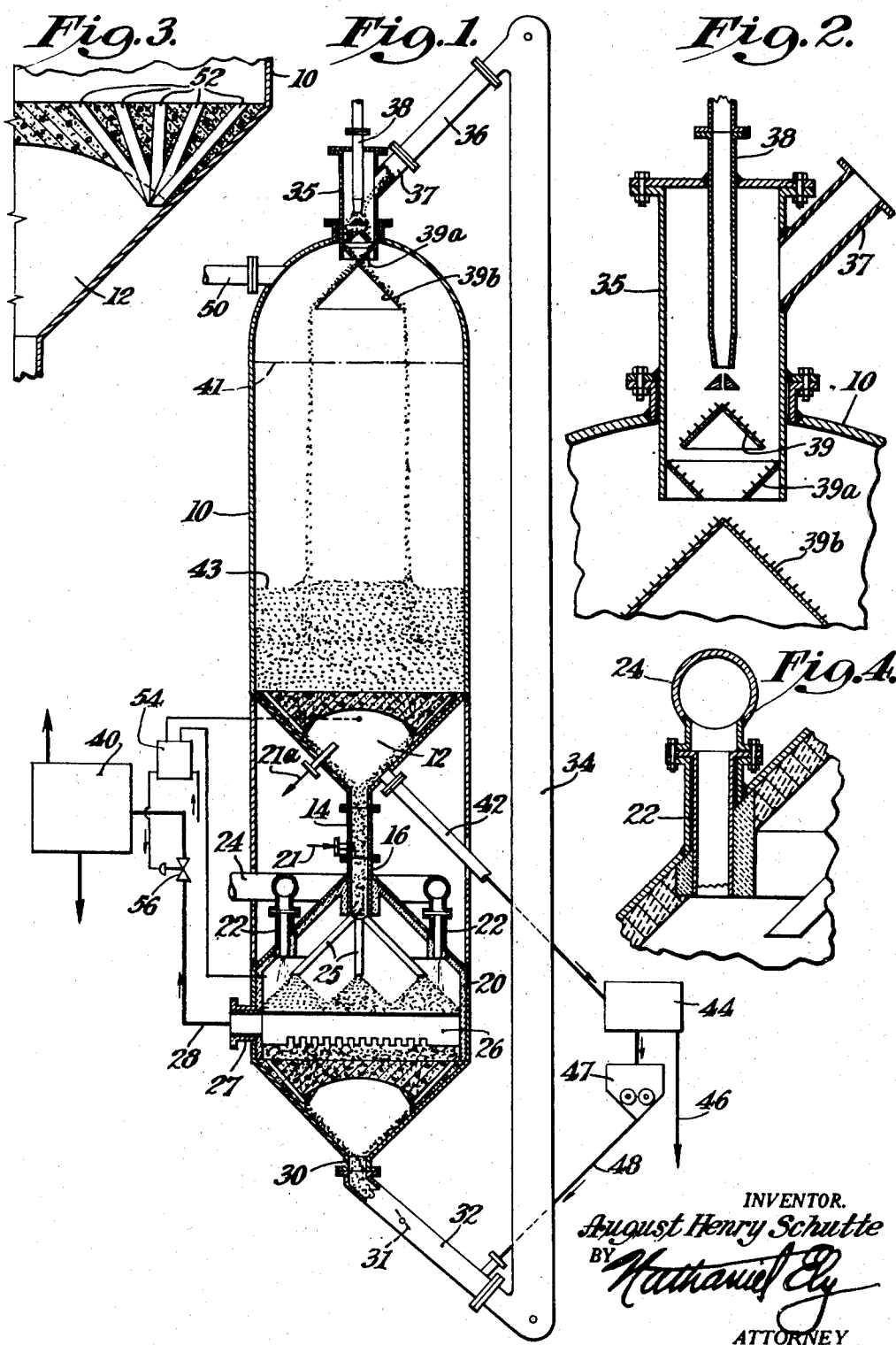


July 24, 1951

A. H. SCHUTTE
CONTINUOUS HYDROCARBON CONVERSION
PROCESS AND APPARATUS
Filed Jan. 7, 1949

2,561,420



INVENTOR.
August Henry Schutte
BY *Nathaniel Ely*
ATTORNEY

UNITED STATES PATENT OFFICE

2,561,420

CONTINUOUS HYDROCARBON CONVERSION
PROCESS AND APPARATUSAugust H. Schutte, Hastings on Hudson, N. Y.,
assignor to The Lummus Company, New York,
N. Y., a corporation of Delaware

Application January 7, 1949, Serial No. 69,657

6 Claims. (Cl. 196—55)

1

The invention relates to improvements in the conversion of a liquid hydrocarbon residuum by continuous contact with a gravity flowing, gravity packed bed of heat supplying particles. It also pertains to an improved apparatus for carrying out such processes.

