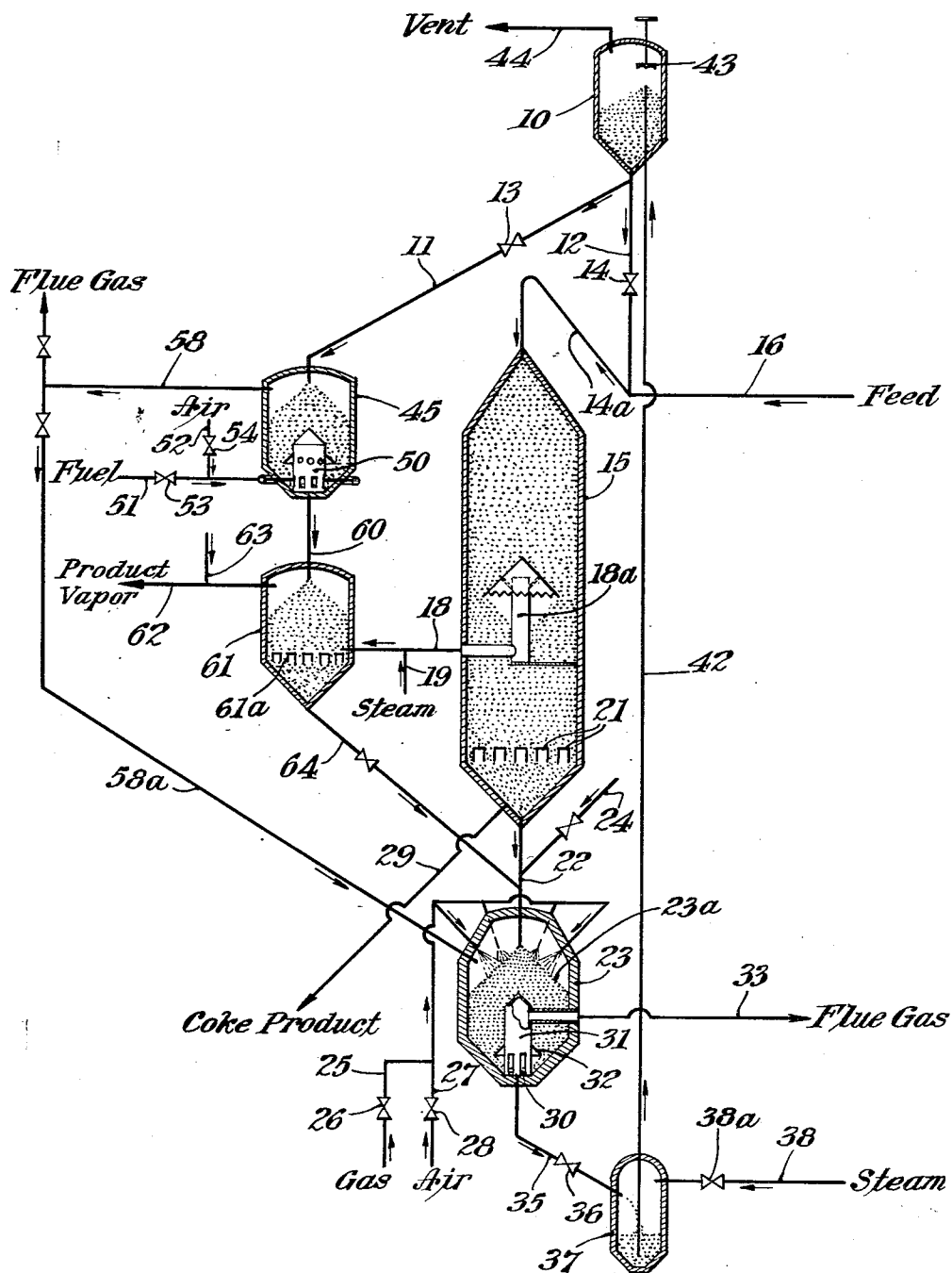


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HYDROCARBON CONVERSION

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2,789,084

HYDROCARBON CONVERSION

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This invention relates to the conversion of hydrocarbons in a freely-flowing, gravity-packed bed of granular materials to simultaneously produce high yields of coke and gaseous unsaturated lower hydrocarbons.

