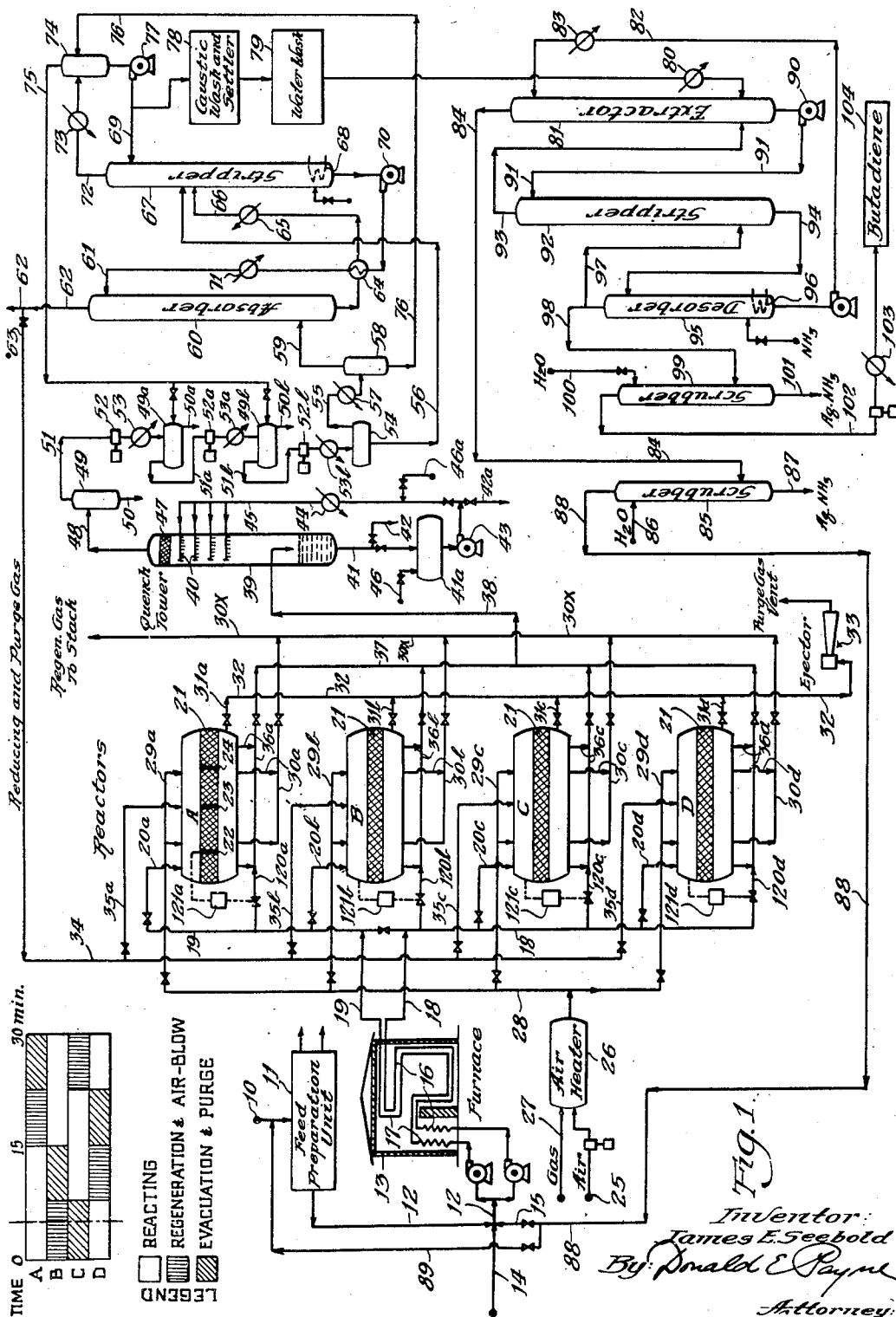


2,474,014

CATALYTIC CONVERSION SYSTEM

3 Sheets-Sheet 1



June 21, 1949.

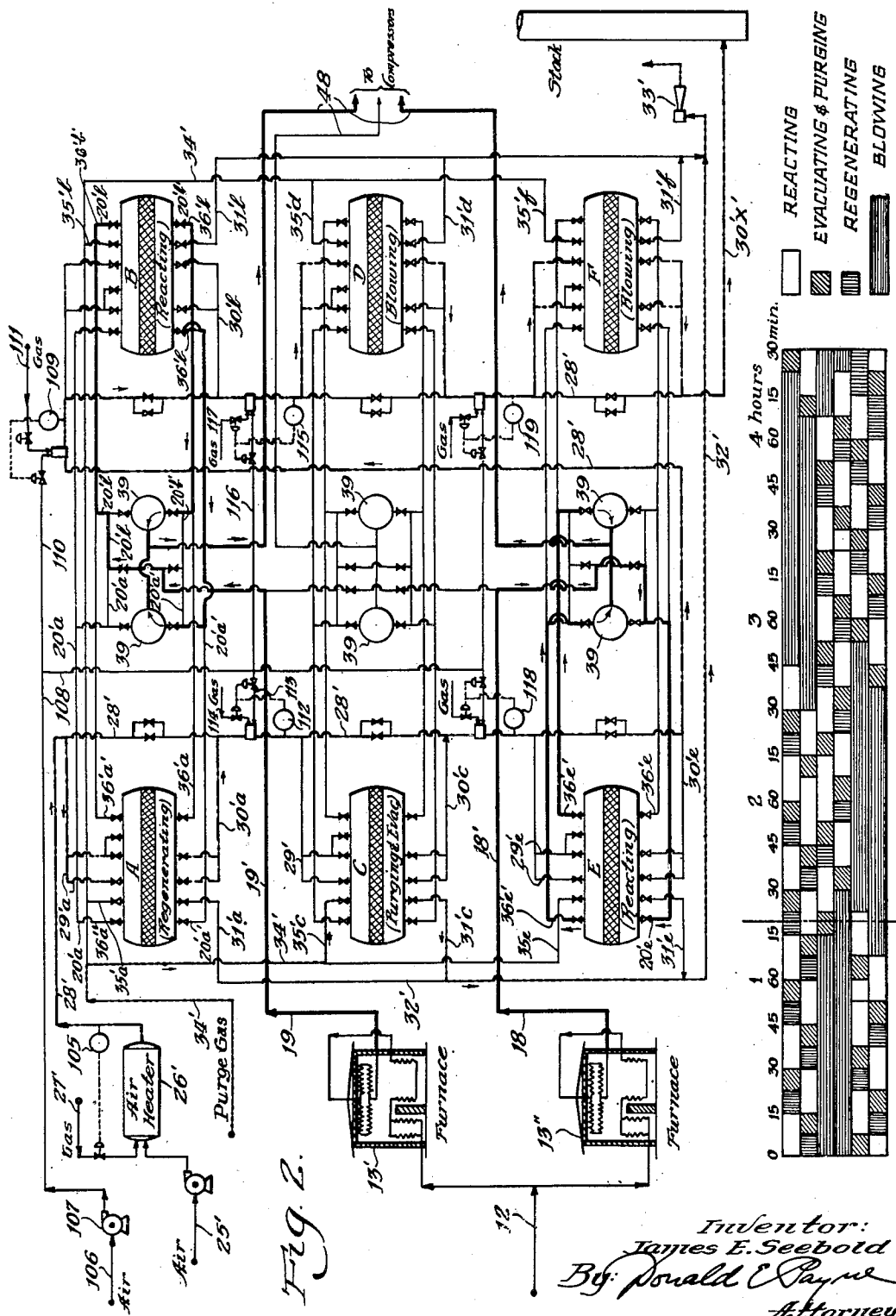
J. E. SEEBOLD

2,474,014

CATALYTIC CONVERSION SYSTEM

Filed Jan. 30, 1943

3 Sheets-Sheet 2



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J. E. SEEBOLD

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CATALYTIC CONVERSION SYSTEM

Filed Jan. 30, 1943

3 Sheets-Sheet 3

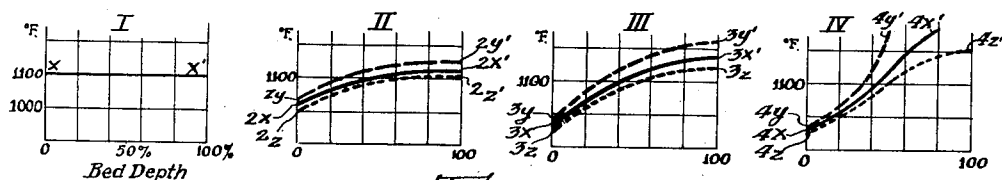


Fig. 3.

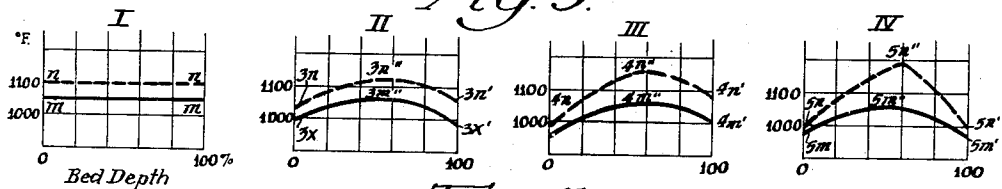


Fig. 4.

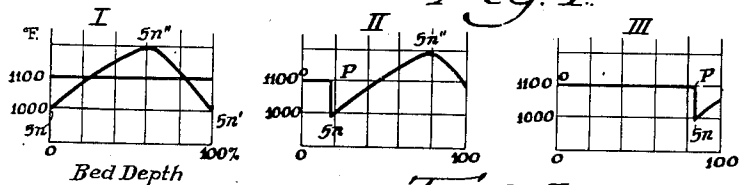


Fig. 5.

