

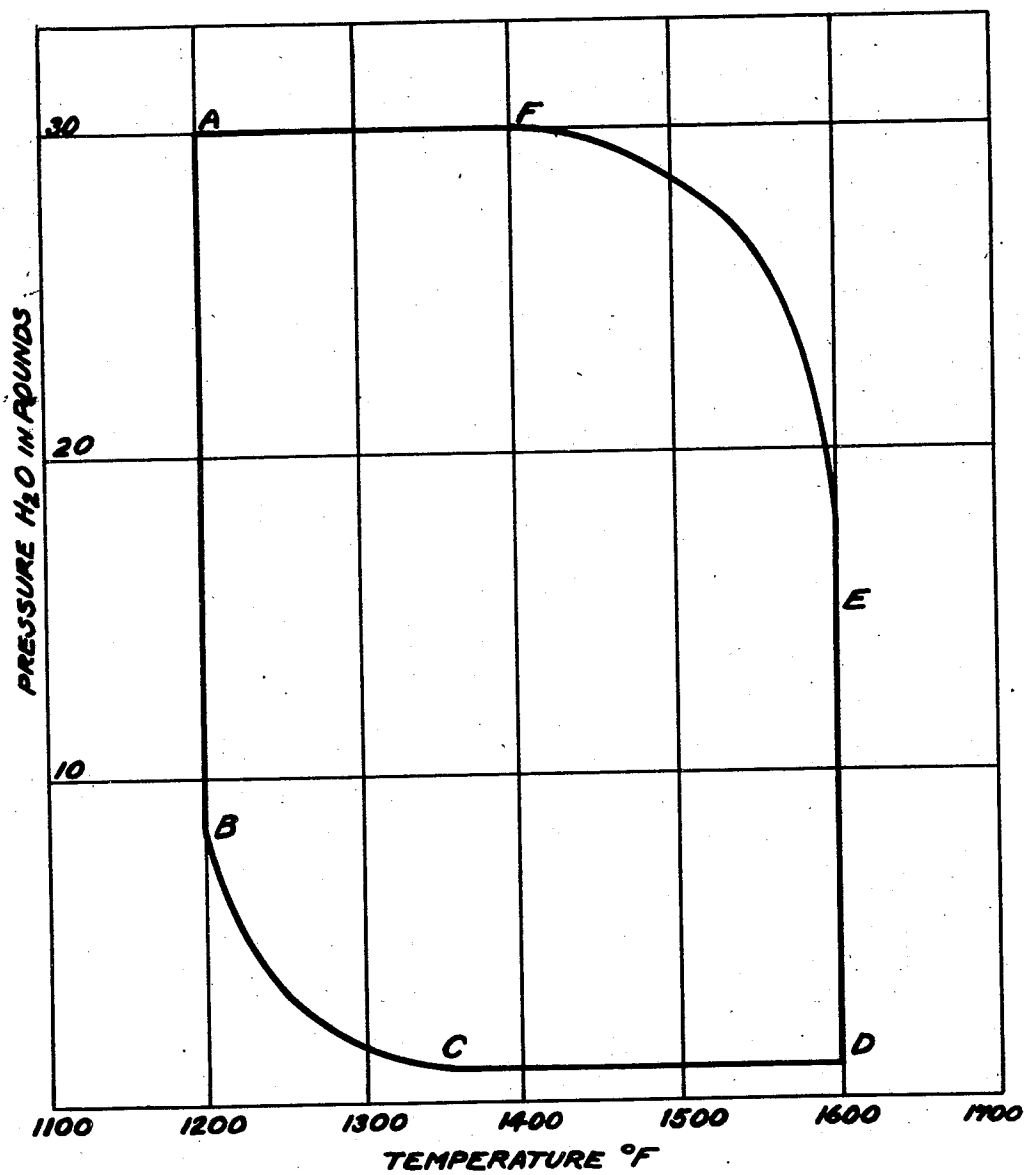
May 6, 1947.