This application is a continuation-in-part of the invention disclosed in my co-pending application, Serial No. 191,543, filed October 23, 1950, now abandoned, and entitled, Hydrocarbon Conversion, which is a continuation-in-part of copending application Serial Number 651,598, filed March 2, 1946, now Patent No. 2,526,696 and entitled "Process for the Simultaneous Production of Coke and Gaseous Unsaturated Hydrocarbons and Apparatus Therefor." In this earlier case, reference has been made to the cracking of various heavy hydrocarbons by the introduction of the hydrocarbon charge to a point below the surface of a preheated continuously-moving bed of porous solids which passes through a confined reaction and regeneration zone solely by gravity. It has been pointed out that the contact material may be inactive or inert, serving only as a heat carrying material and as a coke repository. Proper control of the ratio of charge to contact material prevents gumming, sticking, or cementing of the particles in the bed.

It has also been pointed out that the temperature limits possible in such an operation are dependent only on the character and properties of the contact material and that the normal temperature limitation of cracking in a tubular heater is avoided. It is well known, of course, that except for relatively light stocks, temperatures in a tubular heater cannot be excessive because of the undesirable coke deposition formed on the tubes under these conditions. It is for this reason that charge stocks boiling above 800° F. to 900° F. (at atmospheric pressure), as well as most residual stocks, have usually been sold as residual fuel oil.

In accordance with the present invention, it is found desirable to independently control two portions of the same heated stream of granular materials and to thus operate a liquid phase operation and a vapor phase operation, each under the most favorable conditions. It is possible to conduct operations according to my new process at temperatures substantially higher than has heretofore been the case, as for example, in the so-called thermal cracking as conducted in tubular heaters.

With the substantially higher temperatures at which both the liquid and vapor cracking are accomplished (especially the latter), only a very short time is required for completion of the reaction. Furthermore it is possible to obtain a precise control of the various reactions by independently maintaining the separate zones in such a manner that both the liquid-coking reaction and the vapor-cracking reaction are conducted at maximum efficiency, each at the desirable temperature.

According to my present invention I feed a heavy residual charge stock to an upper part of a liquid-cracking zone and permit a portion of the liquid to crack and distill off, the residue being eventually converted to coke.

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This vapor is passed to a separate bed or zone which may be described as being essentially shallow (in comparison to the liquid-coking bed hereinafter referred to), and is adapted to produce a short-time vapor cracking at comparatively high temperature. Suitable quenching may be provided for the effluent of this vapor cracking.

Simultaneously with this high temperature, short-time vapor cracking, it is also possible in accordance with my invention to include a long-time, less drastic liquid-phase cracking. The liquid cracking bed will be sufficiently deep so that the deposited coke may have time to dry out and to thus produce at the lower end of the bed a substantially dry particle. Vapors produced in the liquid-cracking or coking zone are passed to the vapor-cracking zone along with the vapors formed by flashing the charge stock.

In reheating the granular contact material to the temperatures required for carrying out the respective reactions, the contact material from both reaction zones is preferably combined and passed to a common reheating zone, wherein the contact material is reheated at least to the degree required for the low temperature liquid coking. The portion of contact material used for vapor phase cracking is then passed to an outside high temperature reheating zone for further heating to a temperature sufficient to carry out vapor phase cracking.

Control of combustion conditions in the secondary reheater provides the required heat by the combustion of coke passing through the reheater. It is of course well known that the percentage of carbon monoxide in mixtures of carbon monoxide and carbon dioxide resulting from the combustion of carbon at temperatures above 1400° F. greatly predominates so that at 2000° F. better than 90% CO is formed. Maintaining reheater temperature in such a temperature range provides a flue gas stream which when recycled to the primary or low temperature reheater provides on burning with excess oxygen a substantial amount of the heat required in the primary reheater.

