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W. C. DORSETT ET AL

PROCESS OF CRACKING PETROLEUM

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INVENTORS

WILLIAM C. DORSETT
CURTIS C. SPERLING
ORANGE C. WALKER

VIRGIL E. WOODCOCK
ATTORNEY
This invention relates to petroleum conversion systems, more particularly to systems of the true vapor phase type which are characterized by the use of a gaseous heat carrier which is conditioned with a stream of vapors heated to high temperature. As is well understood by those skilled in the art, systems of the true vapor phase type have been successfully utilized for the cracking or thermal treatment of charging stocks widely differing in character and boiling range.

The present invention is characterized by the fact that the end-products include a large percentage of aromatic compounds, butadiene, and ethylene and by the substantial absence of normally liquid saturates. Further in accordance with the invention, substantially no free carbon is produced which in terms of practical operation means that systems built in accord with the invention may be operated for long periods of time without need of shutting down to clean carbon from tubes or vessels.

In carrying out the invention in one form thereof, any desired charging stock may be utilized although debutanized natural gasoline, a light or heavy naphtha, or an aromatic distillate are preferred charging stocks. A stream of vapors heated to high temperature is commingled with a gaseous hydrocarbon heat carrier which is concurrently heated to a high temperature. By limiting the reaction time to not more than twenty-five one-hundredths (0.25) of a second, preferably from three (0.03) to five one-hundredths (0.05) of a second for a mix temperature of from 1300° F. to 1500° F., under a pressure preferably below one hundred pounds per square inch, and by proper control of the composition of the heat carrier and of the charge, end-products are obtained which consist primarily of the aromatic compounds, ethylene and butadiene.

With regard to the vaporizable charge, a recycle ratio is preferably maintained; that is an aromatic recycle stock may be withdrawn and a portion of it returned to the system preferably in ratio of from 1:1 to 2:1 with respect to the charge. The aromatic distillate must be substantially entirely removed from the reaction products prior to rebubbling operations and prior to the addition of heat for fractionation. With respect to the gaseous heat carrier, it should consist of hydrocarbons to a large extent lighter than C5's and the presence of hydrogen and methane should be minimized. The cycle gas or heat carrier should include a substantially large percentage of unsaturated hydrocarbons having from two to three carbon atoms per molecule. An unusual feature of the present invention is the fact that no gasoline is produced. On the contrary, the principal end-products are benzene, toluene, the xylenes, styrene, butadiene, the butenes, and ethylene.

Each of these end-products is valuable and in accordance with the present invention they may be produced directly from petroleum by means of a relatively inexpensive process and in a form in which they may be readily purified to any desired degree.

For a more complete understanding of the invention, reference should be had to the more detailed description which follows, and to the drawing in which:

Fig. 1 diagrammatically illustrates a system embodying the invention with the connecting pipe lines for the most part shown by single lines; and

Fig. 2 illustrates a curve showing the selective production of certain of the end-products. As indicated above, the conditions of temperature, reaction time, and the character of the hydrocarbons within the reaction zone are of material importance. For convenience, the system will be described starting with the heater 10, diagrammatically shown as a double end-fired heater, and there will be later developed a detailed description of the character of the charging stock and of the heat carrier gas.

A gas-enriched charge enters the convection section 11 of the heater 10 by way of line 12, is vaporized, and during passage through floor tubes 13 and roof tubes 14 is heated in vapor phase to a temperature within the range of 1100° F. to 1400° F., during a time interval insufficient for material cracking to occur. This may be the order of one-tenth of a second at the higher temperature. Concurrently, normally gaseous hydrocarbons enter the floor tubes 15 by way of line 15 and during their passage through the floor tubes and the roof tubes 17 are heated to a temperature between 1400° F. and 1600° F., or higher. It is to be understood that separate heaters may be used for each stream and in many cases separate heaters will be preferred, to provide adequate capacity and wholly independent control of the heating of the two streams. While serial flow of the streams through the respective tube banks is indicated, it is to be understood that the heater tubes will normally be connected in parallel or series-parallel and that they will be of adequate size to minimize pressure drop there through. Furthermore the heating rate must be sufficiently high for the elevation in tempera-
ture of the respective streams to their final outlet temperatures during time intervals (around one-tenth of a second) insufficient for material cracking of either stream to occur prior to their mixture one with the other. Such heating requirements have been attained and heaters are available which will satisfactorily meet these requirements.

