Aug. 5, 1958 C. E. JAHNIG 2,846,360

PROCESS FOR SECURING CHEMICALS FROM PETROLEUM RESIDUA

Filed Oct. 20, 1954 2 Sheets-Sheet 1

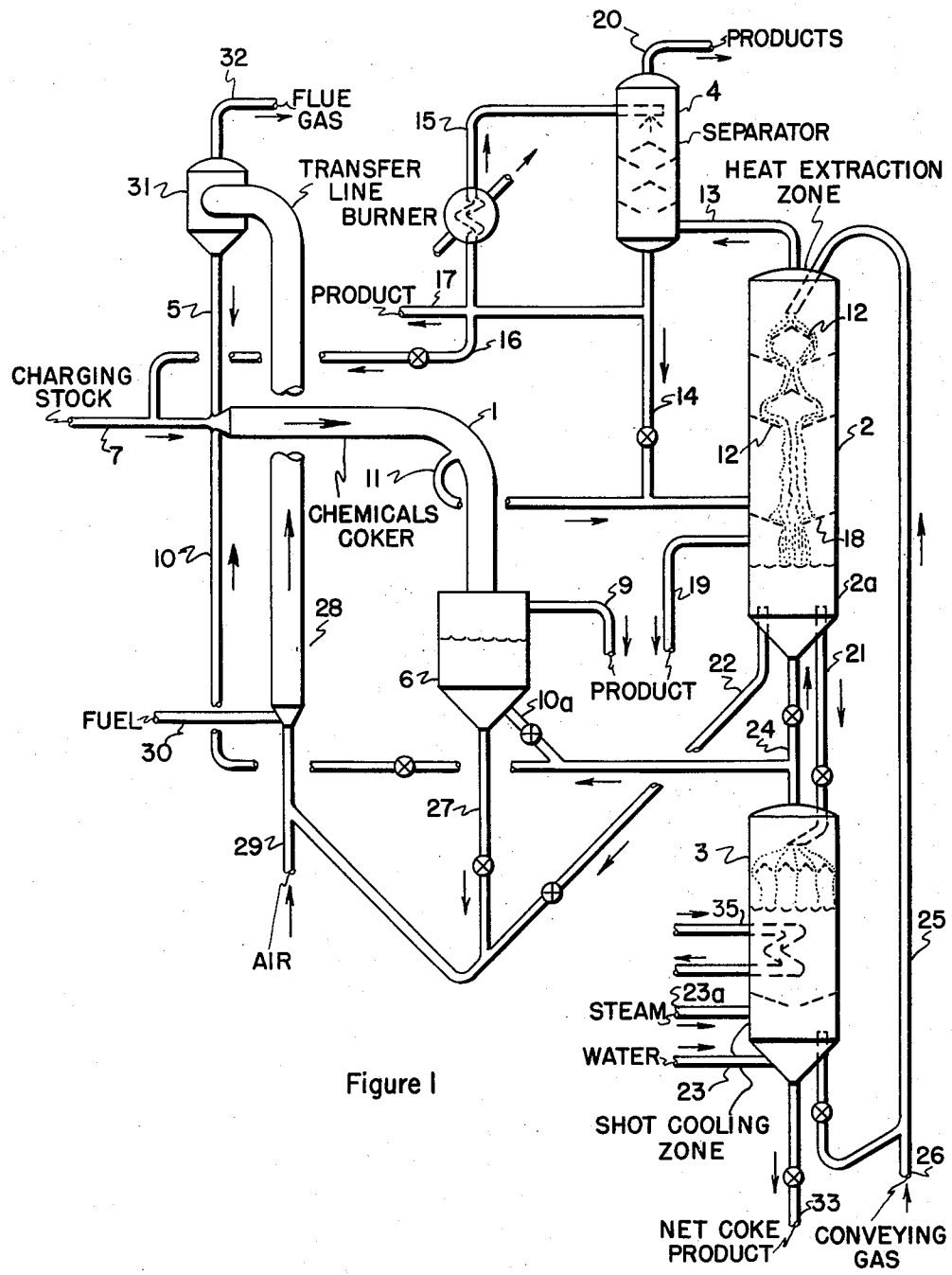


Figure I

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Filed Oct. 20, 1954 2 Sheets-Sheet 2

