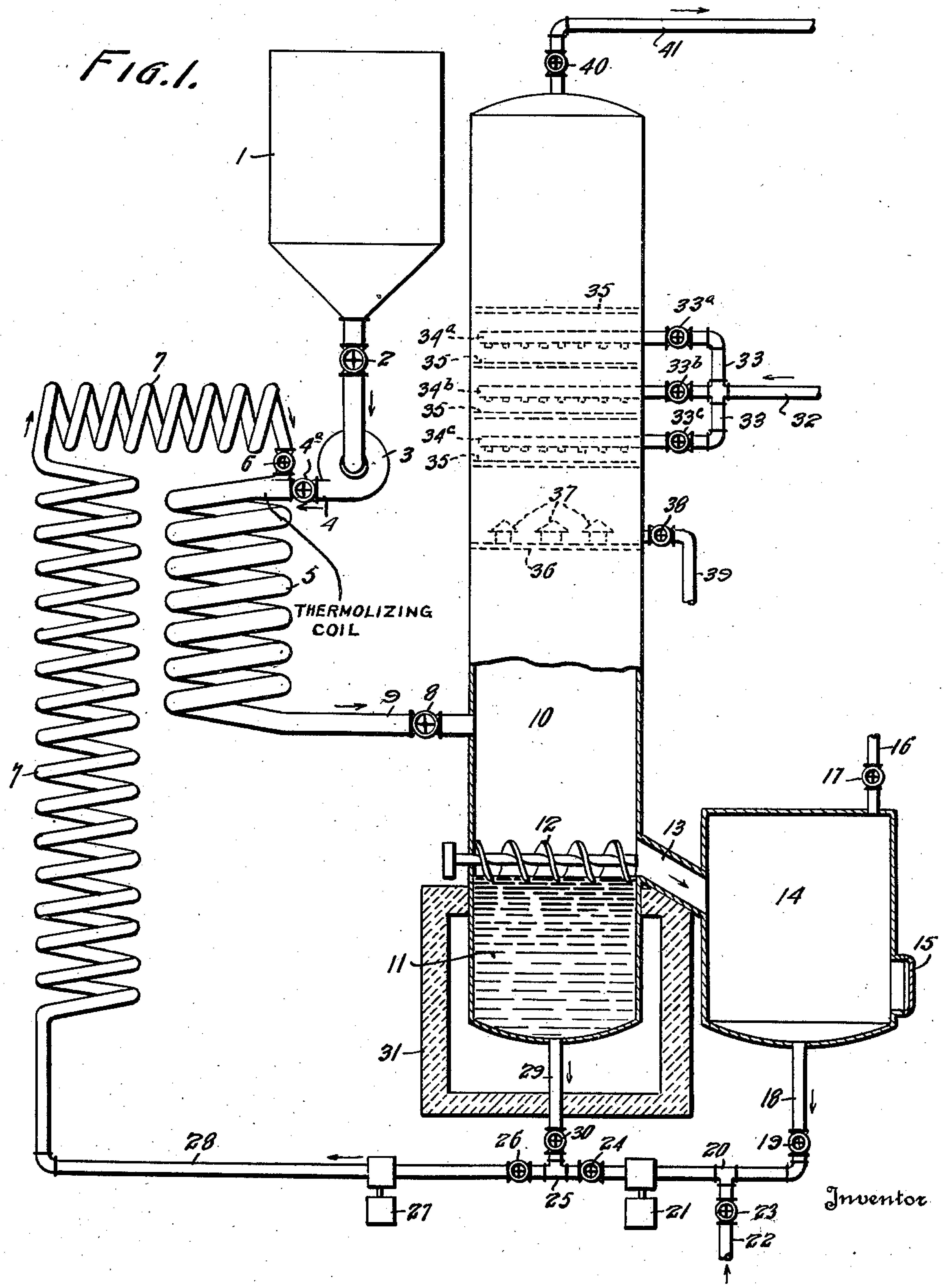

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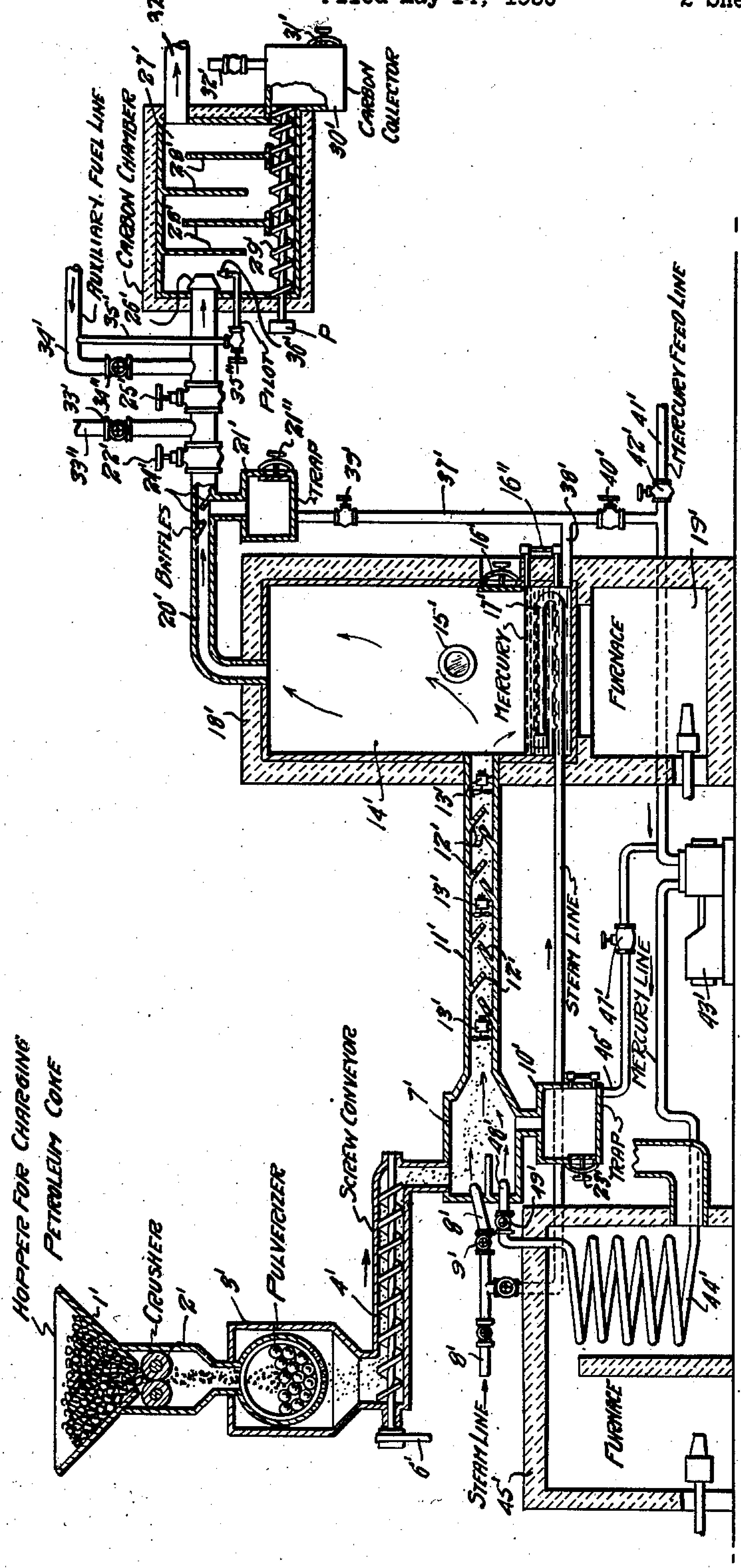
FIG. 2.



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METHOD OF THERMOLIZING CARBONIZABLE MATERIALS

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Application May 14, 1930, Serial No. 452,482

10 Claims. (Cl. 202—18)

This invention relates to a method of thermolizing solid and semi-solid carbonizable materials, such as coal, lignite, peat, petroleum carbon, mixtures of carbon and oil residues, or residues obtained from hydrogenation of oils or coal and oils, also colloidal asphaltenes, carbenes and carboids resulting from cracking of liquid hydrocarbons, or other substances of similar natures in a continuous process.

The objects of the invention are to provide a process and an apparatus wherein the heat required for the changes involved in the process is provided entirely or in part by transfer from mercury, amalgams, or alloys such as Wood's metal consisting of cadmium, tin, lead and bismuth and Rose metal consisting of tin, lead and bismuth, heated to a very high temperature, with which the substance comes into intimate contact in such a manner and under such conditions as to cause the desired changes without danger of superheating, objectionable swelling and caking or other consequent excessive undesirable changes, the conditions of time, temperature and pressure being controlled.