The gas-enriched charge includes gases absorbed from an absorption operation and the charge includes a recycle stock which to large extent consists of an aromatic distillate. The normally gaseous stream of hydrocarbons is utilized not only as a heat carrier but the hydrocarbons enter into the reaction and by their presence they also control the direction and the extent of completion of the complex chemical reactions which occur and which result in the production of end-products to large extent composed of the aromatics, the unsaturates, and butadiene.

After the heating of both streams in the manner aforesaid, the heat carrier is commingled with the highly heated vapors. As shown, the two streams are mixed together in a transfer line 18 preferably of very short length and which leads directly to a reactor or reaction zone or chamber 19. The reaction chamber which may be the transfer line itself is preferably heat-insulated as indicated at 18a and is of a size with reference to the volume of the commingled streams as to provide a time interval of from about three to twenty-five hundredths of a second for the complex reactions to take place. For time intervals within this range, the mix temperature, or the temperature of the mixture should be within the approximate range of 1300°F. to 1500°F.

After the aforesaid time interval, the reaction products exit from the reaction zone or chamber 19 through a transfer line 20 in which is introduced a relatively large quantity of a relatively cool (150°F. to 250°F.) liquid hydrocarbon, which liquid may enter through the line 21. By introducing the cool liquid hydrocarbon into the transfer line rapid and thorough mixing is accomplished and the cracking reactions are abruptly terminated.

We prefer to maintain in the reaction chamber a pressure of about twenty-five pounds and less than one hundred pounds per square inch, gage. If the pressure is less than twenty-five pounds per square inch, the compressor cost becomes excessively high and if the pressure is greater than one hundred pounds per square inch the cost of the heater tubes becomes excessive, even if available for operations at higher temperatures and pressures.

By the concurrence of the aforesaid conditions of temperature and time, and by controlling the character of the hydrocarbons subjected to the cracking reactions, there is produced a yield of butadiene unexpectedly high and higher than heretofore achieved or believed possible in systems of the true vapor phase type. Moreover there is simultaneous production of other reaction products which are of considerable value.

The present invention is further characterized by the fact that charging stock available if large quantity and at low cost may be utilized in con

In accord with the present invention the aforesaid conditions may not only be readily brought about but they may be continuously maintained with a minimum of difficulty. A process or system functioning in accord with the foregoing is relatively simple and the operation as a whole is exceptionally free from difficulties which normally cause the shutting down of the system for the cleaning of vessels and tubes.

The reaction-arresting or quenching medium may be a low gravity residuum circulated from the bottom of a combined scrubber-fractionating column 22 by way of line 23, a cooler 24, and accumulator 25 and by pump 26 forced through the line 21 in the desired quantity. If desired, some of this material may be withdrawn from the accumulator 25, or make-up may be introduced into the accumulator.

Preferably the transfer line 20 includes mechanical means indicated at 29 for the removal of possible carbon or tarry deposits in the transfer line. These ordinarily are negligible and such a provision is precautionary and guards against the formation of such deposits during the starting and shutting down of the unit or system embodying the invention.

The commingled reaction products and the quenching medium are discharged from the transfer line 20 into the lower part of the scrubber section of the column or vessel 22 where there is a separation of the liquid and the vaporous products. The vapors rise upwardly through the column in counter-current relation to descending reflux. The vessel 22 is preferably provided with numerous bubble trays (not shown) which provide for the more efficient fractionation of the rising vapors and in manner well understood by those skilled in the art. The overhead stream from the fractionating column 22 passes by way of line 28 to a condenser 30 where it is materially cooled to between 90°F. and 150°F. It is then introduced into an accumulator 31 where the resulting condensate and gasses separate. Reflux for the fractionating column 22 is derived from the accumulator 31 and is returned to the column 22 by the pump 33 by way of the transfer line 32. The condenser 30 is preferably supplied with cooling water 34 under the control of valve 35.

