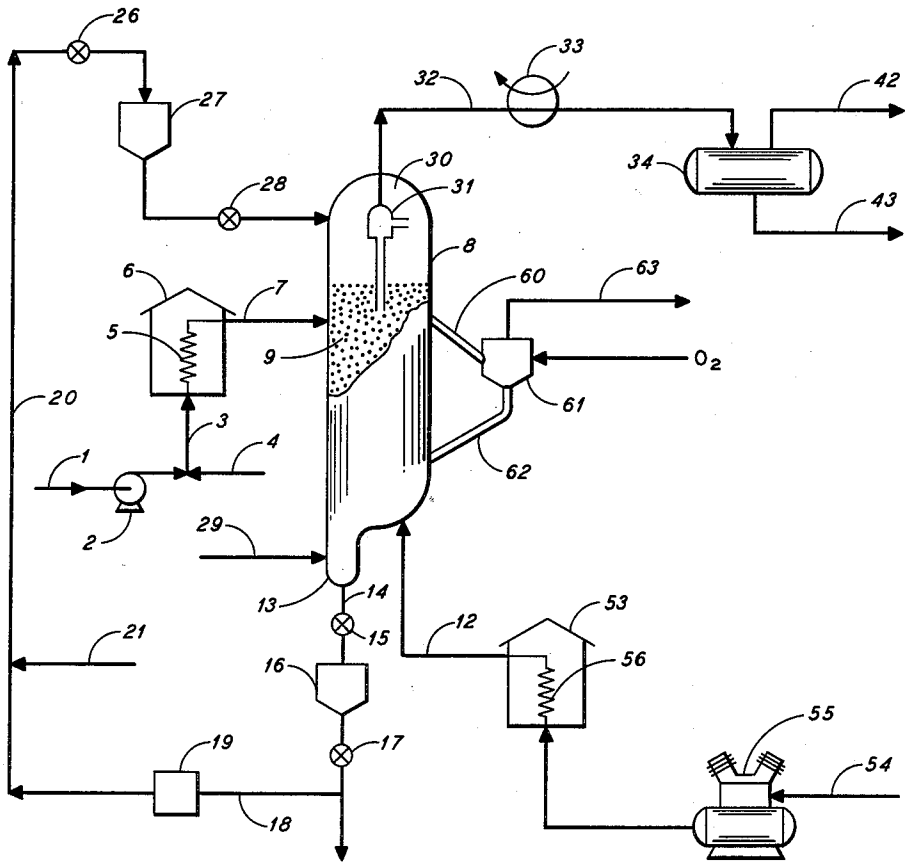
May 23, 1961 J. W. SCOTT, JR 2,985,585

COKING PROCESS

Filed Aug. 7, 1958



INVENTOR
JOHN W. SCOTT, JR.
BY Frank E. Johnston
R. H. Davies
ATTORNEYS

United States Patent Office 2,985,585 Patented May 23, 1961

2,985,585

COKING PROCESS

John W. Scott, Jr., Ross, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

Filed Aug. 7, 1958, Ser. No. 753,813

1 Claim. Cl. 208—127)

This invention relates to an improved coking or carbonization process. More particularly, the invention has to do with a process of coking heavy hydrocarbon oils, such as petroleum residual oils, and those derived from other heavy hydrocarbon-bearing materials, e.g., oil shale, coal, and lignite, to produce lighter, more useful products, including motor fuels.

To an increasing degree, the petroleum industry is finding it necessary to utilize heavy residual oils more effectively, particularly those derived from low A.P.I. gravity crudes containing a considerable amount of very high molecular weight fractions characterized by a low hydrogen content. Although residual oils can be blended to proper viscosity and utilized as fuel, this procedure is often undesirable beyond certain limits, because for the most part the supply exceeds the demand, and in many situations low viscosity distillate oil or cutter stock is in short supply.

In the past the thermal cracking and delayed coking processes were developed to convert heavy residual oils into more salable stocks such as gas oils, gasoline, and light olefinic hydrocarbons useful as charging stocks for synthetics; the relative use of the two processes depended on the relative availability of light and heavy crudes and the demand for heavy fuel oil. Viscosity breaking, a form of thermal cracking, was devised to convert to fuel oil materials initially too heavy for full thermal cracking to gasoline. Destructive hydrogenation, the alternative to coking as a means of lowering the carbon-hydrogen ratio (C/H) of heavy materials, has not yet proved economically feasible.

