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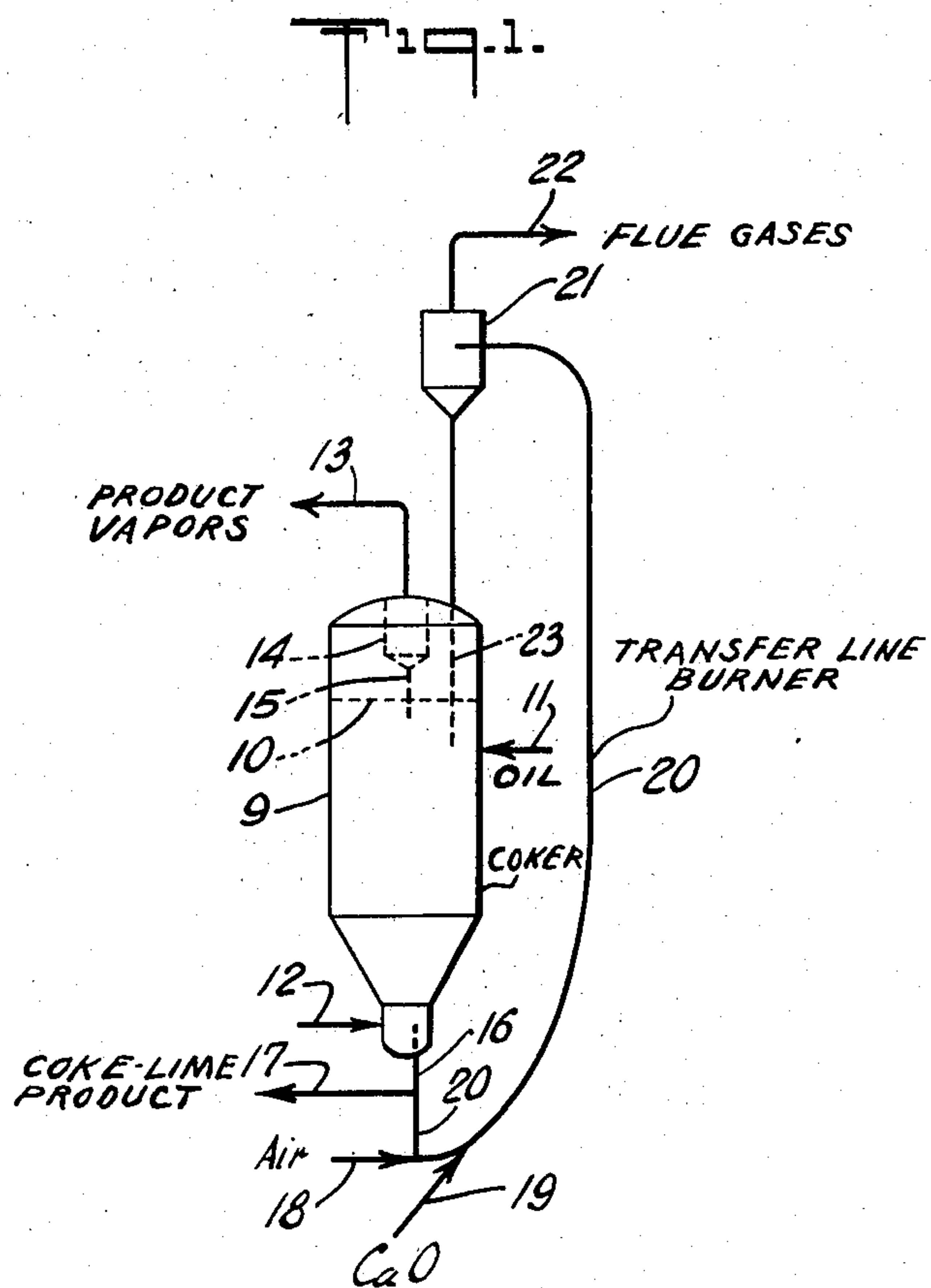
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2,953,518