For convenience, where cooling water is indicated for other condensers or coolers in the system, there has been utilized the reference number 34 to indicate both inlets and outlets and there has been used a reference number corresponding with the particular cooler or condenser together with the subscript "a" to designate the control valve.

Uncondensed gases and vapors from the accumulator 31 are elevated in pressure to from 150 to 300 pounds per square inch gage by a compressor 36 and by way of line 38 pass through a cooler 39 and into an accumulator 40. The cooler 39 is provided with a control valve 38a for the regulation of the supply of cooling water 34.

The vaporizable condensate in the accumulator 31 consists largely of an aromatic distillate; that is, a distillate having a gravity of around 1.0 A. P. I. and which includes aromatics in proportion of about 20-25% benzene, 18-22% toluene, 4-8% unsaturates, and the remainder heavier aromatics such as styrene, the xylenes, etc.

In addition to the condensate, a portion of the vaporizable, aromatic distillate is preferably returned to the reaction zone. For this purpose a pump 37 withdraws distillate from the accumu-
and by way of line 3 and by way of line 29 introduces it into the line 12 which leads to the convection section 11 of the heater 10. Only a part of the aromatic distillate is recycled. The excess is withdrawn by way of line 41 under the control of valve 42. Preferably the recycle stock consists of aromatic distillate in amount which with the gaseous fractions bears a weight relation of from 1:1 to 2:1 with that of the charging stock.

As a result of the cooling of the vapors and gases compressed by the compressor 39, there is a further separation of condensate within an accumulator 40. The undiluted vapors and gases from the accumulator 40 pass by way of line 42 into the lower portion of an absorber 43 where they are counter-currently contacted with the charge introduced into the absorber by way of pump 44, cooler 45, and line 46. The absorber is provided with bubble trays (not shown) or other means for insure intimate contact between the gases and vapors and the charging stock and for the maximum absorption of desirable constituents. One or more intercoolers may also be provided, one of which, the inter-cooler 47 being shown.

The free hydrogen and unabsorbed gaseous hydrocarbons, largely gases having one or two carbon atoms per molecule are withdrawn from the absorber 43 by way of line 50 and under the control of valve 53 may be discharged from the system as the make gas. The make gas is conventionally understood as the excess gas produced by the system, or the gas which in this case it is desired substantially to exclude from the reaction zone. It is important substantially to eliminate from the cycle gas and from the reaction zone recycled hydrogen and methane and these gases are removed from the absorber together with some of the Co's. The latter may comprise as much as 53% by weight of make gas and of the Co's, 85% by weight will be ethylene. The latter is a valuable end-product and may be recovered in a manner well understood by the art. Hence, even from the make gas there may be recovered a valuable end-product.

The charging stock, though it may vary widely in character, is preferably a naphtha or depanthenized natural gasoline which after enrichment by the absorption of gaseous and vaporous constituents within the absorber 43 is withdrawn therefrom by way of line 54 and in line 56 comingling with the condensate from the accumulator 40. The latter condensate consists largely of hydrocarbons having more than three carbon atoms per molecule. The mixture then passes by way of line 56 and with the assistance of a pump not shown through a heat exchanger 57 in which it is heated by indirect heat exchange with a heating medium circulated through the exchanger by way of lines 58. After its elevation in temperature the mixture is discharged into the midportion of a fractionating tower or column 60 operating at from 200 to 400 pounds per square inch gage pressure which has for its function the removal of propane and lighter gases. Heat is supplied to the liquid material in the base of the tower 60 as by a reboiler 61 through which a heating medium circulates by way of lines 58.

It may be again observed that introduction of any aromatic distillate into the tower 60 has been avoided. Instead of such as aromatic distillate contains styrene, the addition of heat by the reboiler 61 and the relatively long time interval within the base of the tower 60 would result in the formation of polymers which would soon clog and choke the trays and lines associated with the tower 60.