The novelty in the invention here disclosed lies in the use of heated mercury, amalgam, or appropriate alloy in a thermolizing tube in which thorough mixing with a carbonaceous material is assured. The control of the pressure, temperature, duration of the treatment in the thermolizing tube and rate of charge, both the degree and the nature of the decomposition can be controlled, in order to assure the maximum yields of gaseous or liquid hydrocarbons, as desired, without interruption of the process. Accommodations can also be made through control of these same factors for the treatment of charges of different natures.

Depending on the character of the charging material, and the control, the process yields smokeless fuel such as is ordinarily produced by low temperature carbonization or active carbon and gaseous and liquid hydrocarbons. In the process here disclosed the material to be treated is blown, or otherwise forced, into the thermolizing coil or tube to come into intimate contact with mercury, which has already been heated in a separate coil and under pressure in the furnace, in such a manner as to insure intimate mixing and efficient heat transfer. The mixture passes through the thermolizing coil and into the tower where the liquid metal and the residual carbonaceous material are separated from the volatile matter. The various products of the process are collected in manners appropriate to their character.

It is distinctly understood that suitable low melting alloys, such as, for example, Rose metal consisting of tin, lead, and bismuth or Wood's metal consisting of cadmium, tin, lead and bismuth, or amalgams may be used instead of mercury in the practical application of this invention.

In this specification, mercury has been chosen as a typical example of the heat conveying substance, although any of the above mentioned materials may be used instead of the mercury, with the various substances to be thermolized without alteration of the process.

The details and advantages of the process will be best understood with the aid of the diagrams and the typical examples.

Figures 1 and 2 are diagrammatic side elevational views of the apparatuses.

Referring to Figure 1, 1 designates a pulverizer or homogenizer for grinding the carbonaceous material or otherwise preparing it for passage through valve 2 and forcing by blower or atomizer 3 and line 4 into the thermolizing coil 5. 1 is so constructed that pressure may be maintained on it and/or heat applied to it if desired. As such features are well known they are not indicated in the diagram.

Line 4 contains valve 4*a*, and may also be provided with any conventional means for preheating the charge and with inlets for hydrogen and/or steam and/or catalyzing material if desired. Line 4 connects the blower or atomizer 3 with the thermolizing coil. Coil 7 is for heating the mercury to a high temperature under pressure up to 4000 pounds per square inch and is connected with thermolizing coil 5 through pressure reducing valve 6. The inlets to coil 5 are so constructed and located that they cause the hot mercury and charging stock to enter this coil tangentially and to cause intimate mixture and turbulence throughout the coil. Coils 5 and 7 are located in a furnace, not shown in the diagram. Coil 7, for heating the mercury is placed in the hottest part of the furnace and the thermolizing coil 5 nearest where the flue gases leave the funace.

Dampers are arranged in the furnace, so that the heating of thermolizing coil can be controlled. Line 9 in which is a pressure release valve 8 connects the thermolizing coil 7 with tower 10 in which the hot liquid mercury and the treated carbonaceous material are separated from volatile matter.

The hot liquid mercury settles to the bottom of tower 10 where it forms a pool 11 on top of which an endless screw 12 is so operated that the carbonaceous residue collecting on top of the mercury pool is continuously discharged through passage 13 which connects tower 10 with tank 14, one of several like carbon collecting tanks which has a manhole 15 for the removal of carbon, a vapor line 16 with a pressure regulating valve 17 for the removal of volatile matter, and a line 18 and a valve 19 through which any mercury which may collect in the bottom of tank 14 is returned to the system by line 20 and pump 21. Tower 10 and tank 14 may be provided with connections (not shown here, but such as are shown in my co-pending application Serial No. 448,704 filed April 30, 1930) for admitting steam at their bottoms. Tank 14 is provided with conventional shut-offs (not shown) so that it may be used alternately with the other like tanks.

Line 22 serves to introduce the mercury into the system through valve 23, pump 21, valve 24, connection 25, valve 26, pump 27 and line 28. The excess of hot mercury which collects in the bottom of tower 10 is continuously withdrawn through pipe 29, valve 30, line 25, valve 26, whence it is again pumped into the system by pressure pump 27. 31 is a furnace by means of which the pool of mercury 11 may be heated if desired. Vapor line 41 with pressure regulating valve 40, serve for the withdrawal of all volatile material and lead to any conventional condenser system (not shown here) for the separation of the liquid and gaseous hydrocarbons.