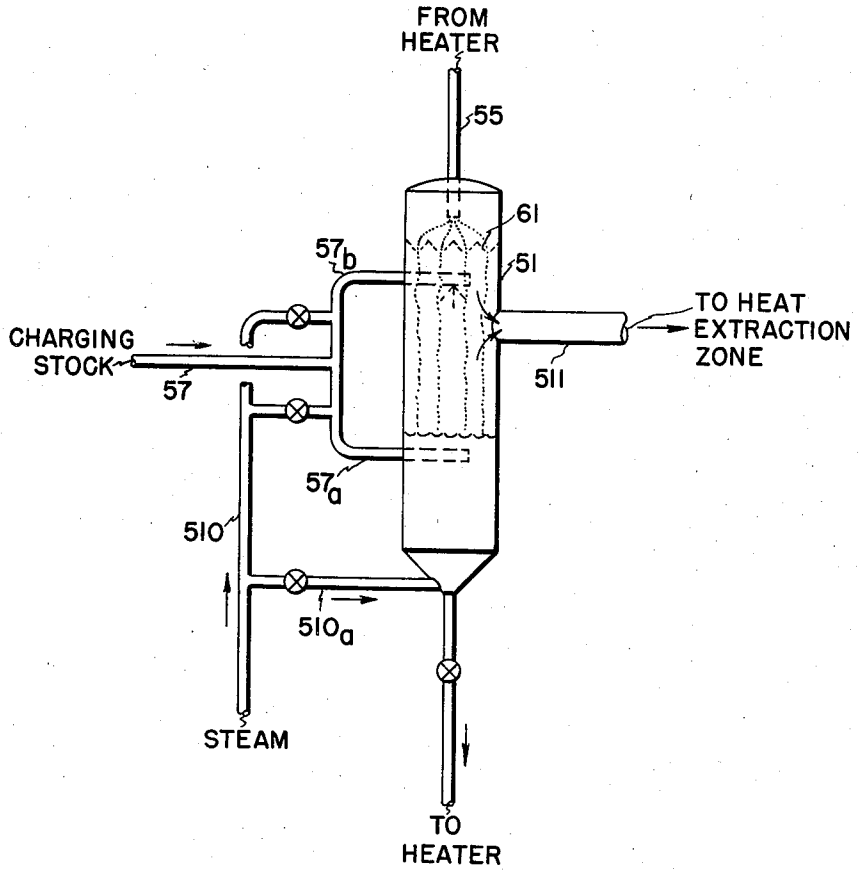


Figure 2

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United States Patent Office

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PROCESS FOR SECURING CHEMICALS FROM PETROLEUM RESIDUA

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Application October 20, 1954, Serial No. 463,529

10 Claims. (Cl. 196—49)

This invention relates to the art of converting hydrocarbons, particularly low value, heavy petroleum residua. It is concerned with a process for converting oils to products suitable for use as chemicals or chemical intermediates in a system utilizing heat carrying particulate solids. In accordance with this invention, heat economies are effected in a coking process converting oils to chemicals by using finely divided solids to quench and extract heat from the conversion products, and by utilizing the heat so recovered to generate steam and/or to preheat and vaporize the oil charged to the process. Minimum cracking times are realized in the practice of this invention leading to improved yields and qualities of the products.

Charging stocks suitable for use in present invention comprise petroleum residua containing refractory constituents and catalyst contaminants that render other methods of upgrading unattractive. Such low value high boiling residual oils are characterized by an API gravity between −10 and 20°, a Conradson carbon between 5 and 50 wt. percent, and an initial boiling point between 850 and 1200° F. Broadly, however, the present invention may find applicability in the converting of charging stocks comprising shale oils, asphalts, tars, pitches, coal tars, synthetic oils, cycle stocks, extracts, recycled heavy ends from the conversion products, whole crudes, heavy distillate or residual fractions therefrom, and mixtures thereof.