The reboiler 61 operates in manner well understood by the art, the material coming from the bottom of the tower 60 being heated in the reboiler, the lighter fractions being returned to the tower through the line 62 and the propane-free material passing by way of line 63 through a cooler 65 and into the final fractionating tower 70 which operates at from 30 to 80 pounds per square inch gage pressure. The tower 70 has for its function the removal of butadiene, or the fraction which includes butadiene and sometimes called the C4 fraction.

The overhead products from the tower 60, largely propane and lighter gases are cooled in a cooler 64 and discharged into an accumulator 65. Condensate is withdrawn by pump 66 and returned as reflux for the tower 60. Gases are withdrawn from the accumulator 65 by way of line 66 and they pass under the control of valve 66a into the line 66 leading to the heater 10. All, or at least the major part, of the cycle gas or heat-carrier is derived from the accumulator 65. In the event there is a deficiency of the heat carrier, make-up gas may be withdrawn from the line 50 under the control of the valve 53a and discharged into the cycle gas line 58.

The cycle gas itself preferably consists of a substantial proportion (80%) of unsaturated Co's and Co's for example, the C4 fraction may consist of about 85% of the unsaturated ethylene, and the remainder of ethane, a saturate. The C4 fraction may consist of about 90% of the unsaturated propylene, and the remainder of propane, a saturate.

A reboiler 71 supplies heat to the material withdrawn from the bottom of the tower 70. The lighter products are returned to the tower by way of line 71a. The overhead products from the tower 70 pass by way of line 72 to a condenser 73 and thence into an accumulator 74. Normally all of the overhead products will be condensed although a valve 75 may be provided for venting the accumulator 74. Some of the condensate is returned by way of pump 76 as reflux for the tower 70 and the remainder of the condensate is withdrawn through the line 77 as an end-product of the system which includes the butadiene fraction.

While the invention has been illustrated in a simple form thereof, it is to be understood that many additional refinements may be made such for example as by the use of additional fractionating equipment in which an additional absorbing menstrum, consisting of bottoms from a debutanizing tower, may be introduced into the absorber below the point of entry of the raw charge.

An unusual feature of the invention is the fact that substantially no free carbon is produced; only traces of carbon may be found in the residuum which is recirculated by the pump 28 as the quenching medium. This material, with gravity of around 6° A.P.I. may be withdrawn as a free flowing liquid even though of such low gravity about 80% will vaporize at 600° F, and at atmospheric pressure. In accord with the invention, the production of free carbon is inhibited by the presence in the reaction zone of a substantial proportion of the unsaturated Co's and Co's and the aromatic distillate. If the aromatic distillate, or the aromatics, are not returned to the reaction zone a considerable amount of free carbon will be formed. If in addition the unsat-
urated C's and C's are not returned to the reaction zone, free carbon will be formed at a substantial rate. However, when both are removed, the formation of free carbon is practically eliminated and for all practical purposes its presence may be neglected. The practical result is that there is no "cooking" problem and from this standpoint the system may be kept on stream indefinitely.

On the other hand it is not desirable to return all of the aromatic distillate to the reaction zone, which means that valuable end products are made available such as benzene, toluene, the xylenes and styrene.

In typical embodiments of the invention there have been produced in terms of weight percentage of the raw charge, benzene, toluene and the xylenes in amounts varying by 4 and 8%, styrene around 1.2%; butadiene from 6 to 10%, and butenes from 12 to 18%. As earlier stated, a feature of the present invention is the production of the relatively large quantities of aromatics and butadiene.