The inlet pipe 32 serves for introducing liquid materials for treating the volatile products in tower 10. For this purpose, the inlet pipe 32 is provided with branch pipes 33, 33 having valves 33*a*, 33*b* and 33*c* controlling the passage of such introduced materials into the pipes 34*a*, 34*b* and 34*c* from which they are introduced into the tower 10. Desirably plates 35 are provided between the pipes 34*a*, 34*b* and 34*c*, so that liquids are thus caused to contact with the materials in tower 10. The liquids drop from one plate 35 to the next lower one, until the plate 36 is reached where they accumulate to be withdrawn either wholly or in part through the pipe 39 provided with valve 38, or pass through the bubble plate risers 37 down onto the pool of liquid metal. The volatile materials generated in the lower part of tower 10 pass up through the openings or risers 37 in plate 36 and into contact with the liquid descending from plates 35.

Figure 2 represents a modification of apparatus especially adapted for thermolizing petroleum carbon or residues although it may be used successfully for treatment of other carbonaceous material.

Referring to Figure 2, 1′ is a hopper into which the petroleum coke or residue is fed, 2′ is a crusher and 3′ is a pulverizer for the reduction of the coke to a relatively fine condition preferably small enough to pass through a 300 mesh screen. A screw conveyor 4′ driven by a motor, not shown, attached to pulley 6′, delivers the finely divided particles to an atomizing chamber 7′ into which superheated steam is introduced by means of pipe 8′, controlled by valve 9′, and heated mercury by pipe 48′ controlled by valve 49′ and supplied from heat coil 44′. A trap 10′ is for collecting the relatively heavier particles or impurities, 11′ is an insulated mixing and thermolizing tube in which are located baffles 12′ and turbulators 13′ which serve to intermix the contents of the tube more intimately. Tube 11′ opens into an expansion chamber 14′ equipped with a peephole 15′, the manhole plate 16′, and a perforated steam pipe 17′, the latter being placed near the bottom of the chamber.

The expansion chamber 14′ is heavily insulated as shown at 18′ and is mounted above the furnace 19′ by means of which the temperature in the chamber may be accurately controlled. Mercury falls to the bottom of chamber 14′ and forms a pool, the depth of which is controlled by withdrawal of excess of mercury through lines 38′, 37′, and valve 40′. Chamber 14′ is also fitted with a gauge 16″. The mercury thus withdrawn is returned to the mercury feed line. The returned mercury is supplemented by mercury which enters the system through line 41′ and valve 42′ and passes through pump 43′ after which it is again supplemented by mercury which collected in trap 10′ and is returned through line 46′ and valve 47′ and is then heated in coil 44′ in the furnace 45′. Vapor line 20′ leads from the top of chamber 14′ and contains baffles 24′ and trap 21′. Trap 21′ serves to collect mercury and any solid material which is carried over mechanically. Line 37′ has an opening of a conventional type which permits entry of the mercury, but not of the carbonaceous product. The mercury is returned to the feed line through line 37′, valves 39′ and 40′. 21″ is a manhole for the removal of the carbonaceous product which may be activated carbon, coke, or other carbonized residue.

The uncondensed gases and steam pass through valve 22′ and valve 25′ through nozzle or jet 26′ into carbon chamber 27′, or after passing through valve 22′ may be diverted through line 33′ which contains valve 33″. Line 34′, containing valve 34″, is an auxiliary fuel line and 36′ is a pilot light fed by line 35′ and controlled by valve 35″. Within the chamber 27 are baffles 28′ and screw 29′ driven by pulley P, for conveying the carbon black into carbon collector 30′ provided with a manhole 31′ for removal of carbon, and a line 32′ for escape of gases. Chamber 27′ is also provided with a gas escape line 32″.

All drawings are only diagrammatic and the dimensions of the various parts may be altered, especially those of the heating and thermolizing tubes or coils. Pyrometers, pressure gauges, and various devices for control and safety may be introduced as and wherever desired.

The underlying principles of the invention are further explained by means of examples illustrating two practical embodiments of the process and of apparatus suitable for carrying it into effect.