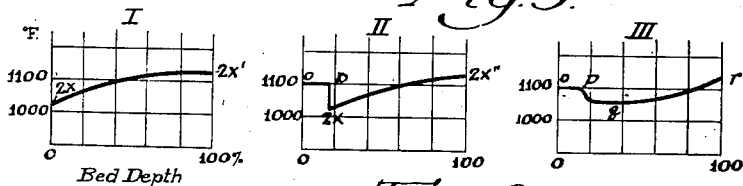


Fig. 6.

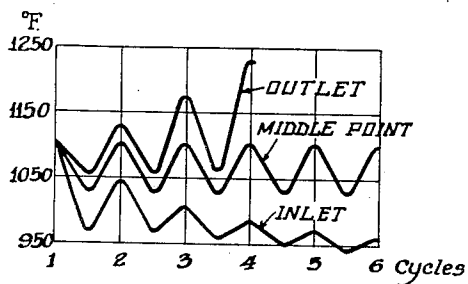


Fig. 7.

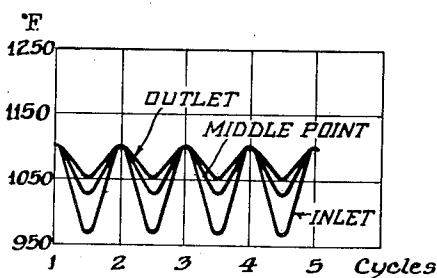


Fig. 8.

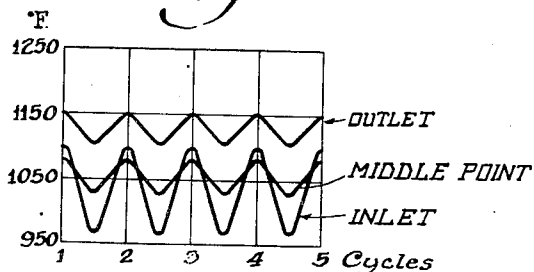


Fig. 9.

Inventor:
James E. Seebold
By: Donald E. Payne
Attorney.

UNITED STATES PATENT OFFICE

2,474,014

CATALYTIC CONVERSION SYSTEM

James E. Seebold, Chicago, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application January 30, 1943, Serial No. 474,120

9 Claims. (Cl. 260—680)

1

This invention relates to a catalytic system and it pertains more particularly to temperature control in cyclic catalytic hydrocarbon conversion systems wherein a carbonaceous deposit is formed in a catalyst bed during an endothermic conversion step and is burned therefrom during an exothermic regeneration step in each cycle, wherein the fluctuation in temperature of a catalyst bed of high heat capacity enables the utilization of the heat generated during the exothermic regeneration period to supply heat required during the endothermic conversion period, and wherein there is a tendency toward the development of hot spots or cool spots in the catalyst bed as the cycles are continuously repeated.

It is known that by admixing a substantial amount of heat retention material with the catalyst, said heat retention material being of about the same particle size as the catalyst particles and uniformly dispersed throughout the catalyst bed, the danger of overheating the catalyst in the burning period of a single cycle can be minimized or substantially eliminated. The exothermic heat liberated in the burning step can be absorbed to a considerable extent by this heat retention material and substantially utilized for supplying endothermic heat of reaction in the subsequent conversion step. In this way heat is carried from one period to the next as sensible heat contained in the catalyst bed and is absorbed and liberated as required by temperature fluctuations in the bed. The heat retention material thus acts as a "thermal flywheel" to absorb heat and liberate heat as required in this cyclic conversion system.

In most reactions of this type there will be a tendency for some points in the line of gas or vapor flow through the bed to become considerably hotter or cooler than other points in this line of flow. The hotter points may get still hotter and hotter and the cool points may get still cooler and cooler in succeeding cycles. The hotter and the cooler temperatures may get so low as to be outside the desired conversion range while the average bed temperature is still substantially constant. An object of my invention is to minimize such temperature changes in the line of flow through a catalyst bed, to maintain substantially all of the bed within desired operating temperature limits during conversion, and to avoid reaching any temperatures in the regeneration step that might impair catalyst activity or damage the conversion system.

A proposed method of solving this problem was to reverse the flow of gases or vapors

2

through the bed in alternate cycles or periodically. This method can be used with some degree of success in small laboratory equipment and within certain rather narrow operating temperature ranges. In the process of converting normal butanes and butenes to butadiene, fairly constant temperature can be maintained in such laboratory equipment at a conversion level of about 1050° F., but this is below the desired conversion level, which is at least about 1100° F. for maximum butadiene production. The reverse flow idea does not solve the temperature control problem at the desired higher temperature conversion level because it is found that the center of the bed gets so hot as to impair the catalyst while the inlet and outlet sides of the bed get so cool as to effect no appreciable amount of conversion. An object of my invention is to provide a temperature control system that will be effective at any desired conversion temperature level.

In beds of relatively small cross-sectional area (as exemplified by small scale or laboratory catalyst beds only a few inches in diameter) adequate temperature control at a relatively low temperature level may be obtained by using reverse flow from cycle to cycle or from time to time after a plurality of cycles and by regulating such controllable variables as composition of feed to the reactor, reactor pressure, space velocity, inlet temperature of streams, etc. However, with the beds of large cross-sectional area which are required in commercial operations the regulation of temperature in one particular bed area does not insure that temperatures in other particular bed areas will be maintained within the desired operating limits. If one particular spot in the catalyst bed gets a little too hot in one cycle of operations there is a tendency for that spot to get hotter and hotter in succeeding cycles of operations so that hot spots may develop at various areas throughout this large catalyst bed. Similarly, if a particular area gets a little too cool there will be a tendency for that area to get cooler and cooler with succeeding cycles so that such area will soon be below the desired operating temperature range. An object of my invention is to avoid the development of hot spots and cool spots in catalyst beds of large cross-sectional area which are thus employed in cyclic conversion systems of alternate endothermic conversion and exothermic regeneration.

I will describe my invention as it is applied to the known laboratory process of producing butadiene from normal butanes and butenes by means

of a mass or bed of dehydrogenation catalyst such, for example, as chromium oxide on alumina in the presence of sufficient heat retention material such as Alundum or fused alumina so that the exothermic heat resulting from catalyst regeneration is stored in the catalyst bed and used to supply endothermic heat for the butane-butene dehydrogenation. For maximum butadiene production the conversion may be effected under a relatively high vacuum of about 25 inches of mercury (absolute pressure of 1 to 4 pounds per square inch) with a space velocity in the general vicinity of 200 to 800 volumes of gas (measured under standard conditions) per hour per volume of active catalyst (exclusive of space occupied by heat retention material) and at a temperature in the general vicinity of 1100° F. During the on-stream or conversion period there will be a drop in temperature in the catalyst bed which may range from about 50 to 100° F. or more. During the regeneration period there will be an increase in temperature and the temperature of catalyst particles in certain parts of the bed may be raised to approximately 1200° F. or more. Usually about 2 volumes of the Alundum or other heat retention material is employed per volume of active catalyst, the heat retention material being of approximately the same size as the catalyst particles and being uniformly distributed throughout the catalyst bed. The on-stream or conversion period under such circumstances is about 5 to 20 minutes, usually about 10 to 15 minutes, and it is desirable to have a catalyst restoration period of about the same length of time. It is to be expected that serious difficulties would occur if this process were used on a commercial scale with beds of large cross-sectional area, that hot spots would develop at various points in the catalyst bed and that these hot spots would not be adjusted or evened out in successive stages but, on the contrary, would become hotter and hotter rendering the process inoperable. In spite of the country's urgent need for butadiene and the efforts of outstanding chemical engineers to make this butadiene process commercially feasible, it was ruled out in connection with the country's synthetic rubber program because of the question of the development of localized areas of overheating and undercooling in various parts of the bed, which would render the process inoperable on a commercial scale. An object of my invention is to provide a method and means for solving this problem and for making the butadiene process commercially successful.

While my invention will be described in connection with the butadiene process hereinabove described it should be understood that the invention is not limited thereto but is applicable to any cyclic, fixed bed, catalytic conversion process wherein the system is subject to overheating and the development of "hot spots." My invention is particularly applicable to processes of catalytic cracking, reforming, aromatization, isomerization, or other catalytic hydrocarbon conversion process wherein said problem of temperature control may arise. The invention is herein described as applied to the butadiene process merely by way of example and not by way of limitation.

An object of my invention is to provide an improved method and means for avoiding or eliminating "hot spots" in a catalyst bed of large cross-sectional area and for insuring substantially optimum temperature conditions throughout the bed for a desired conversion. A further object is to prevent the running away of temperatures in

hot spot areas during regeneration. A further object is to provide improved methods and means of controlling the temperature of a catalyst bed of large cross-sectional area in order to keep it from deviating to any appreciable extent from desired reaction temperatures over a long period of time, i. e., throughout a large number of cycles.

A further object of the invention is to provide a conversion system which will require a minimum amount of steel and other critical materials. A further object is to provide a system which can be built at minimum cost and operated at minimum expense for obtaining maximum conversion and maximum yields of the desired products. Other objects will be apparent as the detailed description of the invention proceeds.