The prior art is familiar with processes wherein petroleum derivatives are converted at high temperatures by contact with heat carrying particulate solids to obtain low molecular weight hydrocarbon products suitable for use as chemicals or chemical intermediates upon separation and purification. In prior processes, because of the temperature of operation, the heat requirements of the processes have been unduly high. Various schemes have been previously proposed to recapture some of the heat from the conversion products, but they usually involve indirect heat transfer between the conversion products and various other streams. Such indirect heat transfer usually prevents rapid cooling of the products and involves fouling of the heat transferring surfaces. When converting petroleum oils at temperatures in the nature of 1400° F., rapid cooling of the vaporous conversion products within a time of about .01 to 0.10 second is desirable to avoid undue degradation of the conversion products.

In conventional fluidized solids systems for the conversion of oils at high temperatures, tubular heat exchangers have been used to recover heat from the high temperature products. The means of heat recovery has not proved practical, however, because the dust in the vapors deposits on the tubes and greatly reduces heat transfer. The present invention avoids this problem and accomplishes the desired recovery of heat from the conversion products by means of a fluidized solids heat exchange system.

It is an object of the present invention to present to the art a chemicals coking process that alleviates this problem of heat conservation and other difficulties. Another object is to propose an efficient chemicals coking process utilizing particulate solids as heat transfer media. Still another object of this invention is to devise a high temperature petroleum oil conversion process wherein vapor phase cracking of the initial conversion products is at a minimum, and maximum conservation of heat energy obtains.

These and other objects and advantages will become apparent as this description proceeds during which the attached drawings, forming a part of this specification, are described in detail. These drawings are presented by way of illustration only and the present invention is not to be limited thereto.

Figure I illustrates a preferred embodiment of the invention wherein the oil being converted flows concurrently through a transfer line coker along with the contact solids and rapid separation of the initial conversion products is obtained by centrifugal force in a simple elbow separator.

Figure II illustrates an alternative design of a chemicals coking reactor that can be used in the practice of this invention wherein there is countercurrent flow of the oil and contact solids and wherein the inertia of the relatively coarse contact solids is again utilized to secure rapid and reasonably complete separation of the conversion products from the contact solids.

In brief compass, this invention proposes a hydrocarbon conversion process which comprises contacting a charging stock with a stream of high temperature substantially catalytically inert particulate solids in a conversion zone, separating and withdrawing gasiform conversion products rapidly from the conversion zone and introducing the conversion products into an intermediate portion of a heat extraction zone, downwardly passing relatively cool particulate solids countercurrent to the conversion products in the heat extraction zone whereby the conversion products are cooled depositing condensate on the relatively cool particulate solids, withdrawing relatively cool conversion products overhead from the zone, collecting particulate solids in the lower portion of the heat extraction zone, cooling and circulating solids from the lower portion of the heat extraction zone to the upper portion thereof as the relatively cool particulate solids, and heating and circulating solids separated from the conversion products in the conversion zone to the inlet thereof as the high temperature particulate solids.

In a preferred embodiment of the invention, the solids that collect in the lower portion of the heat extraction zone are collected in a semi-segregated portion and are

held resident in this portion for a time sufficient to substantially completely convert the condensate on the solids and to dry the solids, the long time conversion products being separately withdrawn from the semi-segregated portion.

In another preferred embodiment of the invention, the solids collected in the bottom portion of the heat extraction zone are stripped and then cooled by contact with a vaporizable liquid medium e. g. water, in a cooling zone, the vapors therefrom being used in the process, and the cooled solids therefrom being circulated to the upper portion of the heat extraction zone.

The present invention is also concerned with an improved coking process wherein petroleum hydrocarbons are converted by contact with high temperature particulate solids, the improvement comprising passing the vaporous conversion products from the chemicals coking zone countercurrent to a stream of relatively cool particulate solids, whereby the products are cooled and the higher boiling portions therefrom are condensed on the relaitvely cool solids. The condensate containing solids are then subject to long time coking in a segregated coking zone to convert the liquid and to dry the solids. The dry solids are then cooled and recirculated to cool further amounts of the conversion products.