COKING OIL WITH A FLUIDIZED BED OF CALCIUM OXIDE

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2 Sheets-Sheet 1



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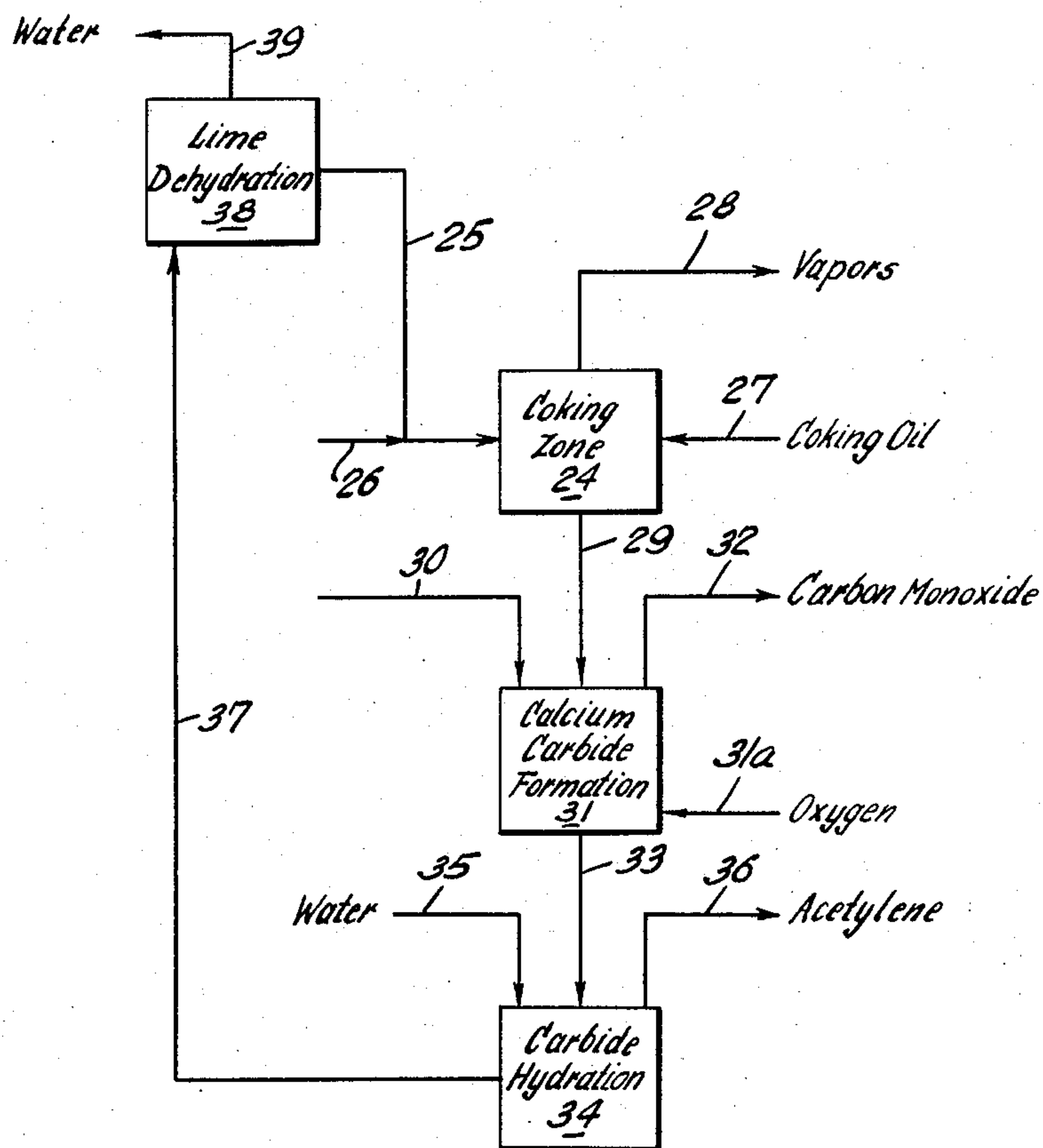
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Fig. 2.



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COKING OIL WITH A FLUIDIZED BED OF CALCIUM OXIDE

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The instant invention relates to improvements in coking heavy hydrocarbon oils. One aspect of the invention concerns coking the oil charge stock by contacting it at coking temperature with hot reactive solid calcareous particles maintained in the form of a dense, turbulent, fluidized bed. More specifically, this aspect relates to a process wherein excessive aggregation or sticking of such bed particles one to another is substantially completely avoided by controlling composition of the particulate matter constituting the fluidized coking bed. Another aspect of the invention relates to production of acetylene and hydrocarbon distillate utilizing a coking step in the presence of reactive solid calcareous particles.