One of the objects of this invention is to provide a new and improved method and apparatus for economically effecting controlled cracking of hydrocarbons by the use of a freely-flowing, gravity-packed bed of granular material, with a resulting conversion of hydrocarbons to coke, used in connection with a separate and independently controlled bed of similar nature wherein vapors from the first bed may be converted to high yields of lower unsaturated hydrocarbons such as ethylene, propylene, and acetylene.

A further object of this method is to provide a hydrocarbon conversion system characterized by a high degree of flexibility and control and wherein the type and quality of the product may be more readily and conveniently controlled than has heretofore been the case.

A more specific object of my invention is to produce as a preferred end product, a high percentage of gaseous olefins by high temperature cracking in a comparatively shallow, continuously moving, gravity-packed bed of granular coke.

A further object of my invention is to treat a residual oil to produce coke and an unsaturated gas as the only major end products.

A further object of my invention is to simultaneously perform a vapor phase cracking at high temperature and of short duration in one part of a continuously moving bed of granular material, while simultaneously obtaining the optimum conditions for liquid phase cracking and coking in a separate and independently controlled bed of the same granular material.

A further object of my invention is to set forth a system wherein a maximum utilization of heat may be main-

tained by virtue of the incremental heating of a portion of a single stream of flowing granular material.

A still further object of my invention is to increase the efficiency of a low temperature and high temperature reheating operation by a more effective utilization of flue gas.

Further objects and advantages of my invention will be apparent from the following description of a preferred embodiment of my invention taken in connection with the attached drawing.

In the customary cracking operation, whether in a tubular heater or in a catalytic fixed or flowing bed, it is well known that some portion of the products will be lighter hydrocarbons having less than four carbon atoms to the molecule. Of these perhaps the most important is ethylene which is of considerable use in the petrochemical industry. Ordinarily the production of ethylene is largely incidental and is somewhat small because of the limited temperature conditions. Conventional cracking methods for producing large yields of gaseous olefins employ very expensive equipment which frequently requires the use of special alloys. Deposition of coke on the heating surfaces necessarily limits the length of the run. In these processes the charge stock is generally propane or some other light distillate such as kerosene which is relatively inexpensive. It is noted however that propane is not available in many sections of the country.

I have found that I can obtain large percentages of the gaseous olefins by feeding a heavy hydrocarbon directly into the hereinafter described unit. This hydrocarbon may be a very heavy oil, or a crude residue, and may include materials containing lighter compounds. This is accomplished by applying the charge to a preheated, gravity-packed, free-flowing body of granular material which is preferably non-catalytic and may, for example, be of a highly refractory nature. Examples of this material include "Alundum," "Carborundum," pumice, fire brick, porous ceramic particles, spent catalyst, "Koppers" coke, petroleum coke, or other normally inactive granular materials which can withstand temperatures up to 2600° F. Coke is an ideal material for this process since it will withstand the extremely high temperatures met in the process and since it may be reheated by partial combustion or partial conversion by the water gas or air gas reaction. It is to be noted that the reactions referred to in this description are essentially non-catalytic in nature, and may be best described as thermal cracking.

By applying the hydrocarbon charge to the hot granular solids as they enter the liquid-coking zone, I obtain a vaporization and cracking of the liquid constituents. Vaporous material removed from the liquid cracking or coking zone is sufficiently suitable in character so that it may be used as a feed stock for the vapor cracking zone. By operating in this manner it is possible to avoid the difficulties arising from coke deposition inherent in the vaporization of these heavier components. Whereas I prefer to feed a liquid charge to the coking zone, it is possible that the charge can consist of a mixture of liquid and vapor.

The conditions existing in gravity-moving beds of inert material are ideally suited to both liquid and vapor cracking in the manner hereinafter described. These conditions are substantially as follows:

(1) There is present a continuous, moving, non-turbulent mass of heated solid particles which presents, in effect, a continuously supplied clean heating surface.