Referring to Figure 1, in a typical operation, carbonaceous material, as coal, to be thermolized, is charged into the pulverizer in which it is ground to the size necessary, passes through valve 2 and is forced by blower 3 through line 4 and valve 4*a* into the thermolizing coil 5 tangentially in such a manner that it is intimately mixed with the heated mercury which is atomized tangentially into this coil through pressure release valve 6 after having been heated to the desired high temperature under pressure in coil 7.

The intimate mixture passes rapidly through coil 5 with a very turbulent motion. The coal is quickly thermolized by heat from the mercury supplemented, as desired, by heat from the furnace and then passes through pressure release valve 8 in line 9 into tower 10 where the liquid mercury settles and forms pool 11 below the residual carbonaceous material and from which the volatile matter is withdrawn through valve 40 in line 41 as fast as formed into any conventional condensing system, before undergoing the undesired changes resulting from too long heating and/or too high a temperature. The mercury pool may receive heat from furnace 31.

The endless screw 12 is so operated that it churns the coked residue and the surface of the hot mercury thus aiding in the removal of volatile constituents and continuously discharges the coked residue through passage 13 into a carbon collecting tank 14. It is an advantage to have two or more collecting tanks so connected with the tower 10 and return line 18 that each one may be operated independently in order that one can be emptied while another one is being filled. The coke or char is removed from collecting tank 14 through manhole 15, the vapor through line 16 which is fitted with pressure regulating valve 17 and any mercury which may have collected in the bottom of tank 14 is returned to the system by line 20 and pump 21. The excess of hot mercury which collects in the bottom of tower 10 is continuously withdrawn through pipe 29, valve 30, line 25, and valve 26, and again pumped into the system by pressure pump 27 and line 28, if necessary, together with added mercury from line 22, valve 23, pump 21, valve 24, connection 25 and valve 26.

The use of the apparatus represented in Fig. 2 is further explained by the following typical operation.

Petroleum carbon resulting from distillation or cracking of mineral oils is fed into hopper 1′, crushed by crusher 2′, and pulverized small enough to pass through a 300 mesh screen by the pulverizer in chamber 3′. The screw conveyor 4′, driven by pulley 6′, conveys the finely divided particles to the atomizing chamber 7′ in which it is mixed with superheated steam from pipe 8′, controlled by valve 9′, and atomized, heated mercury from pipe 48′, controlled by valve 49′, and supplied from heating coil 44′.

A trap 10′ collects the relatively heavier particles and impurities. Any mercury which collects in this trap is returned through line 46′ and valve 47′ and supplements the mercury to be heated. The mixture of steam, petroleum coke particles, and atomized mercury then passes into the insulated mixing tube 11′ in which are located baffles 12′ and turbulators 13′ which serve to further intermix and prevent separation of the mixture and thus aid in the transfer of heat carried by the mercury and steam to the petroleum carbon.

The use of steam aids materially in removing vapors and gases from carbonaceous material and from tube and chamber, activating influence helps turbulence in tube and keeps carbon over the mercury pool in motion.

From tube 11′, the mixture goes into expansion chamber 14′, in which the hot mercury and the heavier carbonaceous product settle to the bottom, the mercury forming a pool in the bottom. The gases and uncondensed vapors and light, very fine, dust like carbonaceous material leave this chamber by line 20′.

The temperature of the mercury pool in chamber 14′ may be elevated by means of furnace 19′ over which chamber 14′ is mounted and also steam may be injected into the chamber through the perforated steam pipe 17′ which is submerged in the mercury. The carbonaceous product which may be activated carbon, coke, or other carbonized residue is removed through manhole 16′ and excess of mercury withdrawn through lines 37′, 38′ and valve 40′. The hot mercury withdrawn is returned to the mercury feed line, where, supplemented by mercury which enters the system through line 41′ and valve 42′, it passes through pump 43′ and to it is added also any mercury from trap 10′, after which it passes into the mercury heating coil 44′ in furnace 45′.

The vapors from the top of chamber 14′ pass through line 20′, which contains baffles 24′ and trap 21′. The mercury, and any solid material which is carried over mechanically, collect in this trap, the mercury being returned to the mercury feed line through valve 39′, line 37′ and valve 40′, and the carbonaceous product removed through manhole 21″. The uncondensed gases pass through valve 22′ and valve 25′ through nozzle or jet 26′ into carbon chamber 27′, or may be diverted through line 33′ which contains valve 33″, after passing through valve 22′. The gases are burned to lamp black in chamber 27′. Auxiliary fuel may be introduced through line 34′ containing valve 34″. Pilot light 36′ is fed by line 35′, or from any other conventional source, and is controlled by valve 35″. The carbon thus formed, in 27′, is collected by baffles 28′ and conveyed into carbon collector 30′ by screw 29′ driven by pulley P. The carbon black which collects in carbon collector 30′ is removed through manhole 31′, and the gases escape from the collector through line 32′. Gases may also escape from chamber 27′ by the line 32″ there provided.