In the butadiene process (and in many other processes) heat produced during the regeneration of the catalyst may be stored within a catalyst bed both by catalyst and by Alundum particles or other heat retention material added for the purpose. A portion of this stored heat is consumed by the dehydrogenation (or other endothermic reaction) occurring during an on-stream period. Heretofore the successful operation of the process has been dependent upon the establishment of an equilibrium condition in which the heat gained during regeneration was equal to the heat lost during reaction. If the heat gained during regeneration exceeded the heat lost during reaction the average temperature of the catalyst bed tended to rise and vice versa. The relationship existing between the heat lost during reaction and the heat gained during regeneration is dependent upon a large number of variables, including: (1) composition of feed to the reactor, (2) reactor pressure, (3) space velocity employed, (4) catalyst activity, (5) temperature of streams. Thus under otherwise constant conditions, increasing the proportion of normal butane (or the inclusion of propane) in the charge will increase the heat absorbed during reaction relative to exothermic heat liberated during regeneration and the bed temperature will tend to fall. Coke or carbon (carbonaceous material) production increases with increase in reactor pressure; thus by increasing the reactor pressure, the heat released during regeneration is increased relative to the heat absorbed during reaction, causing the bed temperature to increase with succeeding cycles. By increasing space velocity, the general conversion level is decreased and the carbon yield per unit of conversion is decreased so that the heat absorbed during reaction is increased relative to the heat released during regeneration. Catalyst activity may be adjusted by changing its composition and method of preparation. By adjustment of the temperature of the streams entering the reactor during reaction and regeneration periods it is possible to obtain some measure of control of the average catalyst bed temperature. By the use of the above techniques it is possible to control the temperature (at a relatively low conversion level) of small sized catalyst beds as used in a laboratory and this has been demonstrated by small sized laboratory operations. However, when relatively large catalyst beds are employed, as are necessarily required in commercial operations, there is a tendency for a decrease in temperature in some parts of the bed and at the same time there is a tendency toward temperature increase in other portions of the bed. At every point of temperature increase, there will be a tendency toward more cracking or other undesirable decomposition which in-

5

creases the carbonaceous or coke deposit during the next on-stream period. The burning of the increased coke deposit during the following regeneration period makes the spot still hotter, thus causing more coke to be deposited during the following conversion period. Thus a hot spot would develop, spread and get hotter and hotter with succeeding cycles. Such hot spots would develop at various points in any large bed. An object of my invention is to avoid the occurrence of such hot spots and to eliminate any incipient hot spots from the bed before unsafe temperatures are reached.

It might be possible to divide a catalyst bed into small sections or segments and to control the temperature of each of these segments or sections by the controlled application of one or more of the above variables to each small section or segment. Such subdivision of the catalyst bed would, however, offer numerous structural and operating difficulties and an object of my invention is to avoid the necessity of such subdivision of the catalyst bed and the necessary separate regulation of the aforesaid major variables with respect to each such subdivided catalyst bed portion.

In accordance with my invention I employ in each catalyst restoration period or from time to time a step of "blowing" the catalyst bed with a hot gas such as air or regeneration gas produced in the process. I introduce this hot gas at approximately the desired conversion temperature. In the butadiene process I introduce it at a temperature in the general vicinity of 1100° F. with provision for varying this temperature between about 900° F. and 1200° F. as a normal operating procedure for establishing the average temperature of the catalyst bed as a whole. The amount of hot gas employed in this step is of an entirely different order of magnitude than amounts previously employed for catalyst regeneration, e. g., is from about 4 to 40 times (in the example herein described about six times) the amount heretofore believed to be sufficient for providing regeneration with a reasonable excess of regeneration gas. An outstanding feature of my invention is the avoidance of any effort toward temperature adjustment by blowing hot catalyst spots with cool gas or cool catalyst spots with hot gas. As opposed to such practice I employ a gas of substantially uniform temperature, preferably the approximate temperature at which conversion is to be effected. If the average temperature of the bed as a whole tends to rise, I may use a blow gas of correspondingly lower inlet temperature. If the average temperature of the bed as a whole tends to fall, I may use a correspondingly higher inlet temperature of this blow gas. I employ an amount of such gas which is sufficient to substantially blow out of the catalyst bed any incipient hot spots and any portions of the "temperature pattern" previously existing across various parts of the catalyst bed which would otherwise lead to undesirable temperatures. This unique and remarkably effective process of "blowing out" incipient hot spots and objectionably high portions of the "temperature pattern" will be described in more detail in connection with Figures 3, 4 and 5 of the drawings after I have explained the operation of the system as a whole in connection with Figures 1 and 2.

My "blowing" step is separate and distinct from the regenerating step heretofore known to the art. For regeneration, the amount of air is dependent in large degree on the amount of car-

6

bonaceous material to be burned. In the butadiene process with two parts Alundum to one part active catalyst the carbon deposits amount to about .05 to 0.2 pound of carbonaceous material per cubic foot of total bed at the beginning of a regeneration period. About 8 to 32 cubic feet of air is sufficient to burn this amount of deposit, but since all of the oxygen is not utilized a reasonable excess of regeneration air is used. The maximum amount of regeneration air heretofore proposed for this purpose (including this reasonable excess) has been in the general vicinity of about 50 cubic feet of air per cubic foot of catalyst bed. With a 7½ minute regeneration period this amounts to a regeneration rate of about 6 to 7 cubic feet of air per cubic foot of catalyst bed per minute.

For my blowing step, the amount of air or hot gas is not dependent on the amount of carbonaceous material but is dependent on the total mass of catalyst plus heat retention material and the location of incipient hot spots or cool spots in the catalyst bed. To blow a temperature pattern entirely out of a bed requires an amount of hot air or gas which has a heat capacity (mass multiplied by specific heat) roughly equal to the heat capacity (mass multiplied by specific heat) of the entire catalyst bed. In the butadiene process the specific heat of one pound of the catalyst bed (catalyst plus Alundum) is roughly equivalent to the heat capacity of one pound of hot air or flue gas. If the bed density is 100 pounds per cubic foot, then approximately 100 pounds of hot gas will be required for a complete temperature pattern blow-out. Thus while 50 cubic feet of air provides a reasonable excess for regeneration, I employ approximately 1300 cubic feet of air per cubic foot of catalyst for a complete temperature pattern blow-out.

Complete temperature pattern blow-outs may be employed after a plurality of intervening cycles, e. g., 6 cycles, when reversed flow is employed from cycle to cycle, but I prefer to use the hot blow step in each cycle in a unidirectional flow system, i. e., in a system where both charge and air enter the same side of the bed at all times. In unidirectional flow, the hottest part of the catalyst bed is adjacent the exit side thereof and the incipient hot spots or dangerously high portions of the temperature pattern may be blown out of this particular Alundum-catalyst bed with only about 200 to 350 cubic feet of hot air or flue gas per cubic foot of catalyst bed in each cycle. For a 7½ minute cycle this means that the blow rate should be about 25 to 50 cubic feet of hot gas per minute per cubic foot of catalyst bed. From these figures simple calculations will show that the amount of blow gas corresponds to about 10% to 25% of the heat capacity of the bed. In other words, roughly about ¼ of the temperature pattern is blown out of the bed in each cycle. In processes such as catalytic cracking it may be necessary or desirable to blow out more of the temperature pattern in each cycle, i. e., to employ even greater blow rates.

The regeneration air may have a small effect in displacing the temperature pattern in a catalyst bed, but its effect for such purpose is negligible. Likewise some regeneration or combustion may take place in my blowing operation. The regeneration step, however, produces hot spots and in repeated cycles makes them get hotter and hotter. My blowing step removes hot spots and on repeated cycles insures that all parts of the bed will be brought to or maintained with-

in the desired operating temperature range. The blowing and regeneration steps may merge into each other and proceed simultaneously for at least a part of a hot air-blow step, but each plays its individual function. A blowing with hot air or flue gas for effecting regeneration is not the "blowing" step of my invention unless a sufficient amount of the hot air or flue gas is employed for blowing out incipient hot spots and undesirably high or low portions of temperature patterns across the bed.

The invention will be more clearly understood from the following detailed description read in conjunction with the accompanying drawings which form a part of this specification and in which:

Figure 1 is a diagrammatic flow sheet of a commercial butadiene plant employing a 4-reactor system and the use of hot air for blowing out incipient hot spots and at least a portion of the temperature pattern across the catalyst bed;

Figure 2 is a diagrammatic flow sheet of a commercial plant employing a 6-reactor system and utilizing hot regeneration gas as well as "blow gas" for blowing out the temperature pattern across certain of the catalyst beds;

Figure 3 is a series of graphs illustrating how the temperature pattern in a vertical line through a horizontal catalyst bed changes from cycle to cycle with unidirectional flow in the absence of my added hot gas blowing step;

Figure 4 is a series of graphs illustrating how the temperature pattern taken in vertical line through a horizontal catalyst bed changes from cycle to cycle with reverse flow;

Figure 5 is a series of graphs illustrating in stages the effect of my hot gas blowing step in blowing out of a catalyst bed a temperature pattern resulting from a series of reverse flow operations;

Figure 6 is a series of graphs illustrating the effect of my hot gas blowing step in partially blowing out of a catalyst bed the highest portion of the temperature pattern in each cycle of a unidirectional flow-operation;

Figure 7 is an idealized chart illustrating the general type of temperature curves that might be expected by continuously recorded temperatures at the inlet, mid-point, and outlet of a catalyst bed employing unidirectional flow but no blowing step;

Figure 8 is a chart as in Figure 7 where the entire temperature pattern is blown out in each cycle and

Figure 9 is a chart as in Figure 7 where only about $\frac{1}{2}$ of the temperature pattern is blown out in each cycle.

The charging stock for the butadiene plant may be normal butane, normal butenes or mixtures of normal butanes and normal butenes. The charging stock may, of course, be obtained from natural gas or from the reduction of carbon monoxide with hydrogen (the so-called Fischer synthesis) or from any other natural or synthetic source. In the example herein described I employ the so-called butanes-butylenes or "B-B" stream of refinery gases including butanes and butylenes from various thermal and catalytic processes as well as from crude oil distillation. Such B-B stream may be introduced from source 10 to feed preparation unit 11.