(2) The rate of heat transfer and the particle surface area provided for heat transfer to the vapor phase cracking zone are both of a high order of magnitude permitting high-temperature short-time cracking.

(3) Time factors are subject to precise control during operation.

(4) Flexibility of operation may be accomplished by the selected removal of the vapors at different levels or distances of flow.

(5) Maximum temperatures possible are greater than with heating in tubular heaters.

(6) The vapor cracking bed is relatively shallow as compared to the liquid bed.

(7) If cracking is desired at low hydrocarbon partial pressures, steam or other gas may be introduced with the charge to produce the required effect. Steam or gas is not required for the purpose of adjusting the cracking time, as in the case of high-temperature, short-time coil cracking.

(8) For deep or severe cracking operations, this method has a unique advantage over coil cracking in that the cracking reaction heat requirements are very small or negligible. Where coke formation cannot be allowed, as in tubular cracking, the reaction heats may be as high as 1000 B. t. u. per pound of charge when running for the optimum production of ethylene.

An illustrative form of embodiment of the apparatus in which I have found it desirable to carry out my invention, is shown in the attached drawing in which the numeral 10 represents a receiver or accumulator for the hot contact material. These hot inert granules pass through lines 11 and 12 under the control of valves 13 and 14 respectively. The major portion of the particles pass to liquid-coking reactor 15 hereinafter referred to as the first reactor, the liquid coker, or merely the coker. The porous, inert, solid particles are conveyed throughout the entire system solely by gravity except as hereinafter referred to.

The reactor 15, as shown, tapers downwardly and outwardly from the inlet to the main portion, and then downwardly and inwardly at the bottom from the main portion to the outlet. This reactor may be fabricated in substantially the same manner as the reactor described in detail in U. S. 2,526,696. It may be round or rectangular as desired. Sealing steam may be applied to the inlet line 12 of reactor 15 and also at other locations, not generally shown, in the lines between the various vessels hereinafter referred to. The purpose of this steam is to prevent the flow of gases and vapors from the vessels into adjoining lines and vessels.

Hydrocarbon feed in line 16 is introduced into the flowing stream of contact materials in line 14 and is mixed therewith prior to introduction into the reactor 15. If desired, feed 16 could be introduced into the upper part of the reactor directly by a feed mechanism such as described in U. S. 2,326,696, so that a substantially uniform distribution of the hydrocarbon charge is obtained throughout the cross-sectional area of the reactor. It has been found however that introduction of the feed into the transfer line, such as 14, is to be preferred since a better distribution of the hydrocarbon on the contact particle can be obtained.

As shown in the drawing, reactor 15 is provided with a vapor disengager 18a which is connected with vapor draw-off line 18. During the course of the conversion reaction a part of the feed is vaporized with the remaining portion of the feed being reduced to a dried surface on the coke particle. Vapors produced in the reaction are disengaged by means of the disengager 18a and are withdrawn through line 18. If desired, steam may be introduced through line 19 for the purpose of controlling partial pressure of the vapor in line 18.

Reactor 15 has a drawoff 29 through which granules may be removed from the reactor. A drawoff 22, leading to regenerator or first heater 23, is joined thereto above by feed line 24 through which fresh granules may be introduced to the system, and line 64 containing granules from a source hereinafter referred to. These combined granules are heated in regenerator 24 by combustion of a fuel gas admitted through line 25 under the control of valve 26 and flue gas recycled from the high temperature reheater 45 by way of line 38a. Air for combustion is admitted through line 27 under the con-

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trol of valve 28. The granules only fill vessel 23 to the extent that an upper surface 23a is present. Thus the burners heat the material at this surface.

Combustion gases pass downwardly through the bed concurrently with the descending granules and leave through the holes 30 in the disengager 31 and pass through the gas outlet 33. Disengager 31 is conveniently centrally located in the chamber 23 and may have a cone top to aid in directing the flow of particles. A short baffle 32 partially covers the holes 30 and further assist the flow of granules. Heated granules intermittently leave the regenerator 23 through line 35 and pass through valve 36 to lift pot 37.

