June 19, 1951

G. E. LIEDHOLM

2,557,748

PROCESS FOR HYDROCARBON CONVERSION

Filed March 28, 1950

2 Sheets-Sheet 1

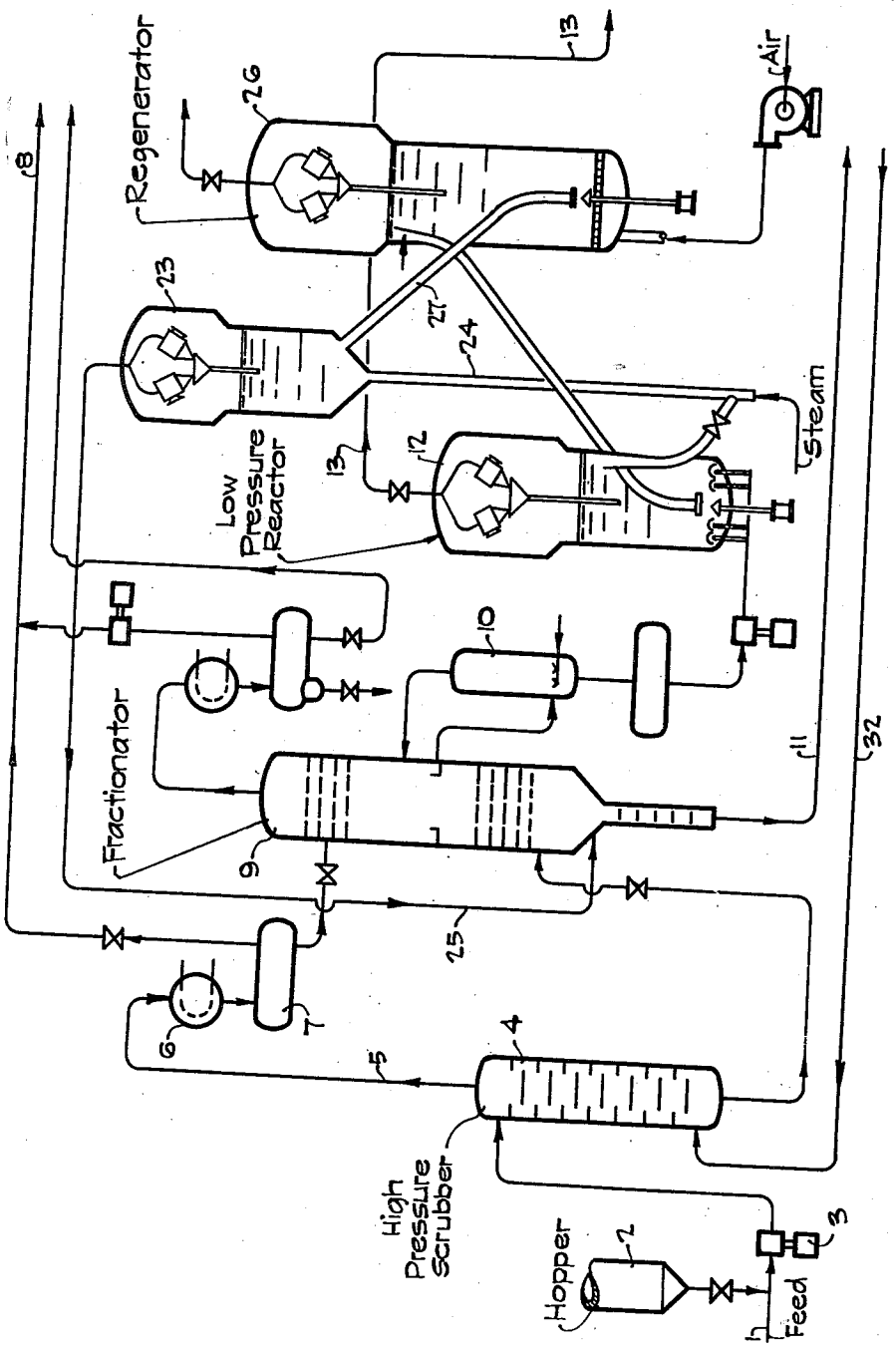

Fig. 1a

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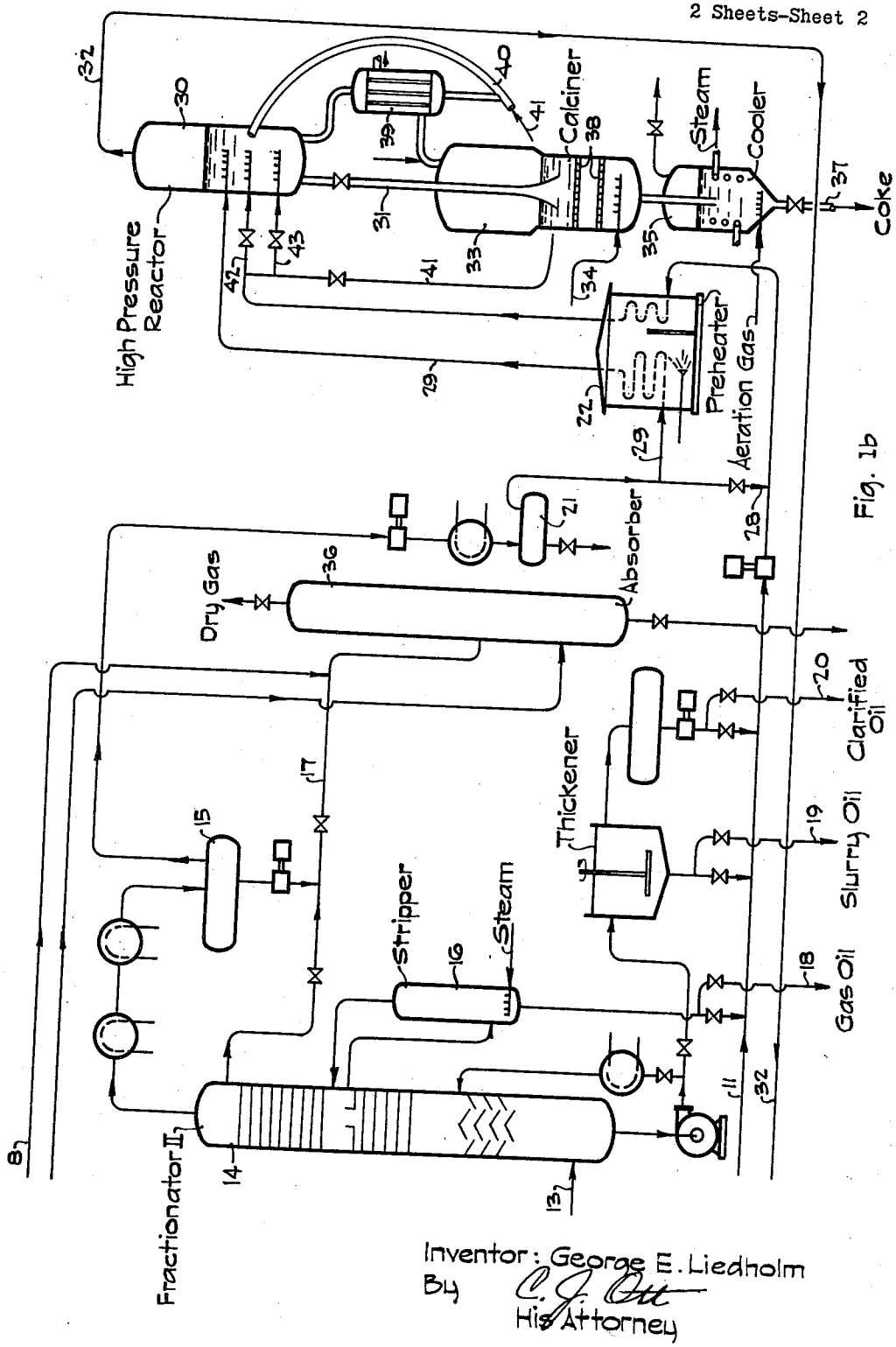

Fig. 1b

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PROCESS FOR HYDROCARBON CONVERSION

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Application March 28, 1950, Serial No. 152,383

5 Claims. (Cl. 196—49)

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The present invention relates to an improvement in the art of converting heavy hydrocarbon oils into more useful products including motor fuels. More particularly, the invention relates to a novel combination of integrated catalytic and non-catalytic hydrocarbon conversion steps carried out under special conditions to obtain a better utilization of the heavy hydrocarbon oil in a practical manner.