In the feed preparation unit the charge may be prefractionated to remove any C_3 or lighter hydrocarbons together with a substantial amount of the isobutane from the heavier normal butane-

butene fraction. This heavier fraction may then be subjected to a cold acid polymerization treatment by treating it at about 100° F. with 65% sulfuric acid in a conventional recycling system. In this treatment the isobutylene is selectively removed. The unpolymerized gases are again fractionated to remove any pentanes and to remove the bulk of the remaining isobutane. The remaining mixture of normal butanes and normal butylenes is then passed from plant 11 by line 12 to pipe still 13. Any C_4 streams which are substantially free from branched-chain hydrocarbons may be introduced to the pipe still from line 14. Recycled butanes and butylenes are introduced into the pipe still from line 15. While cold acid polymerization has been described as a preferred method of removing isobutylene it should be understood that the isobutylene may be removed by polymerization with boron fluoride, aluminum chloride or other known catalyst at sufficiently low temperatures and under such conditions as to selectively remove the isobutylene. Any other known method of obtaining the normal butane-normal butylene stream may be employed and since no invention is claimed in this particular step per se it will not be described in further detail.

The charging stock is passed by separate pumps through separate tubes (convection tubes, wall tubes, and roof tubes respectively) 16 and 17 in pipe still 13 and therein heated to a temperature of about 1000 to 1200° F., e. g. about 1125° F. The hot streams are then introduced through respective transfer lines 18 and 19 to the reactors which are on stream. Reactor A or B is supplied via branch line 20a or 20b from transfer line 19 and reactor B or C is supplied via branch line 20b or 20c from transfer line 18. It should be understood that more than one furnace may be employed in this system, i. e., one furnace may heat the charge to reactors A and B while another heats the charge to reactors C and D.

The reactors in the particular example herein described are cylindrical vessels about 16 feet in diameter by about 45 feet in length, lined with fused Alumina molded bricks. Across the middle of these reactors I provide a horizontal catalyst bed 21 about 3 feet in depth, this bed being supported by a grid and structural elements (not shown) which will retain their necessary structural strength when subjected to the maximum temperatures encountered in the catalyst regeneration. Metal parts in the reactor which are subjected to alternate oxidizing and reducing conditions should be of high chrome (e. g. 27%) or chrome-nickel 25%-20%) or equivalent material. Formation of iron oxide must be avoided in this part of the system. The supporting grid must of course permit the free flow of gases and vapors to and from the catalyst bed. To insure proper distribution of vapors in the bed, this catalyst bed may be subdivided by longitudinal and transverse vertical plates (not shown) into a plurality of individual sections and the gas flow through these sections may be controlled by suitable dampers (not shown) operated from the outside of the reactor by any means known to the art. Such a subdivision of the catalyst bed is usually not required in the practice of my invention although it may be desirable to employ baffles, distributors or dampers for directing the flow of charging stock and hot gases to various parts of the bed so that each part of the bed will function with

maximum effectiveness. When upflow is employed through the catalyst bed it may be necessary or desirable to employ a retaining grid at the top as well as at the bottom of this bed or to weight the top of the catalyst bed to insure that the catalyst will not be blown out of position.

It is not essential of course that the reactor be of the size and shape hereinabove described or that the reactor drum or catalyst bed be horizontally mounted. If the drum is vertically mounted it may be provided with a plurality of horizontal beds of approximately 3 feet in depth and the inlet, outlet and distributor conduits may be so arranged as to maintain the flow of hydrocarbons and hot gases respectively through said beds in parallel or series or series-parallel flow. My invention is not limited to any particular reactor structure or arrangement and it should therefore, be unnecessary to describe alternative reactor designs in any further detail. The term bed "depth" as used herein is hereby defined as the dimension of the bed in the direction of charging stock or blow gas flow. Catalyst beds are of large cross-sectional area, the area of each bed in this case being upwards of about 500 square feet. A series of thermocouples may be placed at spaced points from top to bottom of this bed at various locations therein as illustrated by thermocouples 22, 23, and 24. By means of these thermocouples it is possible to ascertain the temperature pattern across the bed at any instant in the particular area where the thermocouples are mounted.

The catalyst employed for the butadiene process is preferably a chromium oxide on active alumina. Such catalysts may be prepared in the same manner as dehydrogenation catalysts employed for other purposes and since the preparation of such catalysts is well known to those skilled in the art the catalyst preparation requires no detailed description. It should be pointed out, however, that other VIII group metal oxides may be employed instead of chromium oxide and that any other dehydrogenation catalyst of similar properties may be employed. The catalyst material is preferably in pelleted or granular form having a particle size of about 2 to 10 mesh although larger or smaller particles may be used.

Uniformly admixed with the catalyst particles I employ a heat retention material such as fused alumina or Alundum or any other material which has no deleterious effect on the desired conversion and which has the necessary properties of heat capacity and heat conductivity. About two volumes of Alundum may be employed per volume of active catalyst although this proportion may be varied over a relatively wide range, for example, from about 5:1 to about 5:1. In some cases the catalyst or catalyst support itself may serve as sufficient heat retention material. The specific gravity of Alundum is about 2 as compared with an active catalyst specific gravity of about 1. The catalyst bed depth is of course the depth (dimension in the direction of gas or vapor flow) of the mixed catalyst and Alundum mixture and while this bed depth is preferably about 3 feet it should be understood that bed depths may likewise vary throughout a relatively wide range, for example, from about 1 foot or less to 6 feet or more.

Each catalyst bed is first brought to conversion temperature by blowing it with a hot gas until all parts of the bed are at approximately 1050° F. This hot gas may be air from source 25 which is heated in furnace 26 by burning a gas introduced

through line 27. The air is preferably heated to a temperature of about 1050° F. either by direct combustion or indirect heating and is passed through header 28 and branch lines 29a, 29b, 29c or 29d to the desired reactor. The heating step may be effected at approximately atmospheric pressure or about 5 pounds gauge although higher pressures may be employed. During the heating the gases which have passed through the bed are withdrawn through line 30a, 30b, 30c or 30d and are discharged through line 31. The heat energy in these gases may be employed for any desired purpose such as driving a turbine, generating steam, preheating charging stock, etc.

When the catalyst bed has reached conversion temperature the hot gas inlets and outlets are closed and the reactor is evacuated through line 31a, 31b, 31c or 31d leading to line 32 which in turn leads to an ejector 33 or series of ejectors or other commercial means for evacuating the system and reducing its pressure to approximately 25 inches of mercury vacuum (about 1 to 4 pounds pressure absolute). The reaction pressure should be as low as is commercially feasible since butadiene production increases with decreased reaction pressure. When steam or other diluent gas is employed with the B-B charge the reaction pressure refers to the partial pressure of the B-B component of the mixture. By using a sufficient amount of steam carbon dioxide, nitrogen or other diluent gas the system may be operated at atmospheric pressure or even higher and the use of ejectors may be unnecessary.

During the latter part of the evacuation step a purge or reducing gas may be introduced into the reactor through line 34 and branch lines 35a, 35b, 35c or 35d. This purge or reducing gas may be hydrogen, a fuel gas or a mixture of hydrogen and light hydrocarbon gases and it may be obtained from the product absorption unit as will be hereinafter described. The purge step not only displaces any free oxygen in the reactor chamber but it preconditions the catalyst in such a way as to reduce coke deposition in the subsequent processing period; it effects a certain amount of catalyst reduction thereby avoiding undue degradation of charging stock when the reactor is placed on stream.

When a reactor has been brought to conversion temperature, evacuated and purged, the hot charging stock vapors are introduced through appropriate line 20a, 20b, 20c or 20d and passed through the catalyst bed at a space velocity in the general vicinity of about 200 to 800 volumes of gas (measured under standard conditions) per hour per volume of catalyst (exclusive of space occupied by heat retention material). Based on total bed, the feed rate is about 1 to 4 volumes of gas per minute per volume of catalyst bed. The space velocity will be dependent to some extent of course on the nature of feed, i. e., will be lower with increased amounts of normal butane and higher with lesser amounts of normal butane in the feed. Space velocity will depend to some extent on the activity of the particular catalyst employed. Space velocity will also depend to some extent on conversion temperature, i. e., will be higher with higher temperatures. The conversion temperature is preferably of the order of about 1100° F., i. e., is 1100° F. plus or minus about 100° F. or preferably plus or minus not more than about 50 to 75° F.

The reaction products may be withdrawn from the reactors through line 36a, 36b, 36c or 36d to manifold 37 and thence through line 38 to quench

tower 39. If desired of course a separate quench tower may be employed for each reactor or for each pair of reactors. The quench tower operates at substantially the same pressure as the reactor and in this tower the temperature of the reaction products is rapidly reduced to approximately 100 to 200° F. by means of a cooled quench oil which is sprayed in the upper part of the tower at a plurality of levels through sprays or distributors 40. A substantially constant liquid level of quench oil is maintained just below the outlet of line 38 and quench oil is removed from the bottom of the absorber through line 41. A part or all of this oil may be recirculated by pump 43 and cooler 44 through line 45 to distributors or nozzles 40. Quench oil from an external source may be introduced through line 46 or 46a. A quench oil accumulator drum may be employed with each tower or a single drum may be employed for use with a plurality of towers, the hot quench oil preferably being introduced directly into the drum from the base of each tower and quench oil being pumped from the drum through cooler 44 to distributors 40. This quench oil may be a relatively non-volatile hydrocarbon oil such as a gas oil. Other liquids may of course be used for this purpose and when such liquids are not chemically altered they may simply be recycled. If the liquids are chemically altered or converted, the quenching liquid may be used on a once-through basis or on a continuous basis with conversion product removal.