Further described, thermal cracking is a means of converting residual oils into high value-low C/H products and low value-high C/H products with essentially no change in average product CH from that of the charge. The effect of coking, on the other hand, is to produce a marked lowering of average C/H in the total gaseous and liquid products, usually with production of much less gasoline and lighter than in thermal cracking.

More recently, the catalytic cracking process has developed as a means of producing high quality gasoline in high yield from light and heavy gas oils. Catalytic cracking, which may also be regarded in part as a mild coking process, has the peculiarity that only distillate or decarbonized stocks can be charged economically, in part, due to the poisoning effect on the catalyst of minute amounts of metallic compounds in the heavy ends of crudes. Processes employed or proposed for catalytic charging stock preparation from residual stocks include propane deasphalting, vacuum flashing, i.e., residuum stripping, and coking.

Currently, substantially all commercial coking is by the so-called delayed process. In this process the reduced crude oil feed is heated in pipe coils to about 900° F. to 950° F. The oil is then fed to one of two or more vertical, insulated, coke drums. The drums are connected by valves so that they may be put on stream for filling

and then off stream for coke removal. The temperature in the drum will ordinarily be 875° F. to 950° F. and the pressure 40 to 60 p.s.i.g. Hot vapors from the coke drum pass to a fractionator where gas and gasoline, light gas oil, and heavy gas oil are separated. More or less of the heavy gas oil is recycled to the furnace inlet, the ratio to fresh feed being of the order of one, in order to secure adequate heat input to the coke drums. However, the relatively high coke production, semi-batch operation, and generally high operational costs, such as for decoking the drums, seriously detract from the usefulness of the process. As a result, coking processes have recently been suggested along the lines of fluid and moving bed catalytic crackers. However, both fluid and moving bed coking installations still leave much to be desired, particularly in the size of equipment necessary and in the amount of circulating coke that is required.

For example, in a typical fluidized coke unit, in order to achieve a reasonable carbon-burning rate in pounds per hour per unit of volume of reaction space, it is necessary to use a reasonably large bed height, for example 20 feet, because with smaller beds there is not sufficiently goor fluidization to insure the proper rate of carbon burning. Further, the gas velocities required for proper fluidization, in conjunction with the stoichiometry of the system, require a reasonably large bed cross-section. When the above factors are properly taken into consideration, not only does the necessary reactor size present a problem, but the resulting coke circulation rate that is necessary presents a problem, both from the standpoint of equipment, size and cost and from the standpoint of operating cost.

The above disadvantages and others are overcome by the process of the present invention, a preferred mode of operation of which results in obtaining heat for coking in both fluidized and moving bed coking processes by passing at least a portion of the coke particles in the coke bed from said bed into a separate high heat release combustion zone of the centrifugal or cyclone type, burning at least a portion of the coke in said combustion zone at temperatures substantially higher than those prevailing in said bed, and returning heated coke particles from said combustion zone to said bed.

The novel features that are characteristic of the present invention are set forth with particularity in the appended claim. The invention will better be understood, however, and further objects and advantages thereof will be apparent, from the following detailed description of a specific embodiment thereof, when read in connection with the accompanying drawing, the single figure of which illustrates the application of the invention to a fluidized coking process.

Referring now to the drawing in detail, the feed, which may, for example, be reduced crude or flasher pitch or the like, enters through line 1. The feed is pumped to a pressure which is equal to that in the reactor 8 plus the pressure drop in the furnace and its connecting lines under flow conditions by pump 2, and flows through line 3. An oil recycle stream may be passed into line 3 through line 4. This recycle stream may comprise condensed heavier components of the vaporous products of the process, which products may thus be recycled to extinction and thereby prevented from becoming net reaction products of the process. The feed then flows through coil 5 in furnace 6 where it is preheated to a temperature at which no appreciable coking takes place in the furnace, generally, in the range of about 500° F. to about 850° F. The preheated feed leaves the furnace through line 7 which discharges into reactor 8. In reactor 8 the feed is contacted with a highly turbulent, hot fluidized coke mass of about 20 to 200 mesh particle size. The coking or

carbonization temperature in reactor 8 may be about 850° F. to 1200° F., generally at a superatmospheric pressure, for example as high as 400 p.s.i.g. Coke formed in the reaction is deposited on the fluidized coke. The fluidized coke mass 9 may be interspersed with transverse grids, if desired, to slow vertical travel of coke particles and to create hotter zones in the lower portion of mass 9, so that better coke drying may be accomplished.