Reduced crude petroleum and similar residual oils from other sources, e. g., oil shale, coal, lignite, oilsand, represent a large part of the available hydrocarbon oil supply and much effort has been given to improve the utilization of such oils. Such oils when brought to the proper viscosity by known methods are suitable as fuel oil and large quantities are so used. However, the use of such oils as fuel oil is not an efficient utilization and, furthermore, the supply exceeds the demand. It has therefore been the past practice and still is the present desire to convert at least a substantial part of such oils into products which can be better utilized. Several methods for doing this have been used or suggested. The first is to thermally crack such oils in one of two ways. In one method the oil is thermally cracked in one of the known thermal cracking processes, e. g., the Dubbs process, to produce gasoline and cracked gas oil and to leave a so-called black oil which is still suitable for producing fuel oil. In the other method the oil is coked, i. e., thermally cracked to produce gasoline and gas oil and to leave a petroleum coke. These methods, both of which are in present use, produce low quality gas oil and gasoline which require extensive refining with high losses. A better, although more costly, utilization of such oils may be realized through the use of one of the presently used catalytic cracking processes, e. g., the Fluidized Catalytic Cracking Process. There are numerous technical articles and patents relating to the catalytic cracking processes. Many of the patents state that the process may be applied to such oils, but as will be seen from the technical literature, the use of such oils in these processes is entirely unfeasible. In practical operation these processes require a relatively clean oil such as gas oil; this is also borne out by many of the patents which are directed to ways and means for producing relatively clean oils from such residual oils as charging stocks for the process. There are four methods for doing this. The first is to subject the oil to a conventional deasphalting treatment. This method, in current use, produces a relatively clean charging stock and an asphaltic residue. The second method is to vacuum flash the oil. This method, also in current use, produces a relatively clean charging stock and a heavy pitch which can be converted into low grade fuel oil. The third method, which, as far as I am aware, is not used commercially, is to subject the oil to a catalytic decarbonization treatment. This method has not been developed sufficiently. The fourth method is to vaporize the oil by contact with a hot inert solid such as pebbles, sand, pumice or coke. This method is being developed at present.

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It is well known and recognized that the chief fundamental difficulty preventing efficient utilization of such residual oils is the lack of hydrogen. It is known that a 100% efficient utilization of such oils could be obtained by suitable catalytic hydrogenation, e. g., the I. G. Destructive Hydrogenation Process, but catalytic hydrogenation is far too uneconomical to warrant practical consideration. The methods described above achieve the hydrogen balance by the wasteful but far less costly removal of carbon.

The process of my invention is particularly designed for the utilization of reduced petroleum crudes and oils of similar nature regardless of source. Such oils are better utilized in this method by a novel combination of process steps which achieve a better hydrogen balance without the cost and technical difficulties encountered by conventional catalytic hydrogenation. The process of this invention to be described has the advantages of the simplicity and low cost of thermal methods while at the same time achieving a better hydrogen balance and producing valuable by-products; these advantages may be obtained without resort to the use of industrial oxygen or hydrogen.

Broadly speaking, the process of this invention comprises an integration of "flashing," "catalytic cracking," and an operation which is in itself a composite of "contact flashing," "hydrogenation" and "decoking." The feeds for these operations are in each case composites of the products of each. More specifically, the process of the invention comprises the following steps:

1. Pumping the oil to be converted to a pressure of at least 300 p. s. i. g.

2. Contacting said oil under said pressure with a hot mixture of gas and oil vapors and suspended coke, produced as hereinafter specified, thereby to obtain a partially heated liquid mixture of unconverted and partially converted liq-

uid hydrocarbons containing suspended coke and a partially cooled vapor fraction.