Heretofore, it has been proposed to seed a fluid coking operation with finely-ground coke particles, alumina, or the like, the seed supply being being roughly 3–10% of the net coke make. As coking occurs, product vapors are removed from the reaction zone and sent to fractionation for recovery of gas and hydrocarbon distillates. Undistilled material, that is carbonaceous residue from the feed and solids inventory, remains in the system.

The fluidized reactor bed is maintained at a substantially constant volume by withdrawal of excess particles. Temperature is maintained substantially constant by continuously circulating at least a portion of the withdrawn particles through a heating zone and back to the reaction zone. In the heating zone sufficient carbonaceous matter is burned with an oxygen-containing gas such as air to raise the sensible heat content of the circulating solids enough to maintain the system in heat balance.

The nature of the operation is such that the fluid bed particles grow in size during the operation. It is advantageous to provide a finely-divided matrix of particles for deposition of new coke and thereby distribute growth of the individual particles through out the bed. However, it has been found that the coke particles in the coking zone tend to agglomerate or adhere to each other particularly at critical locations such as slide valves, charge entry point, and lower sections of the coking vessel, and so interrupt the smooth running of the operation.

We have found now that operation of the coking process with a fluidized bed containing a very high proportion of calcium oxide, i.e., 45–75% by weight of the entire bed, not only provides a desirable matrix for deposition of newly-formed carbonaceous residue, but also provides particles which resist sticking to each other in the bed in the manner of fluidized coke beds merely "seeded" with a minute fraction of ground coke, etc. The high lime product from our process is suitable for slag-forming combustion operations and the like, and it has special utility in the production of calcium carbide.

One aspect of our process is the maintenance of a very high proportion of calcium oxide to carbonaceous residue in the fluidized bed of the reaction (coking) zone. The efficient mixing in the bed tends to distribute the coke being formed quite evenly throughout the particles constituting the entire bed, but the particular composition of individual particles can vary. The bed composition range

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we use is the average composition of the fluidized mass. All percentages specified herein are weight percentages. Use of substantially below about 45% calcium oxide in the bed produces particles partaking of the undesirable agglomerating characteristics conventionally encountered. On the other hand, thermal inefficiency is encountered with a bed having more than about 75% calcium oxide content, and the coke-lime product formed has substantially inferior resistance to weathering (i.e., spalling and disintegration on exposure to atmosphere) as compared to the product produced from coking operations with the desired kind of bed. Advantageously the proper fluidized coker bed for use in our process is built up from an original fluidized bed of calcium oxide on which the desired proportion of coke is made deposit.

Heavy hydrocarbon oil feeds suitable for our fluidized coking process are the conventional ones, i.e., heavy and reduced crudes, vacuum bottoms, pitch, asphalt and other heavy hydrocarbon residua, or mixtures thereof. The oil feed will generally be of conventional mineral oil stock, but can be also a residuum from shale oil processing. As a general rule, feeds will have an initial boiling point of about 700° F., and API gravity between 0° and 20°, and a Conradson carbon residue content between about 5 and 40 weight percent.

While broadly conventional coking conditions can be maintained in our fluidized reaction zone, e.g., 850–1500° F., 1–10 atmospheres' total pressure, superficial fluidizing gas velocity of 0.2–4 feet per second, average size of bed particles between 75 and 1000 microns, and coke circulation (circulating solids to oil feed ratio) between about 5 and about 15 (by weight), our very large proportion of lime having lower specific heat and higher density than carbon particles affects our preferred operations. Thus, the fluidizing gas velocity in the coker need not be maintained in a range as narrow as 0.5–2 feet per second for our preferred operation, but it can be as high as about 4 feet per second. Preferred total pressure is between 1 and 2 atmospheres absolute. To preclude formation of any substantial amount of calcium hydroxide the coking zone can be maintained advantageously at about 1100–1300° F. and preferably at about 1100° F. for efficiency and economy.