Alterations in temperature, pressure and other controllable factors determine the character of the products and accommodate the process to charges of highly different character.

Temperatures in the thermolizing tube 5 range preferably between 250° and 1000° C.

Hydrogen or steam, and/or any desired catalyst, such as pumice, fireclay, metal-oxides, silicon compounds, iron, cobalt, molybdenum, vanadium, active carbon, mercury, and other suitable catalysts separately or together, may be introduced into the thermolizing coil at its inlet through any added suitable connections not shown in the diagram but such as shown in my co-pending application Serial No. 448,704.

Steam may also be introduced into either or both tower 10 and tank 14 by connections already mentioned but not shown in Fig. 1. Also, introduction of steam into tube 11 and chamber 14 of Fig. 2 may be omitted if desired.

If petroleum carbon is used as charging material, a high grade of active carbon will result.

The charge may advantageously be heated to as high a temperature as technically practical before entering the thermolizing coil.

The chief features of the process are the following: The charge is brought into intimate contact with atomized, highly heated, mercury in such a manner that every particle is thermolized by a very brief contact with the hot metal; the thermolizing tube is kept at such a temperature that heat loss therefrom is avoided and that sufficient heat is transferred through the walls of the tube to supplement that from the mercury but insufficient to cause superheating of the contents of the tube on its inner surface; the mercury prevents the clogging of the tubes and the caking of the residue in the system.

The return of the hot mercury to the system from the bottom of tower 10 is an economy in heat.

The relatively short period of carbonization and the withdrawal of the volatile products as fast as formed as well as the good control of the temperature throughout the process avoids the undesirable changes which take place when this volatile matter is heated too long and/or to too high a temperature.

Dilution of the uncondensable gases by air, thus lowering their calorific value is avoided, as is also the loss of these gases into the air.

Due to the fact that the mercury is non-inflammable and non-combustible, there is a great reduction of fire and explosion hazard.

The use of steam aids materially in the carrying of the mixture, in maintaining turbulence in the thermolizing tube and in separation of volatile matter in the tower or chamber.

The pump in the mercury feed line and the pressure release valve in the entrance to the thermolizing coil make it possible to maintain as high a pressure on the mercury in the heating coil as desired, within reasonable limits.

This feature of regulating the temperature at which the thermolizing coil is kept somewhat independently of the temperature of the mixture of charging material and mercury entering therein, is important.

The pressure in coil **5** is also controllable by means of the outlet valve **40** connected to tower **10**.

Due to the high velocity with which the intimate mixture is passed through the thermolizing tube it is possible to use mercury heated to a very high temperature before it enters the thermolizing tube, thus insuring very effective, although brief, contact of the highly heated mercury particles with the material to be treated before they are expanded in the vaporizing chamber.

There is flexibility in the operation, due to the fact that the heat stored in the mercury is made available in both the thermolizing coil and the tower and also due to the fact that the temperatures of both can be increased as desired by control of the two furnaces respectively.

The use of mercury in this process and apparatus has many advantages, among which are: It is technically possible to heat it to a very high temperature; it gives up its heat very rapidly, especially if atomized or vaporized, because of the intimate contact it can make with the material being treated, without, however, being soluble therein; the amount of mercury and the temperature to which it must be raised are readily determined and controlled; also, because of its liquid state and its high specific gravity, it can be readily fed and transported with the aid of appropriate reservoirs and pumps; it aids in vaporizing any volatile matter held in the residue; its use is economical because it can so conveniently be raised to the temperatures desired in the treatment of carbonaceous material, its recovery is practically complete, and it can be returned to the system at a relatively high temperature; it aids in causing turbulence and prevents clogging and sticking.

It is readily apparent that the process, described above, with various disclosed modifications may be applied to carbonaceous materials of widely varying nature through control of temperature, pressure, and other controllable factors and that the products of the process can also be appreciably varied as desired by control of these same factors.