3. Releasing the pressure on said liquid fraction and fractionating the same at a pressure below 100 p. s. i. g. into a gasoline fraction, an intermediate distillate fraction of unconverted and partially converted oil, and a residue fraction of unconverted and partially converted oil containing the suspended coke.

4. Subjecting said intermediate fraction to catalytic cracking.

5. Fractionating the product of said catalytic cracking into a gasoline fraction, an intermediate distillate fraction of unconverted and partially converted oil, and a residue fraction.

6. Commingling at least a part of the product from said catalytic cracking heavier than gasoline with the above said residue fraction of unconverted and partially converted oil and suspended coke.

7. Pumping said last-mentioned mixture to a pressure of at least 300 p. s. i. g.

8. Heating said last-mentioned mixture.

9. Compressing the gases from step 5.

10. Heating the gases from step 9.

11. Contacting said heated mixture from step 8 and said gas from step 10 with a fluidized mass of coke at a pressure of at least 300 p. s. i. g. thereby to produce a hot vaporized product of normal liquid hydrocarbon and gases containing suspended coke, and to deposit coke in the fluidized mass of coke.

12. Withdrawing coke from the said fluidized mass of coke.

13. Contacting the total vaporous products of step 11 including said suspended coke with the feed oil as specified in step 2.

In a specific modification the coke withdrawn in step 12 is calcined at a graphitizing temperature by partial combustion with air and the hot combustion gases are indirectly heat exchanged with the coke in step 11.

In another specific modification the coke withdrawn in step 12 is combusted under pressure; part of the hot combustion products is heat exchanged with the hot coke in step 11 and the remainder is utilized in a hot gas turbine.

The process will be further described and explained with reference to the accompanying drawings wherein a flow diagram of a typical operation is illustrated. This flow diagram is shown in two parts which are given in Figs. Ia and Ib. Referring to the drawing Fig. Ia, the feed which may, for example, be flasher pitch, reduced crude, or the like, enters via line 1. A small amount of coke or catalyst, to be later described, may be added to the feed from hopper 2. The feed is pumped to a pressure of at least 300 p. s. i. g., e. g., 700 p. s. i. g., by pump 3 and is forced into the scrubbing tower 4. The pumpability of the feed may be insured by preheating it or by adding a distillate fraction (not shown). In scrubber 4 the feed passes downward countercurrent to a vapor stream of gas and oil containing suspended coke and in so doing it scrubs out the suspended coke and a substantial part of the less volatile constituents of the vapor stream and becomes itself preheated. The vapors leaving the scrubber via line 5 are cooled in cooler 6 and passed to a separator 7 from which the uncondensed gas is withdrawn overhead. This uncondensed gas, after expanding somewhat, e. g. to 300 p. s. i. g., is passed via line 8 to the absorber 36 (Fig. Ib). The liquid product from the scrubber 4, as well as the condensate from separator 7, is passed to the fractionator 9. The feed to fractionator 9, it will be noted, consists of the original feed plus gasoline, partially converted oil, heavy residual oil, and coke from a subsequent operation to be described. This mixture is separated in fractionator 9 into a gasoline plus gas fraction which is withdrawn overhead and passed to the absorber 36; also, a reflux condensate fraction which is withdrawn through side stripper 10; also a residue fraction containing suspended coke which is withdrawn from the bottom via line 11. The reflux condensate fraction heavier than gasoline withdrawn through side stripper 10 is an excellent feed stock for catalytic cracking and is catalytically cracked in reactor 12. In the flow illustrated, the catalytic cracking feed oil is injected directly into the bottom of the catalytic cracking reactor by a series of nozzles. While this has distinct advantages over the conventional method for introducing the feed into the catalytic cracking zone, it is to be understood that the invention is not limited to this feature, nor to the use of any particular type of catalytic cracking plant. The catalytic cracking operation may be carried out with any one of the known clay type cracking catalysts. Particularly suitable catalysts are the so-called synthetic silica-alumina composite cracking catalyst, the so-called synthetic silica-magnesia composite cracking catalyst, and the so-called natural cracking catalyst which are special acid treated clays. During use the catalyst gradually becomes contaminated with small amounts of iron oxide, e. g. 0.1–0.2% iron, from traces of iron in the feed oil and from erosion of the plant. In the past, all iron in the catalyst has been considered detrimental and every effort has been made to prevent any appreciable accumulation of iron in the catalyst. In the process of the present invention a catalyst which is free of all but a trace of iron may likewise be used. On the other hand, it is often advantageous in the process of the invention to include a small amount of iron oxide, e. g. 0.5–1% in the catalyst.