Lift pot 37 contains pressuring line 38 through which air or steam may be passed under the control of valve 38a. Lift leg 42 enters pot 37 at the top. At the top of lift leg 42 is located baffle 43 which arrest the flow of ascending material. Line 44 permits the lift gas introduced at 38 to escape.

A portion of the elevated granules are passed to vessel 45 through line 11 under the control of valve 13. This vessel is supplied with air inlet line 52 controlled by valve 54 and a flue gas outlet line 58. Heating vessel 45 is connected to vapor-cracking vessel 61 by line 60. This latter vessel has product outlet line 62 into which quenching medium may be injected through line 63. Vessel 61 is provided with flow control plates 61a similar to plates 21 of vessel 15 to regulate the particle flow.

Vessel 15 may be referred to as a reactor, a coker, a liquid-coker, or as a liquid cracker and coker and the term "coking" will be generally applied to the reactions occurring therein. Vessel 61 is a vapor cracker, or more simply a cracker. Vessel 37 is a lift pot, and vessel 10, an accumulator or separator surge drum. Vessel 23, which may be located above vessels 15 and 45, is a first regenerator or heater and vessel 45 is a second regenerator or heater.

A particular embodiment of this process is designed to feed a West Texas-New Mexico sweet residuum having the following composition:

Gravity, ° API	14.2
Sp. gr., 60/60° F.	0.9713
Color	Black
Pour point, ° F.	75
Viscosity, S. F. S. ¹ @ 210° F.	180
Flash point, ° F., C. O. C. ²	680
Fire point, ° F., C. O. C. ²	755
Carbon residue, wt. percent:	
Ramsbottom	11.8
Conradson	13.0

¹ Saybolt furl seconds.

² Cleveland open cup.

This charge stock, heated to about 650–850° F., was introduced along with the coke particles to the reactor by way of line 14a. The coke particles in line 12 are normally at a temperature of 900–1050° F.

The lighter materials are removed from the charge oil in the manner hereinbefore referred to and the residual coke deposits evenly on the descending bed as it passes through the coker. Due to the comparatively long residence time in coker 15 (which may be 30 or 40 minutes), the coke dries and becomes partially calcined; most of the volatiles are removed therefrom. In this manner, a hard product coke is produced which may be withdrawn from the coker by line 29 under the control of a valve not shown. This product, described more fully in applicant's U. S. Patent 2,600,078, June 10, 1952, may be briefly described as follows: dense (true density 1.9 g./cc.; apparent density 1.39 g./cc.), non-porous; hard (crushing strength for ½" particle 300 pounds, for ¾" particle 400–500 pounds; round—¼" to 1.5" major dimension, regular, smooth, low coefficient of expansion, high specific heat, low volatile (less than 5–8%).

The major portion of the coke from reactor 15 is

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passed downwardly through line 22 to regenerator 23. Fuel, air and flue gas admitted through lines 25, 27 and 58a regenerate the coke by heating it to about 900° F. Flue gases pass downwardly through the bed and leave through ports 30 in the disengager 31 and then through flue gas outlet 33. The heated coke passes downwardly past baffle 32, through ports 30 and line 35 to vessel 37.

When the proper amount of coke has been admitted to the vessel 37, the valve 36 is closed and valve 38a is opened, admitting steam to the bottom of the lift. The regenerated or hot particles will then be conveyed through lift leg 42 to accumulator 10. This lift will operate intermittently or continuously.

Fresh feed coke will be introduced through line 24 either continuously or intermittently as conditions require.

Particles from vessel 10 are returned to the vessels 15 and 45. Under the conditions hereinbefore set forth, from 40% to about 80% of the particles will be passed to the coker 15 although these limits will depend entirely upon the particular operating conditions present and the heat balance requirements for the individual zones.