I claim:

1. A method of thermolizing solid carbonizable material which comprises passing a stream of intimately admixed solid carbonizable material and hot liquid metal through a thermolizing zone, withdrawing said stream of intimately admixed material and hot liquid metal from the thermolizing zone and introducing said admixed stream of material and hot liquid metal into an enlarged zone, and recovering coke and volatile by-products.

2. A method of thermolizing solid carbonizable material which comprises continuously passing a stream of intimately admixed solid carbonizable material and hot liquid metal through a thermolizing zone, continuously withdrawing said stream of intimately admixed material and hot liquid metal from the thermolizing zone, and continuously introducing said admixed stream of material and hot liquid metal into an enlarged zone, and recovering coke and volatile by-products.

3. A method of thermolizing solid carbonizable material which comprises passing a stream of intimately admixed solid carbonizable material and hot liquid metal through a thermolizing zone, withdrawing said stream of intimately admixed material and hot liquid metal from the thermolizing zone and introducing said admixed stream of material and hot liquid metal into an enlarged zone, at least one of the treatments being carried out under superatmospheric pressure, and recovering coke and volatile by-products.

4. A method of thermolizing solid carbonizable material which comprises passing a stream of intimately admixed solid carbonizable material and hot liquid metal through a thermolizing zone under superatmospheric pressure, withdrawing said stream of intimately admixed material and hot liquid metal from the thermolizing zone and introducing said admixed stream of material and hot liquid metal into an enlarged zone, the pressure in the enlarged zone being less than that in the thermolizing zone, and recovering coke and volatile by-products.

5. A process of thermolizing solid carbonizable material as described in a continuously advancing closed stream of hot liquid metal, including intimately mixing the solid carbonizable material and hot liquid metal and conveying the mixture in a confined stream to an enlarged zone, and removing residual solid, liquid, volatile and gaseous material, wherein the mixture of hot liquid metal and the material to be treated is further heated while advancing through a thermolizing coil.

6. A process for carbonizing pulverized semi-solid or solid carbonizable material or fuel yielding material in a continuously advancing stream of hot mercury, consisting in intimately mixing the fuel and hot mercury and conveying the mixture in a turbulent confined stream into an expansion chamber containing a heated mercury bath, distilling and carbonizing the fuel in the expansion chamber, separately withdrawing the vapors and gases from the chamber, collecting the carbonized residue over the mercury bath, and withdrawing the carbonized residue from the chamber.

7. A process for thermolizing solid carbonaceous material, as described, in a continuously advancing stream of hot mercury, in the presence of hydrogen introduced into the system, consisting in intimately mixing the solid carbonizable material and hydrogen with the hot mercury and conveying the mixture in a turbulent confined stream into an expansion chamber, wherein the volatile products are distilled off and the liquid and solid products collected in the base of the chamber over a pool of hot mercury.

8. A process for thermolizing solid or semi-solid carbonizable or fuel-yielding material in a con-

tinuously advancing stream of hot mercury, consisting in intimately mixing the carbonizable material and hot mercury with hydrogen and steam and conveying the mixture in a turbulent confined stream into an expansion chamber containing a heated mercury bath, distilling and carbonizing the material in the expansion chamber, separately withdrawing the vapors and gases from the chamber, collecting the carbonized residue over the mercury bath, and withdrawing the carbonized residue from the chamber.

9. A process for thermolizing solid or semisolid carbonizable or fuel-yielding material in a continuously advancing stream of hot mercury, consisting in intimately mixing the carbonizable material and hot mercury and introducing hydrogen, steam and a catalyst into the mixture of hot mercury and carbonizable material and conveying the mixture in a turbulent confined stream into an expansion chamber containing a heated mercury bath, distilling and carbonizing the material in the expansion chamber, separately withdrawing the vapors and gases from the chamber, collecting the carbonized residue over the mercury bath, and withdrawing the carbonized residue from the chamber.

10. A process for thermolizing solid or semisolid carbonizable material in a continuously advancing stream of hot mercury, consisting in intimately mixing the material to be treated and the hot mercury and conveying the mixture in a turbulent confined stream into an expansion chamber containing a heated pool of mercury, distilling and carbonizing the material in the expansion chamber and introducing steam into the pool of mercury, separately withdrawing the vapors and gases from the chamber, collecting the carbonized residue over the mercury bath, and withdrawing the carbonized residue from the chamber.

ALFRED OBERLE.