The coking temperatures that can be used in the practice of this invention may vary from about 120° to 2000° F. Preferably, temperatures in the range of 1300° to 1600° F. are used. The reheated solids from the heating zone may have an initial temperature 100° to 300° F. above the coking temperature. Generally stated, a higher initial temperature of the reheated solids permits a lower solids to oil circulation ratio to be used.

The heat carrying particulate solids that are used in the present invention may comprise any suitable subdivided material such as metal beads, sand, metal particles, mullite beads, finely divided ceramics, alumina, silicon carbide, etc. Preferably, however, coke produced by the process forms the heat carrying solid. Although substantially catalytically inert solids are preferably used, this invention encompasses the use of catalytic solids, either in the coking zone or in the heat extraction zone, or both. In some applications, particularly wherein lighter oils are being converted, there may be a particular advantage in using catalytically active solids to obtain a higher conversion and better product distribution, or to permit operations at a lower temperature.

As will appear, the solids are separated from the various gasiform streams, preferably, by simple change in direction rather than by the use of cyclones because cyclones have an undesirably long vapor holding time. Therefore, the solids have, preferably, a relatively large particle size in the range of about 400 to 5,000 microns, although the size may range beyond these limits in some cases.

Although the process of this invention may be most advantageously carried out in a four-vessel system, e. g., a chemicals coking zone, a heat extraction zone, a solids cooling zone and a heating zone for the circulated solids, other variations or combinations in the number of reaction of reaction vessels used will be readily apparent to those skilled in the art. Thus, a reduction in the number of vessels can be made by conducting two or more of the operations in separate or segregated zones within one vessel.

Any means of circulating solids between zones may be used as desired. Preferably, the solids are circulated using an extraneous gasiform transporting medium, e. g. steam, as is known in the art. Reference is made to co-pending application Serial No. 439,702 by Whiteley et al, as illustrative of one method of circulating solids applicable to the present invention.

The method of reheating the circulating solids forms no part of the present invention. Anyone of several types of heating systems may be used as desired. Thus, fluid bed burners or gravitating bed burners besides the transfer line burner illustrated may be used to combust a portion of the circulating coke and to heat the remaining portion, or any other direct or indirect heating means may be used. Shot circulation systems may be used in certain applications. Further, extraneous liquid or gaseous fuels may be burned in preference to the coke particles to supply heat thereto.

The operating conditions relating to the following example are conveniently summarized in Table I. Referring now to the attached Figure I, the major items of equipment shown are a chemicals coking zone **1**, a heat extraction zone **2**, with a long time coking zone **2***a* in the bottom portion thereof, a solids cooling zone **3**, and a product separation zone **4**. High temperature solids are admitted to the inlet of the coking zone by line **5** and contact the charging stock supplied by line **7**. Steam, or other conveying gas, is admitted to the coking zone by line **10** and conveys the solids and gases therethrough at velocities above about 10 feet per second, e. g., 40 feed per second.

The charging stock may, of course, be suitably preheated as by heat exchange with the various product streams, and may also be admixed with a dispersing medium, e. g. steam, to obtain better contact between the solids and the liquid. The injected charging stock, upon contact with the high temperature solids, undergoes pyrolysis evolving hydrocarbon vapors and depositing carbonaceous residue on the solids. Initial conversion of a charging stock in this zone preferably ranges from 20 to 50% conversion to propane and lighter products. An elbow separator is used to separate the contact solids from the conversion products. In passing around the bend, the solids are forced to the outside and the conversion products are withdrawn radially from the interior of the bend by line **11**. The solids, after the separation, pass downwardly into an expanded settling zone **6**. Because of the high temperature of the solids, the particles are substantially completely dried. Some stripping steam may be admitted to the base of the settling zone to sweep out hydrocarbons, the vapors being removed as product by line **9**.