To avoid possible entrainment or carry-over of quenching liquid I may employ suitable baffles or a bed of packing material 47 in the upper part of the quench tower. Product vapors leaving the top of the quench tower through line 48 pass through dry drum 49 from which any liquid may be withdrawn through line 50. Gases leave dry drum 49 through line 51 to compressor 52 and are then passed through cooler 53 to dry drum 49a from which any condensate may be removed through line 50a. Gases from dry drum 49a pass through lines 51a, compressor 52a and cooler 53a to dry drum 49b from which any condensate may be removed through line 50b. Gases from dry drum 49b pass through line 51b, compressor 52b and cooler 53b to receiver or separator 54. The condensed liquid is withdrawn from this separator through line 56. Gases from this separator pass through cooler 58 for effecting further condensation and thence to receiver or separator 58. Gases from the top of separator 58 are introduced through line 59 to the base of absorber 60 which is preferably operated at a pressure of about 150 pounds per square inch with a top temperature in the general vicinity of about 100° F. and a bottom temperature in the general vicinity of about 140° F. The absorber oil may be a heavy naphtha, a light gas oil or other suitable hydrocarbon introduced through line 61. Unabsorbed gases, chiefly hydrogen and light hydrocarbons, are withdrawn from the top of the absorber through line 62 and a part of these gases is passed through line 63 to header 34 for supplying the purge or reducing gas for the reactor system.

Rich absorber oil from the base of absorber 60 is passed through heat exchanger 64 and heater 65 and then introduced through line 66 to an intermediate point in stripper 67 which is operated at a pressure of about 60 pounds gauge with a bottom temperature in the general vicinity of 300° F. and a top temperature in the general vicinity of about 120° F. A suitable heater or

reboiler 68 may be employed at the base of this stripper and steam may be introduced through line 68a. Reflux may be introduced at the top thereof through line 69. Condensate from receiver 54 is introduced at an upper part of the stripper through line 66. Lean absorber oil from the base of the stripper is passed by pump 70 through exchanger 64 and cooler 71 to line 61 for introduction at the upper part of absorber 60.

The product stream leaving the top of the stripper through line 72 is cooled in cooler 73 and introduced into receiver 74. Any gases which separate out in this receiver are returned by line 75 to dry drum 49a or 49b. Liquid from separator 58 is introduced by line 76 to receiver 74. A portion of the liquid from receiver 74 is introduced by pump 77 to the top of stripper 67 and the remainder is scrubbed with caustic in caustic treating system 78 and then washed in water wash system 79. The washed product then passes through heater 80 to a low point in extractor 81 wherein it is countercurrently extracted with a selective solvent for removing butadiene from other hydrocarbons. The extractor may be operated at a pressure in the general vicinity of atmospheric to 3 pounds gauge with a bottom temperature of approximately 35° F. and a top temperature of approximately 25° F., the solvent in this case being a cuprous-cupric acetate ammonia composition known to those skilled in the art. It should be understood that any other suitable solvent or agent may be used for this purpose providing that system and the operating conditions thereof are suitably modified to meet the requirements of such solvent. The solvent is introduced through line 82 and cooler 83 to the top of the extractor 81.

The unabsorbed butanes and butylenes leaving the top of the extractor pass through line 84 to scrubber 85 wherein they are countercurrently scrubbed with water introduced through line 86. The scrubbing liquid (aqueous ammonia) leaving the base of the scrubber through line 87 may be suitably treated for recovering ammonia. The scrubbed butanes and butenes may be passed from the top of the scrubber through line 88 to feed preparation unit via line 89 or via line 15 to the charging stock heater. In order to prevent any buildup of isobutanes or isobutenes in the system it is preferred to introduce at least a part of this stream into the feed preparation unit.

The butadiene rich solvent liquid from the base of extractor 81 is introduced by pump 90 and line 91 to the upper part of scrubber 92 which may be operated at a pressure of about 6 pounds gauge with a top temperature of about 34° F. and a bottom temperature of about 46° F. The overhead from the stripper is introduced by line 93 to a low point in extractor 81. The butadiene-solvent liquid passes from the base of stripper 92 through line 94 to an upper part of desorber tower 95 which may be operated at a pressure of about 10 pounds gauge with a bottom temperature of about 180° F. and a top temperature of about 95° F., this desorber being provided with a suitable heater or reboiler 96. A part of the butadiene removed from the top of the desorber is introduced through line 97 to a low point in stripper 92 for maintaining a relatively high butadiene content in the base of the stripper and insuring the removal of butenes. The remainder of the overhead from desorber 95 is removed through line 98 to scrubber 99 and scrubbed with water introduced through line 100. Aqueous am-

monia is removed through line 101. The scrubbed butadiene product is pumped from the top of scrubber 99 through line 102 and cooler 103 to butadiene storage tank 104.

After a reactor has been on stream for approximately 15 minutes the charging stock stream is diverted to another reactor and for about 2½ minutes the reactor chamber may be evacuated to remove as much as possible of the hydrocarbon materials therefrom. Evacuation at this stage is not always necessary and this evacuation step may be omitted. Hot air is then introduced into the system through line 29a, 29b, 29c or 29d for a period of about 7½ minutes in amounts sufficient to effect both regeneration and blowing of the catalyst to remove incipient hot spots and to blow out undesirable peaks in temperature patterns at various lines across the catalyst bed. While about 6 to 7 cubic feet of gas per minute per cubic foot of total catalyst bed is sufficient to effect regeneration, I employ about 25 to 50 cubic feet of gas per minute per cubic foot of catalyst bed. During the first part of this 7½ minute period most of the catalyst deposit is removed. During this 7½ minute period the incipient hot spots and peaks of temperature patterns across various lines of the catalyst bed are effectively blown out of the bed. Of the gas employed during this period only about 1 to 4 cubic feet per minute is required for the complete combustion of carbonaceous deposits, and 6 to 7 cubic feet per minute was about the maximum heretofore employed for producing a reasonable excess and insuring sufficiently complete combustion. This amount of air would not blow out incipient hot spots but would result in overheating and would render the process inoperable, as has been fully demonstrated. The additional 18 to 44 cubic feet per minute which I employ is not for the purpose of burning deposits but is for the purpose of blowing out incipient hot spots as will be described in more detail in connection with Figures 4 to 8.

After the regeneration and blowing step the introduction of hot air is discontinued and the reactor is evacuated for 2 or 3 minutes to remove as much as possible of the free oxygen from the catalyst chamber. Finally, the purge or reducing gas from line 34 is passed through the catalyst bed and discharged through lines 31a, 31b, 31c or 31d and line 32 at low pressure to recondition the catalyst which is now ready to once more go on stream with hot charging stock. This series of steps constitute the catalyst restoration portion of the cycle. The time sequence of the various reactors may be as shown by the legend adjacent Figure 1. If a 2½ minute purge follows each on-stream period, the evacuation and purge following regeneration and blowing may be reduced to 5 minutes. At any instance two reactors are on stream, one reactor is undergoing regeneration and "air-blow" and one reactor is undergoing either an evacuation or reduction and purging operation. The charging system, hot air system and evacuation system are each in continuous operation.

In Figure 2 I have illustrated a 6-reactor system in which I may use hot regeneration gases from one reaction chamber for blowing out the incipient hot spots and peaks of the temperature pattern in other reaction chambers. Also, I may effect regeneration of some beds with hot gases previously used for blowing operations in other beds. In this system the sequence of operations

is somewhat modified to provide for a relatively long blowout period of about 1½ hours after six cycles each of which having a 15-minutes' on stream period and 15 minutes' period of regeneration and evacuating and purging (7½ minute regeneration and 7½ minute evacuating and purging). In this system provision is made for reversing the flow of charging stock in alternate cycles. The flow of regeneration gas is unidirectional since the direction of regeneration gas flow has little or no appreciable effect on the temperature patterns which are developed in the catalyst bed.

In Figure 2 the reactors are designated A, B, C, D, E and F and two furnaces 13' and 13'' are employed for heating the charging stock which is introduced from line 12. Charging stock from furnace 13' may be introduced into any one of these reactors through transfer line and branch lines 20'a, 20'b, 20'c, 20'd, 20'e and 20'f where downflow is desired or line 20'a', 20'b', 20'c', 20'd', 20'e' or 20'f' where upflow is desired. Charging stock may be introduced to any one of the reactors through the same branch lines from furnace 13'' and the lines are so arranged that each furnace may constantly supply the charge to one of the reactors on stream. Products are removed from each of the reactors through lines 36'a, 36'b, 36'c, 36'd, 36'e and 36'f through corresponding quench towers 39 to the compressors. The remainder of the cycle as well as the feed preparation, recycling, etc. will be the same in this case as in connection with Figure 1 and such features will therefore not be repeated in connection with Figure 2. It should be observed that in Figure 2 the arrangement of pipes and valves is such that charging stock flow through the catalyst bed may be in either direction or in alternate directions in succeeding cycles. This arrangement of pipes and valves will be clearly apparent to those skilled in the art from the drawing itself and a more detailed description of this arrangement is therefore unnecessary.