As coke is deposited in the particles of the fluidized coke in zone 9, they tend to increase in size and the larger particles tend to accumulate near the bottom of the vessel in spite of the rather violent agitation therein. Accordingly, a portion of the fluidized coke is continuously or intermittently withdrawn through stripping leg 13 to maintain the desired level of fluidized coke in the reactor. Hot gas, which may, for example, be obtained from line 12, or cold gas from another convenient source, is introduced near the bottom of the stripping leg 13 through line 29 in order to finally dry the coke leaving the system. The use of cold gas effects desirable heat exchange. Coke discharges from stripping leg 13 through line 14 into lock hopper 16, which with its associated valves 15 and 17 permits coke to be withdrawn from the high pressure area comprising the reactor to low pressure coke handling operations to be described below, without material loss of pressure in the reactor. In order to maintain particle size distribution in the system a portion of coke production may be withdrawn through line 18, reduced in size in ball mill of crusher 19 and returned to the reactor 8 by means of gas lift 20, lock hopper 27, and associated valves 26 and 28. Hot inert gas under pressure such as tail gas from line 12 is introduced through line 21 by connections not shown, to operate the gas lift 20.

Coking of the preheated feed from line 7 takes place in the presence of hot gaseous medium flowing upwardly through coke bed 9. As hereinabove indicated this hot gaseous medium comprises hydrogen, and vaporized or normally gaseous hydrocarbons which are derived from the feed introduced into the reactor through line 7 and its reaction products, from coke undergoing drying in zone 9 and/or from superheated tail gas line 12. Line 12 carries a stream of recycled light product gas which has been separated, partially dehydrogenated, and partially polymerized by steps described hereinbelow.

A portion of the turbulent mass of coke particles in bed 9 is withdrawn therefrom and passed through a particle withdrawal leg 60 to a high heat release centrifugal combustion zone consisting of a conventional centrifugal burner 61, supplied with oxygen or an oxygen-containing gas through line 62. Burner 61 is a high heat-release centrifugal furnace of a type known as a vortex burner. The coke is not completely consumed in the vortex chamber, but is heated by partial combustion while passing therethrough. This general type of burner uses centrifugal force to obtain a high relative velocity between the fuel particles and the combustion gases. This, in turn, permits a large increase in allowable heat release per unit volume of combustion space (B.t.u./h./ft.^{3}) compared to that permissible in a fluidized coke bed where only gravitational forces are dominant. Such burners may operate, for example, above 1500° F., and at such temperatures can produce from a given reaction space many times the heat release in B.t.u./ft.^{3} that can be produced in the kiln portion of conventional coking processes. The use of such a burner in a coking installation in accordance with the present invention effectively removes the limits that are present in conventional coking installations on carbon burning rate which, as pointed out above, are set in conventional installations by the gas velocities required for fluidization and by the necessity for a high coke bed with which to obtain good fluidization.

Centrifugal burners of the type referred to have been demonstrated to achieve heat releases in excess of 500,000 B.t.u./hr./cubic foot of reaction space, and sometimes in excess of 1,000,000 B.t.u./hr./cubic foot. It is ecomically feasible to use them in the present invention because although they must be built to withstand much higher temperatures than conventional fluid kilns, their small size means that they require only relatively small quantities of the expensive refractory materials.

Because of the higher temperatures obtainable in the centrifugal burner, the amount of circulating coke can be greatly reduced, for example by 75% or more, from that necessary in conventional coking installations. Further, because the superficial velocities in the system and the solids inventory requirements are entirely different than in the kiln of a conventional fluidized coking installation, the volume of reaction space can be reduced, for example by as much as 90%. The coke in burner 61 is less than 10% of that in reactor 8, by weight.

From burner 61 heated particles are passed back to bed 9 through leg 62, for transfer of the heat they carry to gases rising from the lower portion of bed 9. Combustion product gases are withdrawn through line 63.

In coking zone 9 a certain amount of what is believed to be non-catalytic hydrogenation takes place, as well as cracking, polymerization, and dehydrogenation, the combination of dehydrogenation and polymerization resulting, at the coking zone temperature, in the formation of very high carbon to hydrogen ratio solid and/or liquid materials which deposit out on the fluidized particles in zone 9 to form coke. When operating at higher pressures in the presence of added hydrogen from line 12 the coking reaction is affected and the distribution of valuable lower molecular weight products of the reaction is displaced toward lower boiling ranges.

Following reaction, the mixture of product vapors and gas and fluidizing gas, containing some entrained coke, is withdrawn overhead from disengaging zone 30 through a conventional gas-solids separation zone, such as cyclone separator 31. Recycle oils or feed can then be used to scrub additional coke from the vapors, which then flow through line 32 and heat exchanger 33 to a conventional gas-liquid separator 34, from which gaseous products may be withdrawn through line 42 and liquid products may be withdrawn through line 43.