Operation of the heating zone for the fluid coker is, of course, affected by use of such preferred high coking temperatures. Temperature of the heating zone should be 50° to 300° F. higher than the coking zone. It can be operated as a conventional moving bed or as a distinct fluidized bed by itself. Advantageously it is simply a portion of pipe wherein the particles in process are being transferred from one location to another while being oxidized. The superficial gas velocity in a fluidized heating zone is generally above that of the fluid coking zone, e.g., 1–5 feet per second, and when the aforementioned transfer-type burning operation is used the velocity can even be higher to achieve efficient entrainment.

It is advantageous in our fluid coking process to make up calcium oxide to the system by adding the fresh calcium oxide feed of fluidizing size to the heating zone. By so doing, such calcium oxide is preheated to a desirably high temperature for subsequent admixture with the fluidized bed in the reaction (coking) zone. Correlative with such operation, the coke-lime product is withdrawn from the reaction zone rather than the heating zone. Thus distribution of the makeup lime is quite complete throughout the reaction zone. This withdrawal also aids in preventing agglomeration and particle buildup due to decreased particle residence time in the system.

Alternatively, however, the makeup calcium oxide can be fed to the reaction zone, optionally with preheating, and the coke-lime product can be withdrawn from the heating zone instead of the coking zone. It is also pos-

sible to slurry at least part of the makeup calcium oxide with the oil feed to the coker, or to combine such makeup technique with one of the foregoing ones. The coke-lime product can be calcined in conventional manner if desired, or it can be molded into desirable-sized pieces of fuel or the like. Advantageously, it can be charged while hot as feed to a calcium carbide-forming operation.

Figure 1 is a flow sheet showing the preferred operation of our fluid coking process. Coking vessel 9 is constructed of materials suitable for operation at about 1100° F. A fluidized bed of solid particles composed in bulk of about 60% calcium oxide and the balance carbonaceous residue (from previous operation) is maintained in the coking vessel with upper level of the bed being indicated by numeral 10. The bed is fluidized by introduction of hot flue gas entering at inlet 12. The fluidizing gas plus vapors from the coking reaction pass upwardly through the vessel at a superficial velocity at 2 feet per second.

Coking oil charge stock, a vacuum residuum having an 8.2° API gravity, 20% carbon residue, and a Saybolt seconds universal viscosity of 972 at 210° F., preheated to temperature of 700° F., is introduced into the bed of particles at inlet 11. Vapors and fluidizing gas from the process are withdrawn through line 13 after having been separated from entrained solids in cyclone separator 14. The separated solids are returned to the bed through dip-leg 15. The bed particles do not agglomerate appreciably and remain in dense, turbulent fluidized condition throughout the operation.

A stream of solid particles is removed from the bed through outlet 16, and a fraction of the particles so removed is discharged from the system through line 17 as product. The balance goes through line 20 and is transported upwards in said line in admixture with air, entering line 18, and makeup calcium oxide of 50 to 150 mesh (U.S. Standard) size range, entering line 19. The quantity of makeup calcium oxide is equivalent to that being discharged from the system through line 17. Line 20 constitutes the heating zone wherein a fraction of the combustible material in transit is burned to raise the temperature to a point (in this case 1300° F.) sufficient to supply the necessary heat to the endothermic processing occurring in coking vessel 9 (which is, in this case, at 1100° F.). The solids from the burning zone and transporting gases are separated in cyclone separator 21, flue gases being withdrawn from the system by means of line 22, and the hot solids returned to the fluidized bed by means of dip-pipe 23.

Figure 2 is a flow diagram showing an integrated process employing coking in the presence of calcium oxide. Acetylene and hydrocarbon distillate are the ultimate products, and at least a portion of the lime in process is recovered for reuse. Thus, into coking zone 24 there is charged calcium oxide from a later stage of the process by means of line 25, supplementary calcium oxide and/or calcium carbonate as is needed through line 26 and coking oil charge stock through line 27. Preferably coking zone 24 is of the sort described hereinbefore with reference to Figure 1, that is, a reaction zone having a fluidized bed of solid particles consisting essentially of calcium oxide and carbonaceous residue from the heavy hydrocarbon oil coking charge stock. The endothermic heat reaction and heat for vaporization of hydrocarbon product vapors is supplied in such operation by a burning zone, not shown, as hereinbefore described in connection with respect to such fluidized reaction zone, i.e., a conventional moving bed, a distinct fluidized bed, or a simple transfer type burning operation.