In Fig. 2, a fractional part of a true boiling point distillation curve is shown for the aromatic distillate, with volumes per cent distilled as abscissa and temperature as ordinates. The aromatic distillate represents about 20% of the raw charge. As shown in Fig. 2, as the temperature rises from 160°F. to about 176°F., less than 3% of the distillate has been removed. At around 176°F. benzene is distilled off and as shown the benzene plateau represents about 20% of the distillate. The temperature then rises to about 230°F. at which temperature there is a toluene plateau. The flat toluene portion of the curve represents about 20% of the distillate. Similarly, like plateaus or "flats" (not shown) are present at the higher temperatures. Quantitative analyses confirm the foregoing and show that there are present, styrene above six percent, the xylene around 20%, the heavier aromatics around 55%, and unsaturates about 5%

By way of further illustration of the invention a charging stock of straight run naphtha, gravity 52° A. P. I.; initial boiling point of 200°F.; and an end point of 400°F., was utilized as the charging stock for the absorber. 43. The naphtha after passage through the fractionating equipment including towers 68 and 70 was to a large extent denuded of its C's and lighter fractions. From tower 78, and in mixture with fractions heavier than the C's the naphtha was by pump 142 charged to the heater coil 11. The fractions heavier than the C's and lighter than the aromatic distillate include unsaturated C's and C's, pentanes and hexenes. These comprise a part of the recycle stock, the aromatic distillate comprising the other part.

The cycle or heat-carrier gas was derived from the depropanizer, as at the accumulator 48. It consisted of around 80% of C's and C's, unsaturates; the remainder being methane, ethane and propane, except for negligible quantities of C's.

The charge to the heater coil, line 12, was vaporized and heated to 1375°F. and commingled with cycle gas heated to 1550°F. The cycle gas was maintained in quantity of about 1500 cubic feet per barrel of the charge to the heater coil.

With a reaction time of from 10 minutes to 30 minutes at a temperature of about 1375°F., the following reaction products in terms of per cent by weight of fresh naphtha charge were obtained. The hydrogen 0.42%, methane 14%, ethylene 19.35%, and the ethane 6.55% were to large extent removed from the system as the make gas. The C's, propylene and propane, comprised about 2.36%. The C's fraction included butadiene 6%, the butenes, 12%, the butanes, 1%, and the C's, 1%. The aromatic distillate was 20%, with a residue of 20%, and 0.42% distillation loss.

With a charging stock of West Virginia de-pentanized natural gasoline, gravity 75.2° A. P. I., initial 130°F. and an end point of 260°F., the foregoing products were for the same operating conditions produced in substantially the same percentages.

Gas oil has also been successfully used as charging stock.

The present invention differs from previous true vapor phase systems by the control of the complex chemical reactions for the production of the aforesaid characteristic products. Other than benzene and toluene, it will be observed a very small percentage of products suitable for inclusion in motor fuel is produced whereas in the past such were the major products. The principal differences include the fixing of the time-temperature relationship of a given aromatic distillate within the system and the recycling of a part of the aromatic distillate.

By the use of the heat-carrying cycle gas of the character aforesaid, there is an increase in the yield of hydrocarbons having four and more atoms of carbon per molecule; and an increased yield of material reported above that reported for systems utilizing steam. The heat-carrying cycle gas may be mixed with the superheated vapors as above described for convenient control of the reaction time. That is, the desired reaction time, below twenty-five one hundredths of a second may be fixed and maintained during continuous operation of the system. This results from the use of more refractory cycle gas which may be heated to its high temperature and then used substantially instantaneously to elevate the vapors to their final cracking temperature.

The vaporization reactions may then be quickly and abruptly cooled to terminate the cracking reactions after the cracking time, which produces the high yields of desirable products, as above described.

While we prefer to recycle the aromatic distillate it is to be understood a "once-through" operation may be utilized; and the aromatic distillate may be charged to the process from an external source of supply.

While we have described a preferred embodiment of our invention, it is to be understood other modifications may be made and we therefore intend by the appended claims to cover any such modifications as fall within the spirit and scope of our invention.