In a copending application in the names of A. H. Schutte and V. O. Bowles, Serial No. 3,747, filed January 22, 1948, a process has been disclosed in which a contact particle mass of heat transfer material is passed continuously in a circuit through a reaction unit, a reheating unit, and then returned to the reaction unit. In the process of this earlier invention the contact mass is composed of refractory heat transfer pebbles of one-sixteenth of an inch to one inch ($\frac{1}{16}$ "—1") in size, which pebbles may be of various materials such as spent catalyst, alumina, corundum, or clay, although coke was found to be the most attractive commercially. This particle mass of contact material which is initially heated to a predetermined temperature, acts to vaporize a part of a liquid hydrocarbon charge as it passes the liquid feed zone, thus producing high quality gas oil or olefins, depending on the bed temperature and characteristics of the hydrocarbon charge. The remainder of the charge is subsequently converted to vapors and to dry coke adhered to the contact particles. By correlated maintenance of bed depth, ratio of solids to oil, temperatures of charge oil feed and bed material, and internal pressure, the coke formation is caused to pass to dryness without agglomeration of the bed particles, so that the bed flows uniformly and continuously without rabbling or other mechanical agitating force. The bed can thus be removed in an attenuated free flowing stream.

Heretofore the production of coke has been an important consideration. With a high Conradson carbon content crude charge the carbon removal was especially important because otherwise the heavy crude charge was unfitted for catalytic cracking. Usually the production of petroleum coke is also of substantial economical advantage as a desirable fuel end product. There was a further advantage in the production of coke in that the coke formed or deposited could be used in reheating of the bed material by suitable autocombustion.

2

At times and in certain locations oil refiners have found that coke production is not economical due to prevailing market conditions, and they have produced heavy fuel oil wherever possible. Under these conditions the known prior practices have been followed and the high carbon crude was thermally cracked as far as possible with the best yield of gas oil that could be obtained by such operation. These thermal cracking operations cannot attain the overall yield of distillate fuels obtainable from coking.

By following the contemplated procedures and operations of the invention disclosed in the applications previously referred to, involving a deep bed of contact material in the reaction zone and moderate temperatures, the coke produced on a once-thru basis approximately equaled the carbon residue analysis of the hydrocarbon.

I have found however that with a shallow reaction bed, of five feet or less, and a correspondingly short reaction time no coke was made. I did note though, that a low coke production was always accompanied by a low liquid product recovery and low overall weight balance. It appeared that the loss was not in coke product, but that full coke yield was never obtained, the loss being in liquid product components, in the reheater stack gases.

This discovery has been put to substantial advantage in the present invention by the production of substantial yields of a heavy aromatic component which has relatively high value as a plasticizer and also, being lean in hydrogen, may be used as a valuable source for carbon black.

These desired results can be obtained in a predetermined and controlled manner by varying the time-temperature relation of the coking operation so that there is insufficient time to convert the heavy hydrocarbon deposit to coke. In fact it has been found that where the time-temperature effect is reduced below that required for the production of dry coke, the contact material is discharged with a coating of very heavy pitch that amounts to nearly two to three times the weight of the original carbon residue. Due to the size and mass of the circulated coke or other contact particles and the relative thinness of the pitch film, the free flow of the solids from the reaction unit is not impeded.

This process differs from those hitherto known

for coking the entire charge oil in the presence of combustion gases, for in such previous processes the oil partial pressure in the reactor is lowered by the flue gases so that unwanted heavy oil is vaporized, there is partial oxidation of the entire oil product and all the oil vapors must be recovered from the flue gases. In the process of this invention most of the oil product is made under optimum conditions and at optimum quality, then the final "near-coke" residue is subjected to short-time, high temperature cracking in the form of a film and in the presence of large quantities of flue gases or inert gas.