In the system illustrated, the spent cracking catalyst from the reactor 12 is passed to an elevated hopper 23 via line 24 in a stream of stripping gas, e. g. steam, to remove heavy difficulty volatilizable hydrocarbon materials. These stripped products with the stripping gas pass via line 25 to the fractionator 9. The heavy stripped products are therefore combined with the bottom product in line 11. The stripped catalyst passes to the regenerator 26 via line 27, and after regeneration it is then returned to the reactor for further use.

The vapors from the catalytic cracking reactor pass via line 13 to a conventional fractionator 14 (Fig. Ib) wherein separation is made between a gasoline plus gas fraction which is cooled and passed to a separator 15; also a gas oil fraction which is withdrawn through the side stripper 16; also a residue fraction which is withdrawn from the bottom. The gasoline fraction is passed via line 17 to the absorber 36. The gas oil is preferably combined with the residue fraction from fractionator 9, but some or all of it may be withdrawn via line 18 if desired. The residue fraction from fractionator 14 is preferably separated in the conventional manner into a slurry oil containing a small amount of catalyst and a clarified oil. Any desired proportion of this oil may be combined with the residue fraction from fractionator 9 or may be withdrawn via line 19 or 20.

The uncondensed gases from seperator 15 are compressed to a pressure above 300 p. s. i. g., e. g. 700 p. s. i. g., and after passing through a catchpot 21 they are preheated in furnace 22.

The residue fraction from fractionator 9 contains most of the original feed stock plus a considerable amount of partially converted products and unconverted oil from the other described operations. It also contains suspended coke. The coke is finely divided, e. g. passing a 20 mesh sieve. The amount of suspended coke may vary from a minimum of about 1 lb./bbl. up to the maximum concentration affording a pumpable suspension. While concentrations near or at the minimum may be used it is preferred to operate with concentrations toward the maximum end of the applicable range. Thus, for example, an amount of coke in the order of 100 lbs./bbl. is recommended.

In preheater 22 the gases from the catalyst cracking operation and the composite residual material are preheated. The temperature of the oil is raised to substantially the maximum temperature which can be employed with the particular oil in question without coking the preheater tubes. This temperature is in the order of 350–950° F. The maximum allowable preheat temperature is increased by the presence of the suspended coke and may also be further increased by the presence of catalytic cracking gas introduced via line 28. In general, however, it is preferred to preheat part of the catalytic cracking gas separately to a higher temperature than the oil. Thus, in the flow illustrated, part of the compressed catalytic cracking gas is passed via line 29 through separate coils in the furnace. The preheated mixture of coke, oil and gas under pressure is then passed to vessel 30 which contains a fluidized bed of coke particles. In vessel 30 a certain amount of the hydrogen from the catalytic cracking gas is recombined with the oil. The amount may be, for example, in the order of 100–200 cu. ft./bbl. This hydrogen uptake is apparently non-catalytic since a conventional hydrogenation catalyst is not necessary. Also, a certain amount of cracking (non-catalytic) takes place and coke is deposited in the fluidized bed of coke particles in the vessel. As coke is deposited upon the particles 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. A part of the fluidized coke bed is continuously or intermittently withdrawn via line 31 to maintain the desired level of fluidized coke in the vessel. The vapors of hydrogenated and cracked oil and unused gas pass out of the reactor 30 at the top via line 32 and are passed into the bottom of the scrubber 4 as previously described. In passing out of the fluidized bed of coke particles this vapor stream carries in suspension a certain amount of the more finely divided coke particles. The amount of coke recycled with this vapor may be controlled by controlling the level of the fluidized bed in reactor 30. Thus, as the level of the fluidized bed is increased the carryover of coke is increased. It is necessary that the mass of fluidized coke in reactor 30 be relatively large in order to prevent agglomeration of the coke particles by the oil feed. Also, it is necessary that sufficient heat be supplied with the preheated feed and gas to maintain the fluidized coke in a dry, free-flowing condition.