What we claim is:

1. A process of cracking petroleum which comprises supplying a stream of normally liquid hydrocarbon materials as charging stock, which stock is substantially free of aromatics and unsaturates, mixing with said stream vaporized hydrocarbons predominantly butanes and pentanes in quantity at least one-half that of said charging stock, heating said mixture to a high temperature within approximate range of from 1200°F. to 1400°F., heating to a high temperature within the approximate range of from 1200°F. to 1400°F., heating to a high temperature within the approximate range of from 1200°F. to 1400°F., heating to a high temperature within the approximate range of from 1200°F. to 1400°F., heating to a high temperature within the approximate range of from 1200°F. to 1400°F., heating to a high temperature within the approximate range of from 1200°F. to 1400°F.
as to produce a temperature of the commingled streams within the range of from 1300° F. to 1500° F., commingling said two streams, and within from three hundredths to twenty-five hundredths of a second after said commingling abruptly cooling said commingled streams to terminate the cracking reactions, which reactions are characterized by the production of a maximized quantity of butadiene and a substantial quantity of aromatics.

Claims set forth in claim 1, and in which the reaction products are fractionated and in a stream of said aromatics derived therefrom, and in which the stream of cycle gas consisting largely of unsaturated C4's and C5's is derived from the process.

3. A cracking process in which the end products consist primarily of aromatic compounds, butadiene, butenes, and ethylene which comprises, heating a stream of vaporizable normally liquid hydrocarbons heavier than propane to a temperature within the approximate range of 1200° F. to 1400° F. during a time interval insufficient for material cracking to occur, said stream comprising a charging stock substantially free of aromatics and unsaturates and including a recycle stock predominantly aromatic, concurrently being heated within the approximate range from 1400° F. to 1600° F. and within a time interval insufficient for material cracking to occur, said stream consisting of hydrocarbons having four carbon atoms per molecule, a substantial percentage of which consists of butadiene, commingling said

5. The combination as set forth in claim 3, in which saturates having from one to two carbon atoms per molecule are substantially excluded from said cycle gas, and in which said cycle gas is derived from the process.

6. The method of producing butadiene which comprises heating a stream of vaporizable normally liquid hydrocarbons heavier than propane to a temperature within the approximate range of 1200° F. to 1400° F., within a time interval of heating not in excess of 1/10 of a second above 1200° F. said stream including added vaporizable aromatic hydrocarbons, concurrently heating to within the approximate range of 1400° F. to 1600° F. and within a time interval of heating not in excess of 1/10 of a second above 1200° F., a heat carrier gas consisting of normally gaseous hydrocarbons to a large extent lighter than C4's and heavier than methane, in a reaction zone commingling said heated hydrocarbons, after a reaction time of from about three hundredths to twenty-five hundredths of a second terminating the cracking reactions by rapid quenching of the reaction products, separating from said reaction products said vaporizable aromatic hydrocarbons and separating from said products a stream of C4 hydrocarbons having butadiene in quantity of from fifteen percent to forty percent thereof.

7. The method of producing butadiene which comprises concurrently heating a vaporizable stream of normally liquid hydrocarbons and a normally gaseous stream of hydrocarbons to temperatures which will produce in a reaction zone a temperature of the commingled streams within the range of approximately 1300° F. to 1500° F., said first-named stream including added vaporizable aromatic hydrocarbons, in said reaction zone commingling said streams, terminating the cracking reactions within from three hundredths to twenty-five hundredths of a second after abruptly cooling said commingled streams, and separating from the reaction products a petroleum fraction including the butadiene and a stream including said vaporizable aromatic hydrocarbons.

8. The method as set forth in claim 7, in which all normally gaseous hydrocarbons from the reaction zone are subjected to an absorbing menstrum for the extraction therefrom of hydrocarbons of the approximate boiling range of butadiene and in which the absorbed hydrocarbons are subsequently utilized for the production of a hydrocarbon fraction which contains butadiene in relatively high proportion and in excess of 15% of said fraction.

9. The method as set forth in claim 7, in which the vaporizable normally liquid hydrocarbons are elevated to their temperature during a time interval insufficient for material cracking to occur, and in which said normally gaseous hydrocarbons are elevated to their temperature during a time interval insufficient for material cracking thereof.

10. The method as set forth in claim 7 in which said vaporizable normally liquid hydrocarbons are elevated to a temperature in excess of 1100° F. during a time interval insufficient for material cracking to occur, and in which a sufficient quantity of said normally gaseous hydrocarbons is elevated during a time interval insufficient for material cracking to a temperature adequate to raise the temperature of said heated vaporizable hydrocarbons to said temperature within said range of 1300° F. to 1500° F.