When feeding a charge stock as hereinbefore set forth in detail, an overhead cut may be removed through line 18 which has substantially the characteristics of a synthetic crude oil of 20° to 30° API gravity. Such crude might be made up of essentially the following constituents:

Name	Molecular Wt.	Weight Percent
Gas	37.2	16.1
Gasoline	116	11.5
Gas Oil	300	39.0
Recycle Stock	350	33.4
		100.0

Whereas a reduced crude having the characteristics described will produce such a synthetic crude, if the charge stock to coker 15 were a heavier bottoms, as for example an asphalt, then the overhead in line 18 would be correspondingly heavier than the synthetic crude. Where the feed to the unit is somewhat lighter, as for example a heavy crude, the overhead may consist of more components boiling within the gasoline-naphtha-kerosene range. It is recognized, of course, that the carbon content as measured by the Conradson test will vary for these stocks generally increasing in the order: heavy crude, reduced crude, asphalt.

The vapor product of the conversion in vessel 15 at a temperature of about 900° F. is passed through line 18 to vapor cracker 61. At this point the vapors contact the hot descending particles which have been heated to about 1800° F. to 2000° F. (depending on the precise reaction to be accomplished). These particles are usually cooled by about 600–800° F. as they pass through the reaction vessel 61. The gaseous products leaving vessel 61 through line 62 will contain acetylene, ethylene, propylene and lesser amounts of methane, ethane, carbon monoxide, carbon dioxide, as well as some tar and carbon. The vapor contact time in vessel 61 is from 0.1 second to several seconds.

For maximum yields of acetylene, the average temperature in the bed 61 will be between about 2372° F. (1300° C.) and 2552° F. (1400° C.). At 1350° C. the effluent gas will have about the following composition:

	Percent
Acetylene	35
Ethylene	23
Propylene	2
Benzene	5
Methane	15
CO and CO ₂	2
Residues	18
	100

The high percentage of acetylene found in this gas is believed to be sufficiently great to warrant an economical recovery.

Where ethylene is the desired product, the average temperature in the bed 61 will be between about 1100° C. (2012° F.) and 1250° C. (2282° F.). In this range, e. g. at 1147° C., the composition of the effluent gas will be about as follows:

	Percent
Acetylene -----	16
Ethylene -----	42
Propylene -----	10
Benzene -----	5
Methane -----	15
CO and CO ₂ -----	2
Residues -----	10
	100

Where propylene is the desired product, the temperature is maintained between about 1832° F. (1000° C.) and 2012° F. (1100° C.). In this range the products from vessel 45 are as follows:

	Percent
Acetylene -----	5
Ethylene -----	40
Butylene -----	3
Propylene -----	20
Ethane -----	18
Methane -----	8
Residues -----	6
	100

This represents an economically recoverable yield of propylene.

The possibility of achieving such satisfactory results is indicated by the article to Hasche (Chem. and Met.) pages 78-79 (1942) and other sources.

The effluent vapors leave the vessel 61 at a temperature 200-400° F. below the entrance temperature of the particles. The particles are cooled by as much as 400-800° F. in passing through the vessel 61. They are then passed to the regenerator 23 in which they come in contact with the particles from vessel 15. Since the temperature of the particles in line 64 is higher than those in line 22, they help to reheat the coke from the coking zone. This decreases the load on the regenerator 23. The pressure in the system is generally atmospheric or slightly higher, but seldom greater than 50 p. s. i. g.

The quench line 63 is provided for introduction of liquid quench oil or other quench medium by means of which the temperature of the effluent gases may be reduced to below the reaction temperatures, before being passed to a recovery system.

I prefer to employ coke as the solid, granular bed material and thus make possible the withdrawal of a high quality petroleum coke formed by the deposition of the coke deposits from the feed. Regeneration may also be easily accomplished by burning enough of the bed material to replace the heat consumed in the reaction. Generally regeneration will be accomplished in reheater 23 by burning fuel gases in line 24, thus heating the granules as hereinbefore described.