The hot air may be introduced into each of the reactors from header 28' and branched lines 29'a, 29'b, 29'c, 29'd, 29'e or 29'f. The temperature of this hot air may be automatically controlled immediately prior to each reactor. The temperature of the hot air entering reactor A may be controlled by an automatic regulator 105 controlling the amount of gas introduced through line 27' to air heater 26'. Since one chamber will be undergoing regeneration and two chambers will be undergoing a blowing operation and since it is desirable to have the inlet gas to each reactor which is undergoing the blowing operation at a temperature of approximately 1100° F., I provide a supplemental air system comprising an air inlet 106, blower 107 and cold air main 108. The temperature of the gas introduced into reactor B will thus be controlled by temperature controller 109 which regulates the amount of air introduced through branch line 110 and hydrocarbon or other combustible gas introduced through line 111. If reactor C is to undergo a blowing operation the temperature of the entering gas will be controlled by controller 112 which controls the amount of air from branch line 113 and combustible gas from branch line 114. If reactor D is to undergo a blowing operation the temperature of the entering gases will be controlled by temperature controller 115 which controls the amount of air introduced

through branch line 116 and combustible gas through branch line 117. Similarly the temperature of gases introduced into reactor E is controlled by temperature controller 118 and the temperature of gases entering reactor F is controlled by temperature controller 119.

The purging operations in this cycle will be effected in the same manner as hereinabove described in connection with Figure 1, the purge gas entering through line 34' and branch lines 35'a, 35'b, 35'c, 35'd, 35'e and 35'f and the evacuated gases being removed through lines 31'a, 31'b, 31'c, 31'd, 31'e and 31'f through main 32' to ejector 33'.

In the system of Figure 2 each reactor is on stream for 15 minutes, regenerated for 7½ minutes and evacuated and purged for 7½ minutes in each of six successive cycles with up-flow and downflow of charging stock in alternate successive cycles, and then is subjected to a hot blowing operation for a period of time corresponding to three complete cycles. In this example the air rate for both the blowing and regenerating steps may be of the order of about 15 cubic feet of gas (measured at standard condition) per minute per cubic foot of catalyst bed. The purpose of this blowing step and its function of blowing out incipient hot spots and peaks of temperature patterns will now be described in further detail in connection with Figures 3 to 6.

In Figure 3 I have shown a series of graphs to illustrate how temperature patterns develop across the catalyst bed with unidirectional charging stock flow but in the absence of any hot gas blowing steps. Assuming for example that the catalyst bed has been blown with hot gas introduced at 1100° F. so that all parts of the catalyst bed are at this temperature and that thermocouples are placed in a line through this bed as indicated by points 23 in Figure 1, the temperature reading of each thermocouple will be 1100° F. and the temperature "pattern" across the bed will be straight line *xx'* of graph I. When the catalyst is regenerated after this on-stream period, the front or inlet end of the temperature pattern will be lowered because the heat lost during conversion in the inlet portion of the bed has exceeded the heat gained during regeneration. Near the discharge end of the catalyst bed the temperature will be considerably higher because the heat gained during regeneration in this portion of the bed exceeds the heat lost during reaction. After this regeneration step, therefore, the temperature across the bed in the area of points 23 will be as indicated by line *2x, 2x'* of graph II. After the next cycle of on-stream and regeneration the temperature pattern across the bed this location will be *3x, 3x'* and after another on-stream and regeneration the temperature pattern across the bed will be *4x, 4x'* as illustrated in graphs III and IV of Figure 3.

Even if the temperatures at areas adjacent points 22 and 24 in the catalyst bed were identical to the temperatures in area 23 it will be seen that after three or four cycles the inlet side of the bed is too cool for effecting conversion and the discharge side of the bed is so hot as to impair the catalyst and lead to cracking rather than dehydrogenation. Such unidirectional flow without my blowing step would, therefore, be inoperative even if there were no variations in temperatures at various cross-sectional areas in the bed. The catalyst adjacent thermocouples 24 may be slightly hotter than the catalyst adjacent thermocouples 23 after the first regeneration step so

that the temperature pattern across the bed in the area of thermocouples 24 will be as indicated in line *2y, 2y'* in graph II. During the next cycle the temperature pattern across the catalyst bed in this area will be *3y, 3y'* and after the following cycle it will be *4y, 4y'*. It can readily be seen that a hot spot rapidly develops in the area of thermocouples 24 and that after two or three cycles the catalyst in this area will be ruined by high temperature.

After the first on-stream and regeneration cycle the area adjacent thermocouples 22 in the catalyst bed may be cooler than area 23 so that the temperature pattern across this area will be *2z, 2z'* of graph II. In succeeding cycles the temperature pattern of this particular area would change to *3z, 3z'* and *4z, 4z'*. It will be noted that the discharge side of the catalyst bed will get too hot even in the cooler catalyst area and that while the temperature difference increases from cycle to cycle in these various bed areas the major difficulty is the enormously high temperatures which are reached in a relatively short time on the discharge side of the catalyst bed.

To solve this problem of overheating the catalyst at the discharge side of the catalyst bed it has been proposed to use reverse charging stock flow, i. e., to pass the charging stock downwardly through the bed in the first cycle, then upwardly through the bed on the second cycle, then downwardly on the third, etc. It was thought that by this method of operation a uniform temperature might be maintained in the bed. Tests made in small laboratory apparatus on beds of only a few inches in diameter have shown that with this type of operation temperature patterns are developed across the bed as diagrammatically illustrated in Figure 4. Starting with a uniform bed temperature of *mm'* at about 1050° F. the temperature pattern after the first regeneration will be similar to temperature pattern *2x, 2x'* of Figure 3. With reverse charging stock flow during the next on-stream period and another regeneration, this temperature pattern will be *3m, 3m'* as shown in graph II of Figure 4; it will be noted that both the inlet and outlet temperatures have been considerably lowered and that a peak temperature *3m''* is developed at an intermediate point in the bed. After another on-stream flow and regeneration the temperature pattern is as shown at *4m, 4m'* in graph III of Figure 4. After still another on-stream period and regeneration, the temperature pattern will be as indicated by line *5m, 5m'* in graph IV of Figure 4. It will thus be seen that at this particular temperature a reasonably uniform bed temperature may be maintained in this bed of very limited cross-sectional area.

Using an initial bed temperature of about 1100° F. as illustrated by *nn'* of graph I, it will be found that after two periods of on-stream and regeneration the temperature pattern across the bed will be *3n, 3n'* and that the peak *3n''* of this curve is considerably higher than the peak *3m''* of curve *3m, 3m'*. After another cycle of on-stream and regeneration the temperature pattern will be *4n, 4n'* having a still higher peak *4n''*. After still another on-stream and regeneration period, the temperature pattern will be *5n, 5n'* with a very high peak *5n''*. It can readily be seen that even this small scale laboratory apparatus cannot be successfully employed at temperatures in the vicinity of 1100° F. because of the hot spots that develop near the center of the catalyst bed.

17

If the reverse flow operation were employed on a commercial scale with a bed of large cross-sectional area it might be possible to control such variables as charging stock composition, space velocities, inlet temperatures, pressure, etc. to hold a substantially constant temperature at point 23 in the bed; i. e., this point of the bed might be held to a temperature pattern corresponding to 5m, 5m'. At areas 22 and 24 in the bed slightly higher or lower temperatures would inevitably develop. If the temperature at point 24 became slightly higher, then a hot spot would develop in this area and a temperature pattern of the type illustrated by 5n, 5n' would result, with a peak far above safe operating temperatures. If the temperature at area 22 should get a little lower than that at area 23 then at point 22 the temperature pattern would fall below the desired operating range.

Thus there are two fatal objections to the reverse flow idea for solving the temperature control problem: (1) the bed as a whole cannot be operated at the desired conversion level and (2) hot spots would inevitably develop at various points in the large cross-sectional area catalyst bed. Hot spots do not develop in the reverse flow system as rapidly, however, as they develop in the unidirectional flow system. It is therefore possible to operate a bed of relatively large cross-sectional area with reverse flow for a few cycles before dangerous hot spots are produced. After five or six cycles it is necessary to discontinue the conversion until the bed can be brought back to a more nearly uniform temperature. In order to bring such bed to uniform temperature I blow it with a hot gas introduced at approximately the desired conversion temperature and I use an amount of gas which will have a heat capacity roughly equivalent to the heat capacity of the catalyst bed. The amount of hot air or other hot gas will depend on the particular catalyst bed employed because different catalysts and catalyst-heat retention mixtures will have different heat capacities. Each cubic foot of catalyst bed in the example herein described weighs roughly about 100 pounds (usually about 105 pounds). I have found that the specific heat of this catalyst bed at the desired conversion temperature is roughly equivalent to the specific heat of air at substantially the same temperature. Therefore, I employ about 1 pound of hot air for each pound of catalyst bed in order to effect the blowing out of the temperature pattern in the bed. For complete temperature pattern blow-out this means that for each cubic foot of catalyst bed I employ roughly about 1350 cubic feet of air (measured at standard conditions). Thus in the system of Figure 2 I employed a blowing period of about 1½ hours. After the first 15 minutes of this blowing period the temperature pattern through this bed will be as illustrated by line op 5n, 5n' in graph II of Figure 5. It should be noted that the cool portion of the temperature pattern is not materially warmed up nor is the hot portion of the temperature pattern materially cooled down. The main effect of the blowing step is to simply move the temperature pattern toward the discharge side of the bed. If the blow gas at 1100° F. meets catalyst at only 1050° F., then the catalyst is warmed up by the entering hot gas but the gas is likewise cooled down by the cool catalyst so that it tends to cool the adjacent catalyst further over in the bed. Likewise, when 1100° F. air passes through 1200° F. catalyst the air cools the catalyst but the air it-

18

self is heated to about 1200° F. and it, therefore, tends to heat succeeding parts of the catalyst bed to this high temperature. The net effect of the blowing step is thus to simply blow the temperature pattern through the bed. Graph III of Figure 5 illustrates the temperature pattern after the blow is substantially complete.