In accordance with the process herein disclosed only 5 to 20% of the feed, by weight, need be recovered from the flue gases, and even if this recovered proportion has only fuel oil value, the operation will be profitable.

It will therefore be understood that flexibility of operation in a process of the type described is very important in order to take care of seasonal trends, and particularly so in operations in certain geographical areas. In the Near East, for example, the refiner can obtain maximum yields of catalytic cracking stock from heavy hydrocarbons, in the absence of any local coke market.

One of the principal features and advantages of the present invention is that with minimum cost and no unexpected or difficult mechanical problems it is possible to produce high yields of valuable oils from heavy residuals whenever desired.

More specifically it is an object of this invention to produce a maximum of near virgin gas oil and a minimum of coke from a heavy residual charge by utilizing a continuous, gravity packed, coke heat transfer bed for controlled conversion of the charge.

A further object of this invention resides in the provision of a more flexible continuous contact hydrocarbon conversion system whereby various end products may be obtained from the same charge so that the refiner can effectively satisfy changing market demands.

These and further objects and advantages of the invention will be appreciated from the following detailed description of a preferred form of embodiment thereof, taken in conjunction with the accompanying drawings, in which:

Figure 1 is a schematic diagram of a continuous hydrocarbon residuum conversion unit suitable for carrying out the process of this invention;

Figure 2 is an enlarged cross-sectional view of the inlet chamber and associated parts.

Figure 3 is an enlarged cross-sectional view of the flow control portion of the lower part of the reactor.

Figure 4 is an enlarged vertical section showing a detail of the heating burners.

As more generally shown in Figure 1, the conversion unit or system consists mainly of a vertical reaction section 10, a reheating section 20 connected therewith, an elevator mechanism 34 of conventional endless bucket chain type, and a gas recovery unit 40 of known construction. Preferably the reaction section 10 is at a substantial elevation so that the contact particles forming the continuous bed may flow by gravity through the outlet 12, the connecting conduit 14, and thence into the inlet 16 at the top of the reheating section 20. Superheated steam for sealing and purging the reaction products of section 10 from the contact mass entering the reheating zone

may be introduced through line 21 as indicated with removal at 21a.

The upper portion of the heating section 20 is provided with suitable radiant burners 22 details of which are shown in Figure 4, such burners being supplied with fuel gas through manifolds 24. As the bed particle mass moves downwardly through the inlet 16, it is distributed by the pipes 25 across the section 20 and the gases evolved will pass out through the vapor collector 26 and through the discharge outlet 27. The gas thus removed through line 27 passes through line 28 to the recovery unit 40. The flue gas will be of controlled oxygen content to prevent burning, that is, oxidation of the hydrocarbons.

The particle form contact material in reheating section 20 continues its gravity flow through the discharge outlet 30 controlled by a regulating valve 31 and thence through connecting conduit 32 to the lower part of the elevator 34. At the upper end of the elevator 34 a downwardly inclined inlet conduit 36 extends to the inlet chamber 35 mounted on the top of the reaction section 10 and thus completes the continuous closed path of the bed material through the reaction section 10, the reheating section 20 and the elevator 34. The reheated, granular bed material discharged from the upper end of the elevator 34 flows by gravity down the conduit 36 through the solids feed inlet 37 on the chamber 35 and thence into the reaction section 10.

As shown in Fig. 2, the inlet chamber 35, is immediately ahead of reaction section 10 and affords a very advantageous location for charging the liquid hydrocarbon residuum. For this purpose a single centrally located oil feed conduit 38 discharges into the lower portion of the chamber 35, and at a point below the heated particles which discharge from conduit 36 through inlet 37. As a result, an efficient contacting and wetting of the granular bed material is thus achieved before entry into the reaction section 10. Coke deposits in chamber 35 are prevented by the continuous flow of solids, and, if desired, spreader baffles 39, 39a, and 39b may be used to tumble the feed particles and distribute them over the cross section of the reactor 10. The entire chamber 35 is demountable for cleaning when necessary.