Regeneration in the high temperature reheater is carried out by a controlled combustion of the coke particles at temperatures which produce a flue gas predominating in carbon monoxide. At temperatures of approximately 2000° F. the flue gas will contain better than 90% carbon monoxide. The recycle of this flue gas through lines 58 and 58a to the primary reheater 23 provides an additional source of reheat fuel which substantially reduces overall fuel requirements.

It is of course to be noted that the particles hereinbefore referred to may be employed and that this process as herein contemplated is substantially non-catalytic in nature, its basic nature being thermal cracking.

While I have shown and described a preferred form of embodiment of my invention, I am aware that modifications may be made thereto and I desire a broad interpretation of the invention within the scope and spirit of the description herein and of the claims appended hereinafter.

I claim:

1. The process for thermally treating a heavy hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule which comprises continuously moving a continuous gravity-packed column of heated solid coke particles downwardly by gravity through a coking operation, continuously introducing said heavy hydrocarbon, a portion of which is in the liquid phase, to the upper part of said column whereby a portion of said hydrocarbon charge is vaporized, maintaining the temperature of said column in said coking operation such as to mildly crack the liquid portion of said hydrocarbon charge whereby the unvaporized portion of said hydrocarbon charge is ultimately converted to dry coke on the solid particles and to additional vapors, passing said coked solid particles through a lower part of said coking operation wherein said coke is dried on said coked particles, combining said first-mentioned vapors and said additional vapors to form combined vapors from said coking operation, passing said combined vapors to an independent vapor-cracking operation containing an independent, continuously moving, continuous, gravity-packed column of solid coke particles, maintaining said combined vapors in said vapor-cracking operation for a period of from a fraction of a second to several seconds, maintaining the temperature of said column in said vapor-cracking operation in the range from 1200-2600° F. thereby producing an effluent containing a high percentage of unsaturated hydrocarbons containing less than four carbon atoms to the molecule, quenching said effluent, withdrawing solid particles from said liquid-coking operation and said vapor-cracking operation into a common first heating operation, reheating said particles therein to a temperature in the order of 900° F. to 1050° F. and sufficient to maintain the desired reaction in said coking operation, returning a portion of the reheated particles to the coking operation, passing another portion of said reheated particles through a second heating operation, heating said particles in said second heating operation to a temperature in the order of 2000° F. to 2600° F. and sufficient to effect said short-time, high temperature vapor reaction in said vapor-cracking operation, passing said last-mentioned particles to said vapor-cracking operation, and drawing off the net make of coke particles as product.

2. The process for thermally treating a heavy hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule as claimed in claim 1 wherein said additional vapors and said first-mentioned vapors are passed through said coking operation concurrently with the flow of said particles therein thereby aiding in drying said coked particles, and thence countercurrent to said reheated particles in said independent vapor-cracking operation.

3. The process for thermally treating a heavy hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule which comprises continuously moving a continuous, gravity-packed column of heated solid coke particles downwardly by gravity through a coking operation, continuously introducing said residual hydrocarbon, the major portion of which is in the liquid phase, to the upper part of said column whereby a portion of said hydrocarbon charge is vaporized, maintaining the temperature of said column in said coking operation at approximately 900° F.-1050° F. whereby the liquid portion of said hydrocarbon charge is mildly cracked, the unvaporized portion thereof being ultimately converted to dry coke on the solid coke parti-

cles and to additional vapors, passing said coked solid coke particles through a lower part of said coking operation, wherein said coke is dried on said solid coked particles, combining said first-mentioned vapors and said additional vapors to form combined vapors from said coking operation, passing said combined vapors downwardly through said coking operation and concurrent to the flow of said particles therein thereby aiding in drying said coked particles, withdrawing said combined vapors from said coking operation at a point below the surface thereof, passing said combined vapors to an independent vapor-cracking operation containing an independent, continuously moving, continuous gravity-packed column of solid coke particles, maintaining said combined vapors in said vapor-cracking operation for a period of from a fraction of a second to several seconds, maintaining the temperature of said column in said vapor-cracking operation in the range from 1200 to 2600° F. thereby producing an effluent containing a high percent of unsaturated hydrocarbons selected from the class consisting of acetylene, ethylene, propylene and mixtures thereof, quenching said effluent, withdrawing solid coke particles from said liquid-coking operation and said vapor-cracking operation into a common heating operation, reheating said particles therein to a temperature of approximately 900 to 1050° F., returning a portion of the reheated particles to said coking operation, passing the balance of said reheated particles through a second heating operation, heating said particles therein to a higher temperature than that in said vapor-cracking operation, and passing said last-mentioned particles to said vapor-cracking operation.