If the temperature pattern were only blown out to the extent indicated by curve op 5n, 5n' in graph II of Figure 5, and then charging stock were passed from the bottom to top of the bed in the next cycle, the peak of the curve 5n' would be carried back to a mid-point in the bed by heat capacity of the charging stock stream itself. One volume of C₄ hydrocarbons weighs about twice as much as one volume of air and it has a specific heat at 1100° F. about three times that of air so that 3 volumes of charge per minute would have approximately the same effect in displacing the temperature pattern as would 18 volumes of air. In the reversed flow operations it is therefore essential that the incipient hot spots or unduly high portions of the temperature pattern be completely eliminated in each blowing step. In the system described in connection with Figure 2, I have illustrated such reverse flow operation with substantially complete temperature pattern blow out after each six cycles. I prefer, however, to employ unidirectional flow and to use a blowing step in each cycle sufficient to blow out the unduly high portion of the temperature pattern, i. e., the incipient hot spots. With unidirectional flow the hottest portion of the catalyst bed will always be at the discharge side thereof and it is thus unnecessary to worry about hot spots at intermediate points in the catalyst bed. Furthermore, the flow of charging stock itself helps to displace the temperature patterns in the desired direction.

If only the conventional amount of hot air were employed for regeneration after a first on-stream period in the system described in Figure 1 the resulting temperature pattern in the bed would be as shown by line 2x, 2x' in graph I of Figure 6 (or graph II of Figure 3). By employing a gas blow rate of 25 to 50 cubic feet per minute per cubic foot of catalyst bed (instead of the 6 or 7 cubic feet per minute that would be used for regeneration) I obtain after the first regeneration cycle a temperature pattern as illustrated by line op 2x, 2x' in graph II of Figure 6. It will be noted that the temperature pattern has been partially blown out of the catalyst bed, that the inlet side of the catalyst bed is at the desired conversion temperature and that the discharge side of the catalyst bed is at a lower temperature than it was at the beginning of the cycle. By using this hot gas blow step in each cycle to the extent indicated (using for example a 1/6 "temperature pattern blowout" in each cycle) I obtain an equilibrium temperature pattern roughly as indicated by line opqr in graph III of Figure 6. If a catalyst bed gets too hot at a particular area, the highest temperature will be adjacent the discharge side and the incipient hot spot will be blown out during each cycle. If another area of a large catalyst bed tends to get too cool the hot gas blow step in each cycle brings that particular area of the bed back to the desired operating temperature in only a few cycles of operation. Thus my system avoids the development of unduly hot areas and unduly cool areas in a large catalyst bed and insures substantially uniform temperatures at all cross-sectional areas of the bed. Continued operation

without my hot gas blowing step causes greater and greater divergence of temperatures and inevitable hot spots as illustrated in Figures 3 and 4. With a partial hot blow step in each cycle of unidirectional flow operation any temperature differences are constantly brought into line or eliminated. My system constantly blows out incipient hot spots and the undesirable portions of the temperature pattern curve and it establishes and maintains an equilibrium condition throughout all areas of a large catalyst bed. Without the air blow step the system gets out of balance with the inevitable development of hot spots which would render said system inoperative.

In Figures 3, 4, 5 and 6 I have shown various temperature patterns across the catalyst bed immediately after regeneration steps and before the catalyst goes on stream in subsequent cycles. In Figure 7 I show how a temperature at the inlet, outlet and mid-point of the bed will vary with time in a unidirectional flow cycle operation in the absence of my hot gas blowing step. If operations are so controlled as to bring the temperature of the mid-point thermocouple to a predetermined temperature level at the beginning of each cycle then the average temperatures indicated by the inlet thermocouple will gradually fall and the average temperatures indicated by the outlet thermocouples will gradually rise. In other words, Figure 7 illustrates the type of curve that would be drawn by continuous recorders actuated by thermocouples mounted at the outlet, mid-point and inlet of a catalyst bed in any particular line therethrough in a unidirectional flow operation without my hot gas blowing step.

With complete temperature pattern blowout during each cycle a continuous recording of temperatures measured by said inlet, mid-point and outlet thermocouples would be substantially as illustrated in Figure 8. With unidirectional flow, however, complete temperature blowout is not necessary or even desirable. In Figure 9 I have illustrated the type of continuous recordings that would be registered by inlet, outlet and mid-point thermocouples in the type of operation hereinabove described in connection with Figure 1, i. e., using an air blow sufficient to displace approximately $\frac{1}{6}$ of the temperature pattern in each cycle. It will be noted that substantially all parts of the bed are maintained within the desired operating temperature range. It should be understood that all of the above curves are more or less idealized and that actual recordings will be less regular. The curves in Figure 8 as well as in Figure 9 and in Figure 7 may cross each other and show considerable fluctuations not shown on these idealized figures. The general temperature patterns, however, will be substantially as hereinabove set forth.

I have already stated that the nature of the charging stock has an appreciable effect on the temperatures developed in the catalyst bed. Thus when using a charging stock containing about 58% normal butenes and 42% normal butanes the following data were obtained in a series of cycles using pressure of about 2 to 3 pounds absolute, a charge rate of the order of about 250 cubic feet per hour per cubic foot of catalyst bed (about 750 cubic feet per hour per cubic foot of active catalyst in the bed) and an inlet transfer line temperature of approximately 1050° F.:

Inlet Air Temp.	Inlet Catalyst Bed Temp.	Midpoint Catalyst Bed Temp.	Exit Catalyst Bed Temp.	Average Catalyst Bed Temp. ¹
°F.	°F.	°F.	°F.	°F.
1,110	1,120	1,095	1,135	1,117
1,115	1,120	1,095	1,140	1,118
1,120	1,125	1,090	1,135	1,117
1,120	1,120	1,095	1,130	1,114
1,110	1,120	1,090	1,135	1,116
1,110	1,115	1,090	1,140	1,115

¹ Based on all thermocouples throughout the bed.

When a charging stock rich in butanes, i. e., containing about 30% normal butenes to 70% normal butane was employed at approximately the same pressure and charge rate with an inlet feed temperature of about 1050 to 1075° F. there was relatively less carbon deposition and hence a tendency for the average bed temperature to become cooler. In this case, the average bed temperature was maintained at the desired level by employing an inlet air blow gas temperature in the vicinity of 1200° F. This produced a slightly different temperature pattern across the bed as will be apparent from the following data:

Inlet Air Temp.	Inlet Catalyst Bed Temp.	Midpoint Catalyst Bed Temp.	Exit Catalyst Bed Temp.	Average Catalyst Bed Temp.
°F.	°F.	°F.	°F.	°F.
1,190	1,160	1,090	1,095	1,116
1,185	1,160	1,095	1,095	1,118
1,185	1,160	1,095	1,100	1,118
1,185	1,150	1,090	1,105	1,116

Where charging stocks containing a preponderance of normal butenes is employed, it may be necessary to employ an inlet blow gas temperature as low as 1000 or even lower in order to maintain the average bed temperature at the desired level. Thus the inlet temperature of the blow gas is varied in accordance with the nature of the charging stock and operating conditions and it serves to maintain a substantially constant average bed temperature in addition to its function of blowing out incipient hot spots and unduly high portions of the temperature pattern across the bed.

In starting up the system as described in Figure 1, it is desirable to initially go on-stream at a temperature slightly lower than the final desired operating temperature, i. e., to go on-stream at about 1050° F. If the desired operating temperature is about 1100° F. This is because unduly high temperatures might otherwise be reached near the exit side of the catalyst bed before the desired equilibrium operations are obtained. After a few cycles at about 1050° F. the temperature may gradually be raised to 1100° F. or higher without exceeding safe operating temperatures at any time.

As an additional safeguard for commercial operations I may provide by-pass lines 120a, 120b, 120c and 120d around each conversion chamber. If the temperature in any conversion chamber gets too high, the charge to that reactor may be manually or automatically by-passed by temperature operated control means 121a, 121b, 121c or 121d (Figure 1) so that that particular reactor will undergo the periodic blowing steps for blowing out hot spots or incipient hot spots without having any more carbon deposited in the bed for augmenting these hot spots. The by-passing of a reactor does not disturb any other part of the system and it is discontinued when the blowing

steps have brought the catalyst bed back to the desired temperature. Similar by-passes may of course be employed in the system of Figure 2.

While my invention has been described as applied to a butadiene process it should be understood that the invention is also applicable to other hydrocarbon conversion processes such as catalytic cracking, reforming, isomerization, etc. In these other hydrocarbon conversion processes the temperature patterns may be somewhat different than in the butadiene process. The amounts of carbon deposited may be relatively greater. The relative distribution of the carbon through the catalyst bed may be more uniform. The heat supplied by burning the carbonaceous deposit may be more than sufficient to effect the desired conversion. Nevertheless, by employing my blowing step the unduly high proportions of the temperature pattern or incipient hot spots may be periodically blow out of the catalyst bed or partially blown out of the catalyst bed in each cycle in a manner which will be apparent to those skilled in the art from the above detailed description of my invention as applied to the butadiene process. While my invention has been described in great detail in connection with certain specific examples it should be understood that my invention is not limited to these examples or to any of the details or operations thereof since numerous modifications thereof and alternative methods and operating conditions will be apparent from the above description to those skilled in the art.