This manner of charge feeding is highly advantageous where, as in the present case, the conversion system is flexible in operation, a high-level gravity packed bed as shown at 41 being maintained in the reaction section 10 when maximum coke production is intended in accordance with the process of the copending applications referred to herein, and a low level bed as shown at 43 is used where heavy aromatic oil and minimum coke yield is desired for the purposes of the present invention.

The reaction bed can be conveniently changed from a high to a low level by means including a draw-off line 42 running from the outlet of the reaction section 10 to a particle classifier 44 of conventional construction, the excess being removed through discharge line 46 as indicated. During operating conditions the classifier will maintain the desired range of uniformity of bed particles which may be passed through a roller crusher 47 and the particles of proper size, are returned to the system through a line 48 connected with the conduit 32 at the lower end of the reheating section. The oil vapors generated at either a high or low level operation are re-

moved through vapor line 50 at the upper part of the reactor to minimize cracking.

While a bucket type chain elevator 34 has been indicated in the illustrative embodiment of means for carrying out this invention, it will be understood that a hitherto known gas lift type of elevator can be used for raising the bed material, mixing it with the charge and supplying the upper end of the reaction section.

Uniformity of flow is desirable for uniformity of reaction and on large reactors, as of sixteen feet in diameter and larger, suitable flow control devices may be required. An example of one preferred form is shown in Figure 3. In this case, a series of conduits generally indicated at 52 are focused on a common annular ring from uniformly spaced points in the area of the lower part of the reactor (or reheater). Each conduit 52 thus draws uniformly from the area above it and as they each discharge to a common ring zone, a uniform drawoff in the open chamber 12 of the bottom of the reactor is accomplished.

An exemplary operation of the process of this invention will now be described. Assuming a low level reaction bed and a balanced operation with uniformity of flow and temperature conditions, the preheated bed particles enter the upper end section of reactor 10 carrying the reduced crude in liquid form as applied thereto by the feed pipe 38 during downwardly inclined gravity flow through the inlet 37. The oil vapors generated by contact with the preheated bed particles discharge through line 50 at the upper end of the reaction zone and the bed particles with the remainder of the liquid charge move continuously downward by gravity as a compact, gravity packed bed.

Now with the time-temperature relation in reaction zone 10 insufficient to produce dry coke, the coke bed particles will leave the reactor 10 through outlet 12 with one and one-half to four times the weight of the original carbon residue. Due to the size of the circulated coke particles and the thinness of the film of pitch, the free downward flow of solid coke in packed bed form is not impeded.

As the pitch covered coke particles enter the reheating zone, a radiant atmosphere is maintained at operating temperatures of the order of 2000° F., the pitch coatings or films will crack and vaporize rapidly, yielding dense yellow vapors in draw-off line 27, and very little carbon or coke. This result is demonstrable because otherwise the coke yield represented by accretion on the bed particles would have been normal, or the stack gases would have carried large quantities of soot. These vapors are quite aromatic due to the short reaction time, high temperature conditions, and they may be readily condensed and recovered in the recovery unit 40. For example, in a typical case it is necessary only to condense these vapors to 500° F. in a steam generator or scrubbing system to recover a condensate having a 650° F. initial boiling point. Further scrubbing will recover the light aromatics.

Where maximum yield of coke is desired, as in the processes of the earlier applications, a deep bed of 30 feet or more is required in the reactor and the solids residence time will range from 20 to 30 minutes. The oil charge is heated to temperatures of the order of 700° to 900° F. and the bed particles introduced to the reaction space will be at a temperature of 900° to 1100° F. to provide the main portion of the coking heat, the reaction bed being maintained at 850° to 1050°

F., below the point of hydrocarbon charge feed.