The primary gas stream to fluidize the mass of coke particles enters through line 12. This may comprise steam or hydrocarbon effluent from furnace 53, and this furnace may be operated as a thermal cracker, thermal reformer, dehydrogenation unit, or other process unit with high process effluent temperatures. A portion of recycle tail gas in the system can be passed to the inlet of furnace 53 where, if desired, it may be joined by a stream of hydrogen and/or a light hydrocarbon-containing gas from an extraneous source through line 54 by means of compressor 55. The combined stream at the furnace inlet flows through coil 56 in furnace 53, where it is subjected to dehydrogenating and polymerizing conditions, for example 1000° to 1500° F., and at superatmospheric pressures up to 600 p.s.i.g., and thence through line 12 to the coking reactor 8.

In general, the system is operative with gas velocities in the reactor of 0.5 to 2.5 linear feet per second at temperatures of 850° to 1100° F., at pressures of 15 to 500 p.s.i.a., with reactor coke inventories of 0.5 to 3 pounds per pound of feed per hour, and with solids particle sizes of 20 to 200 mesh. The recycle gas furnace is operated at temperatures between about 600° F. and 1500° F. at superatmospheric pressures up to 600 p.s.i.g. depending on the amount of dehydrogenation and polymerization of hydrocarbon components of the recycle gas desired, the amount of gas being circulated, and the required heat input to the reactor.

Further to illustrate the invention, the following specific example is given:

Example

Feed, 11° A.P.I. ---------- Boscan crude.
Feed preheat in furnace 6 ---------- 850° F.

Fresh feed through line 1	20,000 b./d.
Recycle through line 4 (recycle steam-stripped to 800° F., initial boiling point at atmospheric pressure)	3,000 b./d.
Average temperature in reactor	950° F.
Average pressure in reactor	375 p.s.i.g.
Average coke particle size in reactor	20–200 mesh.
Coke inventory in reactor	1.5 lbs./lb./hr. of feed.
Superficial gas velocity in reactor	1.6 ft./sec.
Fluidizing gas, line 12	4227 s.c.f.[1]/bbl. fresh feed.
Furnace (53) outlet temperature (line 12)	600° F.
Furnace (53) average pressure	400 p.s.i.g.
Coke from burner 61:	
(*a*) Temperature, ° F.	1500.
(*b*) Lb./lb. feed	10.
Coke in burner 61, lb./lb. in coking reactor	0.01.
Net yields, wt. percent on charge:	
Coke (including that burned)	16.
Stabilized gasoline	26.
Light gas oil	30.
Heavy gas oil	19.
Gas (net)	9.

[1] S.c.f. = standard cubic feet.

If desired, the temperature of coke from the burner may be increased to 1800–2000° F., with a substantial reduction in coke circulation rate.

If desired, the oxygen-containing gases to burner 61 may first be heated to obtain high burner temperatures with less combustion. Also, if desired, the off gases in line 63 from burner 61 may be used to drive turbines, or to heat the coke stream in line 60, the latter expedient serving to still further reduce combustion space requirements.

The burner 61 operates in a temperature range which is feasible for the production of synthesis gas, and the burner may be used for this purpose.

Instead of substantially all coke, the particles inventory in the system may comprise inert particles on which coke is laid down. If the inert particles are selected to have a higher heat carrying capacity than coke itself, particle circulation requirements may be further decreased, particle size may be better controlled, and fines problems may be decreased.

What is claimed is:

In a process for converting a liquid hydrocarbonaceous charge stream in a conversion zone in the presence of a dense phase fluidized bed of coke particles, wherein said coke particles are contacted with said stream at a temperature of from about 850° F. to about 1200° F. at which said charge is converted into lower boiling vaporous products and coke with the transformation of at least a portion of said coke particles into coarser particles, resulting vaporous conversion products are withdrawn from said zone for recovery of the constituents thereof, coarse coke particles are withdrawn from said bed, and fine coke particles are added to said bed to maintain the coke inventory therein, and wherein at least a major portion of the heat required to maintain said contacting temperature is derived from burning a portion of the coke in the system, the improvement which comprises passing a portion of said coke particles, amounting to less than 10% by weight of the total coke in said conversion zone, from an upper portion of said bed to a separate high heat release centrifugal combustion zone, burning a portion of the coke in said combustion zone at a temperature above 1500° F. in the presence of an oxygen-containing gas, and returning heated coke particles substantially free of combustion gases from said combustion zone to a lower portion of said bed.

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