The conversion products enter heat extraction zone **2** from line **11** wherein they contact cool free falling solids and are thereby rapidly cooled below cracking temperatures, e. g., below 800° to 1000° F. Baffles **12** or similar mixing means may be conveniently used in this sector to promote the efficiency of contacting. The heavier portions of the vapors are condensed on the solids, and the condensate and the solids collect in the lower portion **2***a* of the zone. The now cooled conversion products at vapor temperatures in the range of 500° to 800° F. are removed from the heat extraction via line 13. The conversion products may be separated as desired to obtain the various products fractions desired. As shown, they are initially scrubbed in separator zone **4** with a reflux oil to remove the higher boiling portions of the vapors. This higher boiling portion may have initial boiling point in the range of 500° to 800° F. A portion of the oil so condensed may be passed by line **14** to line **11** to partially quench the temperature conversion products, as is hereinafter described. Another portion may be recycled and cooled via line **15** to serve as a reflux or scrubbing oil. Desirably, the remainder is recycled via line **16** to the coking zone to be treated substantially to extinction therein although some of this condensed material, which will be highly aromatic, can be removed from the process as product by line **17**.

Returning to the heat extraction zone, the wet solids collected in the lower zone **2***a* may be stripped and then transferred to cooling zone **3**. However, this permits mingling of the long time conversion products with the primary conversion products which may be disadvantageous in certain applications. Preferably, the lower portion of the heat extraction zone is separated from the

upper portion by baffle **18** or other means, and the coke and the condensate collected thereon are held resident in the lower zone at a temperature of about 1000° to 1400° F. to substantially completely convert the condensed material. The long time gasiform conversion products formed therein are removed by line **19** and may be separated by conventional means. Both the products in line **19** and the products removed from separator **4** via line **20** can be separated as by fractionation, absorption, crystalization extraction etc. to obtain products of the desired purity and boiling range.

The solids in the bottom of the heat extraction are withdrawn and transferred to cooling zone **3** via line **21** or other means. A portion of these solids may be transferred by line **22** to the heating zone, as described hereinafter. Water is injected into the cooling zone by line **23** and contacts the high temperature solids therein. Preferably, the solids are maintained as a fluidized bed, or they can be in the form of a moving fixed bed. In some cases steam only may be injected into the zone to be super-heated as by line **23***a*, or steam-water mixtures may be injected. The steam generated in the cooling zone is removed from the upper portion of the zone by line **24** and may be utilized to fluidize the solids in the lower portions of zone **6** and heat extraction zone **2**. Because it is desirable to use a diluent when coking to produce chemically, a major portion of the steam is preferably transferred to vessel **1** by line **10**. Dependent upon the circulation rate a sufficient amount of water is introduced in the zone to cool the solids to a temperature in the range of about 300° to 700° F. Additional heat may be removed via exchanger **35**, and used to preheat feed, etc. The cool solids are circulated from the zone by line **25** to the upper portion of the heat extraction zone. A conveying gas, e. g. steam, is admitted to line **25** by line **26** to aid in the transportation of the solids as is known by the art. The net coke product of the process can conveniently be removed from the cooling zone by line **33**.

To supply heat to the process, solids are transferred from the bottom of the coking zone by line **27** to a heating zone, e. g., transfer line burner **28**. Air is admitted to the base of the burner by line **29** and serves not only to partially combust the particles but also to convey via entrainment the particles through the elongated burner at velocities above about 10 feet per second, e. g., 40 feet per second. As previously mentioned, extraneous fuels can be admitted to the heating zone by line **30**. After passing through the burner the heated solids are removed from the flue gases in cyclone **31**, the flue gases being withdrawn via line **32**. The heated solids are then transferred by line **5** to the coking zone.

In some applications, particularly when relatively high temperatures are being used, it may be desired to at least partially quench the initial conversion products in line **11**. Steam, water, cool solids etc. may be used to accomplish this quenching. It is preferred, however, to use a heavy oil fraction to attain this quenching. Thus, line **14** can inject sufficient amount of the heavier ends separated from the vapors in separator **4** to cool the initial conversion products. Preferably, the products are only cooled in this alternative mode of operation only by about 200° F. to avoid undue heat loss.

From this description it will be apparent that two different types of solids, e. g., catalytic and non-catalytic, of perhaps different particles size may be circulated in the chemicals coker-heating zone circuit and in the heat extraction zone-cooling zone circuit.

The following Table I summarizes the pertinent range of operating conditions applicable to the present invention illustrated in Figure I and presents a specific example of operating conditions. Table II illustrates the products obtainable from the charging stock indicated when the process is operated in accordance with the example of Table I.