Coking conditions in the fluidized bed reaction (coking) zone will be broadly 850–1500° F., 1–10 atmospheres total pressure, fluidizing gas superficial velocity of 0.2–4 feet per second, average size of bed particles between 75 and 1000 microns, and coke circulation (circulating solids to oil feed ratio) between about 5 and about 15 by weight. Preferred total pressure will be, however,

between 1 and 2 atmospheres absolute, fluidizing gas superficial velocity preferably between 0.5 and 4 feet per second, and temperature about 1100° F. and broadly advantageous between about 1100 and 1300° F.

Alternatively, the coking step in our integrated process can be one wherein coking accumulates in a static bed, e.g., a conventional delayed coking or a conventional pressure coke stilling (also called coking plus thermal cracking) operation, modified by the input of calcium oxide to such static coking operation. Thus, the lime and coking oil can be charged into a coke drum maintained at temperature between about 850° and 1000° F. whereby coke-lime residue accumulates while hydrocarbon distillate is taken overhead from the coke drum, fractionally distilled to produce a light hydrocarbon distillate (and normally gaseous hydrocarbons) as one product and a bottoms product of gas oil as another. A fraction of the gas oil bottoms is heated and recirculated to the coke drum to provide at least part of the heat for such delayed coking process. The proportions of lime and coking oil feed are, in any static coking step used in our process, regulated to form a coke-lime residue having proportions suitable for production of calcium carbide, e.g., 45–75% calcium oxide, there being fed from about 0.8 to about 3 pounds of CaO (and/or equivalent CaO in terms of calcium carbonate, calcium hydroxide or the like) per pound of carbon residue available from the oil feed stock under the coking conditions being employed. A basic description of conventional delayed coking and pressure coke stilling can be found on pages 279–281 of the text "Progress in Petroleum Technology," published August 7, 1951, by the American Chemical Society, Washington, D.C.

In a pressure coke stilling operation as applied to our process a light clean gas oil is heated to a temperature as high as 1100° F. under pressure as high as 500 p.s.i.g. This hot gas oil is mixed with coking charge stock and the calcium oxide feed, then sent to a reaction (coking) chamber maintained, for example, at 800–875° F. and 25–250 p.s.i.g. whereby coking takes place to provide coke-lime residue and thermal cracking also occurs. The overhead distillate from the coking chamber is fractionally distilled into a hydrocarbon distillate (and normally gaseous hydrocarbons), a light, clean oil for heating and recycling to the coke chamber to supply heat thereto, and a bottoms product of heavy oil which can be recycled for further coking in the coke chamber.

The hydrocarbon distillate from coking zone 24 is shown symbolically as being withdrawn through line 28. Also it is to be understood that these vapors can be fractionally distilled as hereinbefore described with respect to the static coking operations, or condensed and stored, or otherwise handled. The coke-lime residue from the coking zone is withdrawn through conduit 29 and charged into a calcium carbide formation operation, indicated in the drawing by item 31. Should the particle size need to be adjusted for the particular calcium carbide formation process employed, the coke-lime product can be graded to selected size, comminuted if too large or aggregated by briquetting or the like if too fine, to obtain desired size range. Thus, for example, the large lumps from a static coking operation will need to be broken down for a conventional electric furnace carbide operation, whereas the coke-lime product from our fluidized coking operation ordinarily will need to be agglomerated into desired lump size of about 1–3" mesh, particularly if intermediate processing such as calcining at 1600–2400° F. and subsequent forming are not practiced.

The calcium carbide formation can be a conventional production operation using a conventional electric furnace of open or closed type, a conventional induction furnace, or a shaft furnace. (Operation of the shaft furnace can be in accordance with the method shown in U.S.P. 2,738,256 wherein an oxygen blast is injected annularly into the furnace near the base through a plurality of nozzles at a

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velocity of 40–100 meters per second and at an angle of between 10° and 30° to the horizontal.)