I claim:

1. In a hydrocarbon conversion process wherein a hydrocarbon charging stock stream is heated to conversion temperature and passed in vapor form through a zone of small cross-sectional area to at least one on-stream reaction zone of large cross-sectional area while at least one other reaction zone is not on-stream, wherein each of the reaction zones contains a large hot mass of particles of catalytically inactive heat retention material with particles of solid catalyst material substantially uniformly distributed therein and said stream is passed through said mass under conditions for effecting endothermic conversion by heat absorbed from said mass and a consequent temperature drop in said mass accompanied by the deposition of a combustible deposit therein, and wherein the catalyst in said mass is regenerated by combustion of said deposit with an air stream and subsequently purged during an interval when the zone is not on-stream, the regeneration liberating heat for absorption in said mass and causing the temperature of the outlet side of said mass to become higher than the temperature of the inlet side thereof and there normally being a change in the temperature patterns in the line of flow through the mass with portions thereof getting hotter and hotter as these operations are repeated from cycle to cycle so that there is a tendency toward the development of at least one hot spot in an intermediate portion of said mass, the improved method of operation which comprises periodically blowing each mass immediately after the regeneration and before the purging thereof, employing in the blowing step a hot blow gas having an inlet temperature of about the desired conversion temperature, introducing the blow gas at the low temperature side of said mass, employing an amount of blow gas such that the product of its weight multiplied by its specific heat is substantially less than the product of the weight multiplied by specific heat of the mass of heat retention material and cata-

lyst in the zone undergoing the blowing step and sufficient to remove the highest portions of temperature patterns in the mass with said blow gas but insufficient to impart a substantially uniform temperature across the bed throughout its entire mass, employing a sufficient number of zones so that conversion, regeneration, blowing and purging may be effected continuously and continuously fractionating products of the conversion.

2. In a hydrocarbon conversion process wherein a hydrocarbon charging stock stream is heated to conversion temperature and passed in vapor form through a zone of small cross-sectional area to at least one on-stream reaction zone of large cross-sectional area while at least one other reaction zone is not on-stream, wherein each of the reaction zones contains a large hot mass of particles of catalytically inactive heat retention material with particles of solid catalyst material uniformly distributed therein and said stream is passed through said mass under conditions for effecting endothermic conversion by heat absorbed from said mass and a consequent temperature drop in said mass accompanied by the deposition of a combustible deposit therein, and wherein the catalyst in said mass is regenerated by combustion of said deposit with an air stream and subsequently purged during an interval when the zone is not on-stream, the regeneration liberating heat for absorption in said mass and causing at least part of said mass to reach high temperatures in an intermediate portion thereof which normally tend to exceed safe limits as these operations are repeated from cycle to cycle, the improved method of operation which comprises periodically blowing said mass after regeneration and before purging, employing in said blowing step a hot blow gas having an inlet temperature of about the desired conversion temperature, employing such amount of blow gas for each six cycles of operation that the product of the weight of the blow gas multiplied by its specific heat is approximately equal to the product of the weight multiplied by the specific heat of the mass of heat retention material and catalyst in the zone undergoing the blowing step, employing a sufficient number of zones whereby conversion, regeneration and blowing and purging may be effected continuously and continuously fractionating the conversion products.

3. In a hydrocarbon conversion process wherein a hydrocarbon charging stock stream is preheated to conversion temperature and passed in vapor form through a zone of small cross-sectional area to at least one on-stream reaction zone of large cross-sectional area while at least one other reaction zone is not on stream, wherein each of the reaction zones contains a large hot mass of catalytically inactive heat retention material intimately admixed with solid catalyst material in portions within the range of 1:5 to 5:1, wherein said preheated charging stock stream is passed through said mass under conditions for effecting endothermic conversion by heat absorbed from said mass, said conversion being accompanied by deposition of combustible carbonaceous deposits within the mass and by drop in the temperature of said mass and wherein the catalyst in said mass is regenerated by combustion of said deposit with an air stream and subsequently purged, the regeneration liberating heat for absorption in said mass and causing the temperature of the outlet side of said mass to become higher than the temperature of the inlet side thereof, there normally being a

change in the temperature pattern in the line of flow through said mass with portions thereof getting hotter and hotter as these operations are repeated from cycle to cycle so there is a tendency toward the development of at least one hot spot in an intermediate portion of said mass, the improved method of operation which comprises preheating an air stream to a temperature of approximately the conversion temperature, passing an amount of said preheated air stream through said mass for effecting said regeneration by combustion of said carbonaceous deposit, passing an additional amount of said preheated air stream through said mass in an amount by weight of approximately but not substantially greater than one-sixth of the product of the weight of the mass multiplied by the specific heat of the mass and divided by the specific heat of the preheated air stream whereby the inlet side of the mass is preheated to approximately conversion temperature and the outlet side of the mass is reduced to a safe temperature which is higher than the inlet temperature.

4. In a hydrocarbon conversion process wherein a hydrocarbon charging stock stream is preheated to conversion temperature and passed in vapor form through a hot mass of catalyst and catalytically inactive heat retention material, said mass being of large cross-sectional area and the ratio of catalyst to heat retention material being within the range of 1:5 to 5:1, at a conversion temperature, pressure and space velocity for effecting endothermic conversion by heat absorbed from said mass accompanied by deposition of carbonaceous deposits which are subsequently burned with a hot oxygen-containing gas stream passed through said mass in the same direction as the charging stock whereby heat is restored in said mass and wherein there is a tendency for at least one hot spot to form in an intermediate portion of said mass, the passage of gases and vapors through said mass tending to shift the temperature patterns from the inlet toward the outlet side of the mass, and wherein the mass is purged of oxygen-containing gas between the regeneration and on-stream periods, the improved method of operation which comprises preheating said oxygen-containing gas stream to a temperature approximating the conversion temperature and blowing through said mass an amount of said preheated oxygen-containing gas sufficient to effect combustion of said carbonaceous deposits and an additional amount by weight of said preheated gas equivalent per cycle to approximately but not substantially greater than one-sixth the weight of the mass times its specific heat divided by the specific heat of the preheated oxygen-containing gas whereby the highest portions of the temperature patterns are reduced without imparting a uniform temperature through the entire mass.

5. A method for producing butadiene which comprises preheating a normal butane-butylene stream to a conversion temperature of about 1100 degrees F., passing said preheated stream at a pressure of about 1 to 4 pounds absolute through an Alundum-catalyst mass, the catalyst comprising chromium oxide on alumina and the catalyst being intimately mixed with about two parts of Alundum, said mass being of large cross-sectional area and about three feet in depth and said mass having been brought to temperature conditions by the blowing step hereinafter specified, effecting

endothermic conversion of at least a part of the stream into butadiene by heat liberated from the catalyst-alundum mass while depositing carbonaceous material in the mass, employing a flow rate of about 200 to 800 volumes per hour of the butane-butylene stream (measured at standard conditions) per volume of catalyst in the mass, discontinuing the flow of the butane-butylene stream through said mass after an on-stream period of about fifteen minutes, then blowing through said mass a stream of air which has been preheated by partial combustion with fuel to a temperature approximating said conversion temperature, blowing said preheated air through said mass for a period of approximately seven and one-half minutes at a rate of about 25 to 50 volumes of preheated air (measured standard conditions) per minute per volume of Alundum-catalyst mass whereby the carbonaceous deposits are burned, the inlet side of the bed is raised to substantially conversion temperature and the outlet side of the bed is cooled to a safe temperature which is higher than the temperature of the inlet side of the bed, purging the mass for a period of about seven and one-half minutes without materially altering the temperature thereof, continuously repeating the cycle, and employing at least four separate masses of Alundum-catalyst so arranged so that two are on stream while one is being blown and one is being purged.

6. In a hydrocarbon conversion process wherein a hydrocarbon charging stock stream is heated to conversion temperature and passed in vapor form through a zone of small cross-sectional area to at least one on-stream reaction zone of large cross-sectional area while at least one other reaction zone is not on-stream, wherein each of the reaction zones contains a large hot mass of particles of catalytically inactive heat retention material with particles of solid catalyst material substantially uniformly distributed therein and said stream is passed through said mass under conditions for effecting endothermic conversion by heat adsorbed from said mass and a consequent temperature drop in said mass accompanied by the deposition of a combustible deposit therein, and wherein the catalyst in said mass is regenerated by combustion of said deposit with an air stream during an interval when the zone is not on-stream, the regeneration liberating heat for absorption in said mass and causing the temperature of the outlet side of said mass to become higher than the temperature of the inlet side thereof and there normally being a change in the temperature patterns in the line of flow through the mass with portions thereof getting hotter and hotter as these operations are repeated from cycle to cycle so that there is a tendency toward the development of at least one hot spot in an intermediate portion of said mass, the improved method of operation which comprises periodically blowing each mass immediately after the regeneration, employing in the blowing step a hot blow gas having an inlet temperature of about the desired conversion temperature, introducing the blow gas at the low temperature side of said mass, employing an amount of blow gas such that the product of its weight multiplied by its specific heat is substantially less than the product of the weight multiplied by specific heat of the mass of heat retention material and catalyst in the zone undergoing the blowing step and sufficient to remove the highest portions of temperature patterns in the mass with said blow gas but insufficient to impart a substantially uniform temperature across

25

the bed throughout its entire mass, employing a sufficient number of zones so that conversion, regeneration, and blowing may be effected continuously and continuously fractionating products of the conversion.

7. The method of claim 6 in which the hydrocarbon charging stock and the air stream are passed through the mass of particles in the same direction and additional amounts of the air stream are employed as blow gas.

8. The method of claim 6 in which the hydrocarbon charging stock and the air stream are passed through the mass of particles in the same direction in which additional amounts of the air stream are employed as blow gas and in which the amount of blow gas employed in each blowing step is such that its heat capacity is in the range of about 10% to 25% of the heat capacity of said mass.

9. The method of claim 6 wherein the hydrocarbon charging stock is a butane-butylene gas, the conversion temperature is about 1100° F., the

26

catalyst material is chromium oxide on alumina, the heat retention material is fused alumina, the conditions for effecting endothermic conversion include an absolute pressure of about 1 to 4 pounds per square inch, and the air stream contains combustion products.

JAMES E. SEEBOLD.

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