Table I

	Range	Example
Pressures, p. s. i.:		
In chemicals coker @ vapor outlet	0–400	7
In heat extraction zone @ vapor outlet	0–400	5
In shot cooler @ vapor outlet	0–400	15
Inlet of transfer line burner	1–10	3
Temperatures, ° F.:		
Outlet of transfer line burner	1,400–2,000	1,500
Solids settling zone of chemicals coker	1,200–1,800	1,300
Vapors passed to heat extraction zone	1,200–1,800	1,325
Bottom of heat extraction zone	1,000–1,700	1,125
Vapors from heat extraction zone	400–900	600
Shot cooler at bottom	250–500	400
Coke Circulation, lbs./lb. fresh feed:		
Heated solids to chemicals coker	5–20	15
Cool solids to heat exchange zone	0. 5–10	2
Solids from heat exchange zone to cooling zone	0. 5–10	2
Solids from heat exchange zone to heating zone	0–5	1
Net product coke	0. 05–. 49	.20
Conversion, [1] basis C_3−:		
In chemicals coking zone	20–60	30
Overall conversion	25–80	35
Steam, wt. percent of fresh feed:		
To chemicals coker	5–50	10
To heat exchange zone	1–5	3
Recycle stock, wt. percent of fresh feed:	5–50	20
Initial boiling point, °F	400–800	650

[1] C_3− conversion is defined as: 100 wt. percent feed less wt. percent of products having 3 carbon atoms and less, excluding coke, based on fresh feed.

Table II

Charging stock: 2.4% South Louisiana residuum

Inspections:

10.7, ° API gravity
17, Conradson carbon
1100° F., initial boiling point
0.74, wt. percent sulphur
0.48, wt. percent ash @ 1100° F.
396, ° SSF viscosity @ 210° F.
105° F., pour

Products: Wt. percent of fresh feed:

Nonhydrocarbons	0.9
H_2	0.6
CH_4	5.8
C_2H_4	10.6
C_2H_6	2.4
C_3H_6	8.9
C_3H_8	0.5
C_4H_6	3.1
C_4H_8	3.7
C_4H_{10}	0.2
C_5—430	[1] 16.7
Benzene	3.1
430°—650° F	7.6
650° F.+	15.9
Gross coke	20.0

[1] Excluding benzene.

Referring now to Figure II, there is shown an alternative apparatus for carrying out the chemicals coking reaction. Parts similar to those in Figure 1 have the same numerical designation, being differentiated by the prefix **5**. The charging stock is injected into the coking zone via lines **57** and **57***a* wherein it contacts high temperature fluidized solids in the lower portion of the zone and undergoes pyrolysis. Steam supplied by line **510** may be used to disperse the oil. The reheated solids are admitted to the upper portion of the zone by line **55** and may be suitably dispersed throughout the zone by distributing bars or grid **61**. The vapors generated in the lower portion rise countercurrently to the falling solids and are further cracked. The conversion products are then rapidly removed from the contact solids by being transversely withdrawn from the coking zone via line **511** and are passed to the heat extraction zone. The contact solids used in this arrangement are, preferably, relatively coarse so as to favor this separation.

The contact solids are collected as a fluidized bed in the lower portion and are stripped with steam supplied by line 510*a* before being circulated to a heating zone to be reheated.

Having described the invention, other variations will become apparent to those skilled in the art. For example, the system of Figure II is adaptable to processing mixed feed streams. Thus, a more refractory material such as a cycle stock may be introduced into the lower portion of the reactor of Figure II as shown wherein it can have a longer contact time, and a lighter stock such as a gas oil may be introduced into the upper portion via line 57*b*. Further, the reheated solids need not only be introduced into the coking zones as illustrated, but a portion of the reheated solids may be separately introduced into the settling zone of the coking zone of Figure I and into the lower portion of the coking zone of Figure II containing the fluid bed whereby independent temperature control can be maintained in these portions.