11. A method of producing butadiene by the conversion in the substantial absence of all gaseous products lighter than propane of normally liquid hydrocarbons in vapor phase and characterized by the use of a heat-carrying cycle gas, which comprises cooling and fractionating the reaction products to produce an aromatic distillate, withdrawing a part of said distillate as an end-product, another part of said distillate forming a source of supply of recycle stock, in an absorbing zone utilizing vaporizable uncracked liquid hydrocarbons for absorption of substantially all of the hydrocarbons having three and more carbons per molecule, withdrawing from the absorbing zone the lighter unabsorbed gases, heating and then fractionating said liquid hydrocarbons and their absorbed gases for the separation therefrom of normally gaseous hydrocarbons having less than four carbon atoms per molecule, the so-separated gases forming the principal supply of the heat-carrying cycle gas, in a subsequent fractionating zone separating hydrocarbons having five or more carbons per molecule, a substantial percentage of which consists of butadiene, commingling said
aromatic distillate and the remaining hydrocarbons having more than four carbon atoms per molecule, applying heat to the aforesaid mixture to vaporize the same and to elevate the temperature thereof to at least 1100° F. during a time interval insufficient for material conversion to occur, concurrently heating said cycle gas to raise its temperature materially above 1300° F., commingling said cycle gas with said mixture to produce simultaneous conversion of all of said commingled hydrocarbons, and in less than twenty-five one-hundredths of a second terminating the cracking reactions by abrupt cooling thereof.

12. In a vapor phase cracking system in which a heat-carrying cycle gas consisting of gaseous hydrocarbons is commingled with a stream of heated hydrocarbon vapors to produce controlled cracking thereof, the method which comprises counter-currently contacting a debutanized uncracked charging stock normally gaseous hydrocarbons made during said cracking for absorption of a substantial quantity of said gases and for substantially eliminating gases lighter than C's, that is, hydrocarbons having three carbon atoms per molecule, commingling said enriched charging stock with a condensate containing reaction products, in successive fractionating zones separating from said mixture the C's and the C's, the C's and lighter gases forming the principal source of supply of said cycle gas, and the C's containing a substantial percentage of butadiene, commingling aromatic distillate with the remaining hydrocarbons heavier than the C's, heating the mixture to a high temperature in a short time, concurrently heating said cycle gas to a temperature within the range of 1400° F. to 1600° F. and in quantity adequate for the elevation of said heated mixture to within the range of 1300° F. to 1500° F., commingling said cycle gas and said highly heated vapors, within twenty-five one-hundredths of a second terminating the cracking reactions by rapid cooling thereof, separating therefrom an aromatic distillate 30% to 40% of which comprises benzene and toluene and 30% to 45% of which includes heavier aromatics, withdrawing from the process a part of said aromatic distillate, another part of said distillate forming the supply of said aromatic distillate commingled with the hydrocarbons heavier than the C's, that is, those having four carbon atoms per molecule.

13. The method of producing butadiene which comprises heating a stream of vaporizable normally liquid hydrocarbons heavier than propane to a temperature of approximately 1375° F. within a relatively short time interval of heating above 1200° F., said stream comprising a charging stock substantially free of aromatics and unsaturates, and including a recycle stock predominantly aromatic, concurrently heating to approximately 1500° F. within a relatively short time interval of heating above 1200° F. a heat carrier consisting of normally gaseous hydrocarbons to large extent lighter than C's and heavier than methane, in a reaction zone commingling said heated hydrocarbons, after a reaction time of approximately four one-hundredths of a second terminating the cracking reactions by rapid quenching of the reaction products, separating from said products a stream of C hydrocarbons which includes butadiene in quantity of approximately thirty percent thereof, and separating from said reaction products a recycle stock predominantly aromatic for mixture with said stream.

WILLIAM C. DORSETT.
CURREN C. SPERLING.
ORANGE C. WALKER.