For the purpose of producing a minimum of coke, a somewhat lower yield of gas oil and a small yield of recovered aromatics the controlled solids residence time must be quite different. A shallow bed, namely five feet or less, is employed in the reactor, the solids residence time is 5 to 6 minutes when the temperature of the charge residuum and the bed temperature are maintained at the same level as in the previous case. A typical analysis of runs is as follows:

[Yields, Weight Per Cent on Feed]

Run #	10	12	160	18
Charge, Red. Cr.	III.	III.	III.	W. Tex.
API	18.1	18.1	18.1	10.7
Per Cent Ramsbottom Carbon	8.3	8.3	8.3	11.5
G. O. Product, Weight Per Cent	76.8	72.1	64.9	63.4
Coke Product, Weight Per Cent	1.6	2.2	0.5	0
Loss, Weight Per Cent	5.0	6.1	10.1	6.0+
Total Liq. Product, Weight Per Cent	85.1	81.6	74.5	76.9
Per Cent Ramsbottom Carbon in Total Liq.	3.5	4.1	5.9	6.4
Per Cent Ramsbottom Carbon in Total/FF	2.9	3.3	4.4	4.9
Per Cent Ramsbottom Carbon unaccounted for *	3.8	2.8	3.4	6.6
Distillate and Gas Oil "Loss"	90.1	87.6	84.6	82.9
Gas + Coke Produced	9.9	12.2	14.8	17.1
	99.9	99.8	99.4	99.0
Per Cent "Loss"/Per Cent C. Res. not formed ⁽⁵⁾	1.3	2.2	2.9	-----

* C₄ and heavier.

* Per cent C in feed (C in liquid product + C made as coke).

* C₄ and lighter.

Instead of merely reheating the bed discharged from the reactor in any way that is sufficient for reintroduction to the initial reaction section, the present invention requires rapid heating by radiant heat and by contact with essentially inert gases at 1500° to 2500° F. in order to produce a predetermined second reaction and rapidly vaporize and convert the pitch coating of the bed particles to recoverable vapors with minimum coke. This high temperature is a surface effect and, as the heat soaks into the particles after the vaporization and cracking of the pitch film, the resulting particle temperature will be 900 to 1100° F., or that required for reintroduction of the particles to the zone of oil feed.

The oil charge, which is fed at a uniform rate, will be in the same ratio to solids as in the operations to dry coke formerly described in earlier applications.

If stripping of the products from the particles discharged at 14 is desired, this of course can be readily accomplished with superheated stripping steam as previously mentioned and in such case, condensation of the steam at 40 is all that is necessary. Control of the pressure in the bottom of reactor at 12 and in the upper part of reheater section 20 can be accomplished by a differential pressure controller 54 operating valve 56 in line 27, provision being made to maintain a higher pressure at 12 to assure solids flow into reheater 20.

While the foregoing exemplary data are illustrative of the process of this invention, it is to be understood that the invention is not hereby limited except as may be required by the scope of the following claims.

I claim:

1. A process for converting heavy residue hydrocarbon into maximum yields of more valuable liquid products and minimum yields of coke which consists in preheating the charge residuum to 700-900° F., then contacting it with sufficient

7

quantity of preheated solid contact material so that primary vaporization evolves vapors of gas oil boiling range and the unvaporized liquid portion of the charge is applied to the particles of contact material, causing the contact material particles thus wetted to flow downward as a compact gravity packed bed in a sealed reaction zone without further addition of heat for a time sufficient to convert the liquid hydrocarbon carried by the particles into lower boiling vapors and a very heavy residuum amounting to one and a half to four times the carbon residue content of the original charge, but not sufficient for complete conversion to dry petroleum coke; removing the wet coke from the reaction zone and passing it through a gas sealed zone, removing the lower boiling vapors from the upper end of the reaction zone, introducing the contact particles carrying the very heavy residuum into a second sealed zone, subjecting said particles to rapid heating and contact with inert gases at 1500° to 2500° F. to rapidly vaporize and convert said heavy residuum to recoverable vapors with a minimum of coke, withdrawing the recoverable vapors from the second zone, and returning the reheated contact particles from said second zone to the zone of initial charge oil contact at a temperature suitable for obtaining the proper extent of initial vaporization.