Having described the invention what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. A hydrocarbon conversion process for the production of chemicals which comprises contacting a heavy hydrocarbon oil charging stock with a stream of high temperature substantially catalytically inert particulate solids in a conversion zone at a temperature in the range of 1200° to 2000° F., rapidly separating and withdrawing gasiform conversion products and introducing the conversion products into an intermediate portion of an extraneous heat extraction zone, downwardly passing relatively cool, substantially non-entrainable, particulate solids countercurrent to said conversion products in said heat extraction zone whereby said conversion products are cooled depositing condensate on said relatively cool particulate solids, withdrawing relatively cool conversion products overhead from said zone, collecting particulate solids in a lower segregated portion of said heat extraction zone, long term conversion products being separately withdrawn from said segregated portion, the solids remaining resident in said segregated portion at a temperature in the range of 1000° to 1700° F., and for a time sufficient to substantially completely convert the condensate thereon and to dry said solids, cooling and stripping solids from the lower portion of said heat extraction zone in an enlarged settling zone and recirculating them to the upper portion of the heat extraction zone as said relatively cool particulate solids, and reheating and returning solids separated from said conversion products to said conversion zone.

2. The process of claim 1 wherein said conversion zone comprises a transfer line zone and wherein the gasiform conversion products are separated by centrifugal force in an elbow separator, the gases being withdrawn radially from the inner part of said separator.

3. The process of claim 1 wherein said charging stock comprises petroleum hydrocarbons having an API gravity in the range of −10 to 20°, a Conradson carbon in the range of 5 to 50 wt. percent, and an initial boiling point in the range of 850° to 1200° F.

4. The process of claim 1 wherein said conversion zone is vertically disposed, wherein said particulate solids fall downwardly therethrough, and wherein said conversion products are separated by being withdrawn from an intermediate portion of said conversion zone transversely to the flow path of the solids.

5. The process of claim 1 wherein said particulate solids comprise petroleum coke produced by the process having a particle size substantially in the range of 400 to 2000 microns.

6. The process of claim 1 wherein said particulate solids circulated from the lower portion of said heat extraction zone to the upper portion thereof are cooled by contact with a vaporizable liquid medium in the settling cooling zone, the vapors therefrom being used in the process.

7. The process of claim 6 wherein said vaporizable liquid medium comprises water, and the steam generated thereby is utilized as stripping and diluting media in said conversion and heat extraction zones.

8. The process of claim 1 wherein the higher boiling portion of said relatively cool conversion products is separated therefrom, and is utilized to partially quench the gasiform conversion products withdrawn from said conversion zone.

9. A process for the production of petro-chemicals and intermediates comprising the steps of heating particulate solids to a temperature in the range of 1400° to 2000° F., passing the solids so heated through a conversion zone, contacting a charging stock with the heated solids in proportions of 5 to 20 lbs. of solids per pound of said charging stock thereby forming gasiform conversion products and carbonaceous residue which is deposited on the solids, withdrawing said gasiform conversion products from said conversion zone transversely to the path of flow of the solids, passing the conversion products countercurrently to a stream of relatively cool particulate solids in proportions of 0.5 to 10 lbs. of solids per pound of said charging stock whereby said conversion products are cooled to a temperature below 900° F. depositing condensate on said solids, withdrawing said conversion products so cooled overhead from said heat extraction zone, collecting solids in a separate lower portion of said heat extraction zone and permitting the solids to remain resident therein for a time and at a temperature in the range of 1000° to 1700° F. sufficient to convert said condensate, separately withdrawing from said lower portion the long time conversion products, stripping and passing solids from the lower portion of said heat extraction zone to a cooling zone, introducing water into the cooling zone to cool the solids therein to a temperature below 500° F. and to generate steam, utilizing the steam so generated in the process, passing cool solids from said cooling zone to the upper portion of said heat extraction zone, and transferring stripped solids from said conversion zone through a heating zone to the inlet portion of said conversion zone, the initial C_3— conversion of charging stock in said conversion zone being in the range of 20 to 60 wt. percent, and the ultimate C_3— conversion of said charging stock being in the range of 25 to 80%.

10. The process of claim 9 wherein the average residence time of said gasiform conversion products before being cooled is less than 0.1 second.

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