The coke withdrawn from reactor 30 via line 31 may be handled in one of several ways. One advantageous method is to pass the coke into a lower vessel 33 wherein it is blown with air introduced via line 34. The coke is maintained in a fluidized state and by partial combustion its temperature is raised to a graphitizing temperature in the order of 2500° F. A substantially pure, dry, graphitized coke suitable for use in the production of electrodes may be produced by this method. The hot calcined coke is then passed to a cooling chamber 35 and is finally withdrawn via line 37.

In order to insure proper calcination of all of the coke it is desirable to provide the calcination vessel with one or more refractory grid plates 38; such plates, even if of quite open structure, substantially decrease top-to-bottom mixing and thereby insure a more uniform residence time in the vessel.

This method of handling the coke is particularly advantageous from two standpoints. In the first place, a valuable graphitized coke is obtained rather than the usual grade of petroleum coke which is of very low value. In the second place, this method of handling allows additional heat to be supplied to the high pressure reactor by heat exchange with the hot effluent combustion gases from the calcination vessel. Thus, in the system illustrated, Fig. *Ib*, a stream of hot fluidized coke is continuously withdrawn from reactor 30 to a heat exchanger 39, and then recycled back to the reactor via line 40. A part of the hot gases under pressure may be passed via line 41 to act as a carrying medium to effect the recycle of the coke. The hot combustion gases from the calcination vessel 33 are passed through the heat exchanger to heat the recycled coke.

If it is not desired to produce graphitized coke another advantageous variation is to operate the vessel 33 at substantially the same pressure as vessel 30. Part of the hot combustion gases can be indirectly heat exchanged, as illustrated, and the remaining hot gases can be utilized in a hot gas turbine (not shown). In this case all of the coke may be consumed. It will be seen that this arrangement affords an exceptionally advantageous application of the use of a hot gas turbine with a solid fuel.

The process of the invention, it will be seen, is a combination process in which catalytic cracking is involved. The process is designed and intended to be also applicable with existing catalytic cracking plants. Conventional catalytic cracking plants are invariably provided with a suitable absorber. In general, a rectified absorption system is used rather than a simple absorber such as illustrated. However, for the sake of simplicity, a simple absorber 36 has been shown. The absorber will normally be part of the catalytic cracking plant. If the gases from the catalytic cracking portion were passed to the absorber in the usual way, the capacity of the absorber would not be sufficient to handle the gas from the high pressure scrubber 4. In the present method the catalytic cracking gas can be passed through the usual absorber in the conventional way and an additional absorber may be provided for the gas from the scrubber 4. However, in the system illustrated this additional absorber is dispensed with by passing the catalytically cracked gases directly to the preheater 22 without absorption and passing the gases from the scrubber 4 to the absorption system. This is possible in the case illustrated because the high pressure in separator 21 serves to condense a substantial part of the

material which would normally be removed in the absorption system.

The greatest problem overcome in the combination process described is that of maintaining a fluidized bed in the high pressure reactor 30. Numerous attempts to operate such a fluidized bed have failed due to the particles of coke agglomerating into large masses. This difficulty is overcome in the present method by maintaining a large fluidized bed of coke so that the residence time of the coke in the reactor is at least several minutes. Other features of the described process which cooperate in preventing difficulty due to the agglomeration with coke particles are as follows:

1. Coke is cycled with the feed oil through the preheating coils. This allows a greater amount of heat to be supplied with the oil without coking the preheater tubes.

2. A portion of the catalytically cracked gas may be preheated with the coil and coke in the preheater tubes. This gas creates turbulence in the tubes and increases the amount of heat which may be supplied with the oil without coking the preheater tubes.