4. The process for thermally treating a heavy hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule which comprises continuously moving a continuous gravity-packed column of heated solid coke particles downwardly by gravity through a coking operation, continuously introducing said heavy hydrocarbon, the major portion of which is in the liquid phase, to the upper part of said column whereby a portion of said hydrocarbon charge is vaporized, maintaining the temperature of said column in said coking operation at approximately 900° F.-1050° F. whereby the liquid portion of said hydrocarbon charge is mildly cracked, the unvaporized portion of said hydrocarbon charge being ultimately converted to dry coke on the solid coke particles and to additional vapors, passing said coked solid coke particles through a lower part of said coking operation wherein said coke is dried on said solid coked particles, combining said first-mentioned vapors and said additional vapors to form a combined vapor from said coking operation, passing said combined vapor to an independent vapor-cracking operation containing an independent, continuously moving, continuous, gravity-packed column of the said solid coke particles, maintaining said combined vapor in said vapor-cracking operation for a period of from a fraction of a second to several seconds, maintaining the temperature of said column in said vapor cracking operation in the range from 1200 to 2600° F. thereby producing an effluent containing a high percentage of unsaturated hydrocarbons containing less than four carbon atoms to the molecule, quenching said effluent, withdrawing solid coke particles from said liquid-coking operation, reheating said solid coke particles therein to a temperature of approximately 900° F.-1050° F., returning a portion of the reheated coke particles to said coking operation, passing the balance of said reheated coke particles through a second heating operation, heating said coke particles therein to a temperature sufficient to effect said short-time, high temperature vapor reaction in said vapor-cracking operation, and passing said last-mentioned coke particles to said vapor-cracking operation.

5. The process for thermally treating a residual hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule as claimed in claim 4 wherein the temperature of said vapor-cracking operation is maintained between approximately 2000° F. and 2300° F. to produce predominant yields of ethylene.

6. The process for thermally treating a residual hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule as claimed in claim 4 wherein the temperature of said vapor-cracking operation is maintained between approximately 2400° F. and 2500° F. to produce predominant yields of acetylene.

7. The process for thermally treating a residual hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule as claimed in claim 4 wherein the temperature of said vapor-cracking operation is maintained between approximately 1800° and 2000° F. to produce predominant yields of propylene.

8. The process for thermally treating a residual hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule as claimed in claim 4 wherein the amount of coke passed to said coking operation is from about $\frac{2}{3}$ to 4 times the amount passing to said second heating operation.

9. The process for thermally treating a residual hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule as claimed in claim 4 wherein said heavy hydrocarbon charge is asphalt.

10. The process for thermally treating a residual hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule as claimed in claim 4 wherein said heavy hydrocarbon charge is a reduced crude.

11. The process for thermally treating a residual hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule as claimed in claim 4 wherein said heavy hydrocarbon charge is a heavy crude.

12. The process for thermally treating a residual hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule as claimed in claim 4 wherein products of combustion from the second heating operation are utilized in reheating coke particles from the liquid-coking operation.

13. The process for thermally treating a residual hydrocarbon charge to simultaneously produce coke and predominant yields of gaseous unsaturated hydrocarbons having less than four carbon atoms to the molecule as claimed in claim 4 wherein the ratio of oxygen to combustible carbon in the second heating operation is such that the products of combustion include a major portion of carbon monoxide and such combustion products are in part introduced to the first heating operation wherein the heat value thereof is utilized.

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