Molten calcium carbide fluxed with some excess lime is withdrawn from the calcium carbide formation operation, and, after cooling and granulating, the carbide can be used as feed to carbide hydration zone 34. Should a shaft furnace operation be employed it will be necessary to supply tonnage oxygen, i.e., oxygen of at least about 90% purity and usually above 95% purity, this supply shown symbolically by line 31a. In any event, carbon monoxide is given off as a by-product from the formation of the calcium carbide. The carbon monoxide so produced can be used in a number of ways, e.g., for fluidizing a fluidized bed in the preceding coking operation, for dehydrating lime conventionally or by the process shown, for example, in our copending U.S. patent application Serial No. 648,905, filed March 27, 1957, used directly with steam in a catalytic water-gas shift operation to manufacture hydrogen, used in reduction of certain ores, or used for the manufacture of phosgene or the like. It may be necessary in the calcium carbide formation operation to make major or minor adjustments in the ratio of coke to equivalent calcium oxide being charged from zone 24. Accordingly, supplementary coke, carbon, anthracite, quicklime, calcium carbonate, dolomite, or the like can be charged through inlet 30. Calcium carbonate and dolomite are useful in this respect when a shaft furnace operation is employed for calcium carbide formation, but are generally avoided when an electric furnace is being used. Temperature above about 3400° F. generally in the range of 3600–4500° F. are used with substantially atmospheric pressure for the formation of the carbide.

Calcium carbide is passed through conduit 33 into carbide hydration zone 34. The hydration can be by a conventional "wet" process, or a "semi-dry" or "dry" process as, for example, is shown in U.S.P. 2,343,185 or 2,415,328. The necessary water for the carbide hydration operation is shown entering through line 35, and the acetylene product is withdrawn through line 36. Calcium hydroxide formed from the carbide hydration is passed through line 37 into lime hydration zone 38. A portion of the lime so withdrawn can be purged from the system by means not shown to maintain a low level of impurities such as silica or the like which would otherwise accumulate to an undesirable extent. Also, a portion of the calcium hydroxide from the carbide hydration can be charged, if desired, into the coking zone through line 26 and/or into the calcium carbide forming operation through line 30. The balance of the by-product calcium hydroxide is dehydrated in conventional manner, that is, at temperature of about 1100° F. or higher, the water being expelled from the system through outlet 39.

The resulting recovered calcium hydroxide from the dehydration operation is recycled to coking zone 24 through line 25. In the instance where coking zone 24 is being operated as a fluidized system with a burning zone emitting flue gases, the hot flue gases so produced can be used in heat exchange with the lime being dehydrated for thermal economy in the overall process.

We claim:

1. In a process for coking a heavy hydrocarbon oil feed wherein the feed is contacted in a reaction zone at a

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coking temperature within the range of from about 1100° to about 1300° F. with a fluidized bed of solid carbonaceous particles, product vapors are removed from the reaction zone, carbonaceous particles from the bed are circulated through a heating zone, therein subjected to combustion conditions with an oxygen-containing gas, and returned to the reaction zone for supplying heat thereto, the improvement which comprises: preventing agglomeration of the bed particles by establishing and maintaining in said reaction zone a fluidized bed consisting essentially of calcium oxide and carbonaceous residue from said feed, the proportion of calcium oxide in said fluidized bed being 45–75%, and withdrawing a coke-lime product from the process the coke portion thereof being substantially uniformly distributed throughout said product.

2. The process of claim 1 wherein the temperature of said reaction zone is maintained at about 1100° F.

3. The process of claim 1 wherein makeup calcium oxide is fed to the heating zone and the coke-lime product is withdrawn from said reaction zone.

4. The process of claim 1 wherein makeup calcium oxide is fed to the reaction zone and the coke-lime product is withdrawn from the heating zone.

5. A process for manufacturing acetylene and hydrocarbon distillate from heavy hydrocarbon oil feed which comprises coking said heavy hydrocarbon oil feed in a fluidized bed reaction zone under coking conditions including a temperature within the range of from about 1100° to about 1300° F., said fluidized bed consisting essentially of calcium oxide and carbonaceous residue from said feed, the proportion of calcium oxide in said fluidized bed being within the range of from 45 to 75% whereby the agglomeration of said bed particles is prevented, withdrawing from said reaction zone the resulting hydrocarbon distillate and coke-lime residue, the coke portion of said residue being substantially uniformly distributed throughout the residue subjecting said coke-lime residue to calcium carbide forming conditions in an elevated temperature zone whereby said residue is converted into calcium carbide, generating acetylene and forming by-product hydrated lime by treating said calcium carbide with water, converting at least a portion of said hydrated lime into recovered calcium oxide by dehydration, and returning recovered calcium oxide to said reaction zone.

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