3. Part of the catalytically cracked gas may be separately preheated to a higher temperature than the oil and coke mixture thereby further increasing the amount of heat which may be supplied to the reactor 30 with the feed streams. This is possible since the heavier less refractory hydrocarbons, such as butane and pentane, are largely removed from the catalytically cracked gas through the substantial compression and separation in vessel 21.

4. Sensible heat in the combustion gases from the calcination step may be used to supply additional heat to the coke without changing the pressure.

5. Such larger particles as may be produced by agglomeration tend to collect at the bottom of vessel 30 and are removed substantially as soon as formed.

6. The preheated catalytically cracked gas is introduced in part at a lower level in vessel 30 than the mixture of oil and coke. Thus, in the plant illustrated, the mixture of oil and coke is passed to the reactor 30 via line 29, whereas the catalytically cracked gas (or a part of it) is introduced at lower points via lines 42 and 43. This tends to hasten the vaporization of the oil, to dry the coke particles beyond the point of sticking, and to prevent sticking by considerable agitation.

I claim as my invention:

1. The process for the conversion of hydrocarbon oils to lower boiling hydrocarbon oils which comprises the steps of (1) pumping the oil to be converted to a pressure of at least 300 p. s. i. g., (2) contacting said oil under said pressure with a hot mixture of normally gaseous and normally liquid hydrocarbons and coke produced as hereinafter specified thereby to obtain a partially heated liquid fraction of a mixture of unconverted and partially converted hydrocarbons containing suspended coke and a partially cooled vapor fraction, (3) releasing the pressure on said liquid fraction and fractionating the same at a pressure below 100 p. s. i. g. into a gasoline fraction, an intermediate distillate fraction of unconverted and partially converted oil and a residue fraction of unconverted and partially converted oil containing the suspended coke, (4) subjecting said intermediate fraction to catalytic cracking, (5) separately fractionating the product of said catalytic cracking into a gaseous fraction, a gasoline fraction, an intermediate distillate fraction of unconverted and partially converted oil and a residue fraction, (6) commingling at least a part of said fraction from the catalytic cracking heavier than gasoline with the above said residue fraction of unconverted and partially converted oil and containing suspended coke thereby to produce a mixture of unconverted and partially converted oil and suspended coke, (7) pumping said last-mentioned mixture to a pressure of at least 300 p. s. i. g., (8) heating said last-mentioned mixture, (9) compressing said gaseous fraction from step 5 to at least 300 p. s. i. g., (10) heating said gaseous fraction from step 9, (11) contacting said heated mixture from step 8 and said gas of step 10 with a fluidized mass of coke at a pressure of at least 300 p. s. i. g. thereby to produce a hot vaporized product of normally liquid hydrocarbons and gases carrying suspended coke and to deposit coke in the fluidized mass of coke, (12) withdrawing coke from said fluidized mass of coke, (13) contacting the total vaporous product of step 11 including said suspended coke with the feed oil as specified in step 2.

2. Process according to claim 1 in which the coke withdrawn in step 12 is withdrawn to a separate calcination zone operating at substantially atmospheric presure in which the coke is heated to a graphitizing temperature by partial combustion with air, and the hot combustion gases resulting therefrom are heat exchanged with the coke in step 11.

3. Process according to claim 1 in which the heating of the gaseous fraction in step 10 is carried out in two portions, one portion being commingled with the oil plus coke in step 8, and the other portion being separately preheated to a higher temperature.

4. Process according to claim 1 in which the catalytic cracking in step 4 is carried out with a siliceous cracking catalyst containing between 0.5 and 1% of iron oxide (Fe_2O_3).

5. Process according to claim 1 in which the coke is withdrawn in step 12 without substantial reduction in pressure and the hot gases of combustion are utilized in part to heat the coke in step 11 and in part to produce energy.

GEORGE E. LIEDHOLM.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,222,682	Nash	Nov. 26, 1940
2,361,891	Watson	Oct. 31, 1944
2,380,897	Murphree et al.	July 31, 1945
2,445,328	Keith	July 20, 1948
2,461,069	Marisic et al.	Feb. 8, 1949