2. A process for converting heavy residue hydrocarbon into maximum yields or more valuable liquid products and minimum yields of coke which consists in preheating the charge residuum to 700-900° F., then contacting it with sufficient quantity of preheated solid contact material so that primary vaporization evolves vapors of gas oil boiling range and the unvaporized liquid portion of the charge is applied to the particles of contact material, causing the contact material particles thus wetted to flow downward as a compact gravity packed bed in a sealed reaction zone without further addition of heat for a time sufficient to convert the liquid hydrocarbon carried by the particles into lower boiling vapors and a very heavy residuum amounting to one and a half to four times the carbon residue content of the original charge, but not sufficient for complete conversion to dry petroleum coke; removing the lower boiling vapors from the upper end of the reaction zone, removing the wetted contact particles from the lower end of the reaction zone, introducing the contact particles carrying the very heavy residuum into a second sealed zone, subjecting said particles to radiant and convection heating and contact with inert gases of controlled oxygen content at 1500° to 2500° F. to rapidly vaporize and convert said heavy residuum to recoverable vapors with a minimum of coke and without substantial oxidation of the hydrocarbons, withdrawing the recoverable vapors from the second zone, and returning the reheated contact particles from the second zone to the zone of initial charge oil contact at a temperature suitable for obtaining the proper extent of initial vaporization.

3. A process for converting heavy residue hydrocarbon into maximum yields of more valuable liquid products and minimum yields of coke which consists in preheating the charge residuum to 700-900° F., then contacting it with sufficient quantity of preheated solid contact material so that primary vaporization evolves vapors of gas oil boiling range and the unvaporized liquid portion of the charge is applied to the particles of contact material, causing the contact material

8

particles thus wetted to flow downward as a compact gravity packed bed in a sealed reaction zone without further addition of heat for a time sufficient to convert the liquid hydrocarbon carried by the particles into lower boiling vapors and a very heavy residuum amounting to one and a half to four times the carbon residue content of the original charge, but not sufficient for complete conversion to dry petroleum coke; removing the lower boiling vapors from the upper end of the reaction zone, removing the wetted contact particles from the lower end of the reaction zone, stripping vaporous materials from the contact particles with an inert gas, introducing the contact particles carrying the very heavy residuum into a second sealed zone, subjecting said particles to radiant and convection heating and contact with inert gases of controlled oxygen content at 1500° to 2500° F. to rapidly vaporize and convert said heavy residuum to recoverable vapors with a minimum of coke and without substantial oxidation of the hydrocarbons, withdrawing the recoverable vapors from the second zone, and returning the reheated contact particles from said second zone to the zone of initial charge oil contact at a temperature suitable for obtaining the proper extent of initial vaporization.

4. A method of reducing heavy hydrocarbon residual charge which comprises preheating the charge to a temperature in excess of 700° F. and applying said charge to a continuously moving gravity packed column of particle form solids moving through a sealed reaction zone, maintaining a time and temperature relation within said zone sufficient to vaporize the lighter ends of said charge but insufficient to convert the heavier ends to dry coke, removing said column of particle mass solids covered with a heavy pitch continuously from the lower end of the zone in an attenuated stream, introducing said pitch covered particles to a second sealed zone as a continuously moving gravity packed column, subjecting said particles in said second zone to temperature conditions in excess of 1500° F. for a period sufficiently short to convert the pitch to heavy vapors without combustion of the particles or the pitch, condensing the vapors from the second zone and returning the contact particles to the first zone.

5. In combination with a reactor for converting heavy liquid hydrocarbons into vaporous products in the presence of discrete particles of granular material forming a gravity packed free-flowing bed which comprises a sealed upright enclosure having an inlet chamber at its upper end for incoming bed material and having an outlet at its lower end for delivering bed material therefrom, a downwardly directed particle feed conduit attached to the upper portion of the inlet chamber and through which the bed material is supplied by gravity to the reactor, a liquid hydrocarbon feed inlet device having its discharge opening in the lower portion of the inlet chamber, and a conduit to feed the hydrocarbon charge liquid to said feed inlet device, said feed inlet device being substantially centrally positioned in the inlet chamber whereby the passage of bed material over said feed inlet device tends to prevent formation of coke in said inlet chamber.

6. In combination with a reactor as claimed in claim 5, a stripping chamber in communication with the reactor outlet, and a second sealed enclosure in the particle path between the stripping

chamber and the first mentioned inlet chamber, radiant heat burners to apply radiant heat to the particles in the second sealed enclosure, and a conduit to remove the vapors therefrom.

AUGUST H. SCHUTTE.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,323,501	Tuttle	July 6, 1943
2,339,932	Kuhl	Jan. 25, 1944
2,390,031	Schutte et al.	Nov. 27, 1945
2,418,679	Utterback	Apr. 8, 1947
2,461,104	Bates	Feb. 8, 1949