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2,419,997

CATALYTIC DEHYDROGENATION OF ALIPHATIC HYDROCARBONS

Filed March 5, 1943



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UNITED STATES PATENT OFFICE

2,419,997

CATALYTIC DEHYDROGENATION OF
ALIPHATIC HYDROCARBONS

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Application March 5, 1943, Serial No. 478,071

4 Claims. (Cl. 260—683.3)

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The present invention relates to that field of catalysis in which a hydrocarbon, and in particular a hydrocarbon gas, is dehydrogenated in the presence of a dehydrogenating catalyst and has special reference to operations of this type in which no indirect heat exchange material is employed to control catalyst temperature.

The catalytic dehydrogenation of hydrocarbons has heretofore been proposed and extensively discussed in the art. In these procedures, while it is often not mentioned, carbonaceous material is deposited within the catalyst during dehydrogenation. Such processes are therefore run in a cycle with alternate periods on-stream and in regeneration, during the latter of which the carbonaceous material is burned from the catalyst.

It has heretofore been proposed to run catalytic cracking operations on an adiabatic cycle, that is, without the use of an indirect heat exchange material for removing or introducing heat. Exact adiabatic balance is attained when the heat produced in the regeneration of the carbonaceous material is exactly equal to the heat consumed in the endothermic catalytic reactions occurring. It has been the past experience in catalytic cracking that the heat production is in excess of the heat consumption. Accordingly, it has been proposed to run on a modified adiabatic cycle by introducing the inlet materials at a lower average temperature than the average catalyst temperature. In this way a theoretically perfect heat balance is obtainable which works out satisfactorily in catalytic cracking operations.

When it is attempted to employ an adiabatic cycle, modified in this manner to the dehydrogenation procedures of the prior art, major difficulties are encountered. It has been found in commercial operation difficult to avoid having the temperature start upward on a steep gradient. Nice control is necessary and in some cases, such as dehydrogenation of particular hydrocarbon gases, it has been found desirable to use supplemental heat dissipating means, for example, a long blow with air at a temperature below the catalyst temperature after regeneration is in fact complete. This phenomenon has been termed "running away." Due to this running away, adiabatic dehydrogenation of aliphatic hydrocarbons has been considered commercially undesirable.

It is accordingly an object of the present invention to provide dehydrogenation processes which do not have this tendency to run away. It is a further object of this invention to provide catalytic dehydrogenation procedures in which the characteristics of catalysts are modified so that more advantageous conversions are obtained. Other objects and advantages will be apparent from the following description:

In accordance with the present invention an

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aliphatic hydrocarbon material is catalytically dehydrogenated on an operating cycle in which the catalyst is alternately in periods of dehydrogenating and regenerating by burning, whereby heat produced in said regenerating supplies heat for said dehydrogenating. Conditions of dehydrogenation are so controlled that the heat of regeneration is less than the heat of dehydrogenation.

It is a demonstrable fact that under any particular operating conditions the amount of dehydrogenation effected and the amount of coke deposited are constant for any given catalyst. As the temperature of operation varies, both the extent of dehydrogenation and the amount of coke vary. I have found that as the temperature varies, the extent of dehydrogenation and the amount of coke do not remain in constant ratio. Therefore the ratio of endothermic and exothermic heat varies. For similar reasons, the ratio of endothermic and exothermic heat varies as the time of contact varies. Under operating conditions heretofore proposed the exothermic heat is greater than the endothermic heat. I have further found that either reduction in temperature or reduction in contact time reduces the exothermic heat to much greater extent than it reduces the endothermic heat. By sufficiently reducing the temperature or time of contact or both from values which produce a net exothermic heat while maintaining the temperature within suitable range for dehydrogenation, I have been able to reach a point at which the endothermic heat is exactly equal to the exothermic heat. This point, for the purpose of the present description and in the accompanying claims, is termed "perfect adiabatic balance." This would appear to be the perfect condition for adiabatic operation, since the heats of reaction in the catalyst bed are at all times equal. When adiabatic operation of a dehydrogenation process was attempted in this manner it was found that the catalyst temperature would hover around the desired temperature for a limited period and then, due to minor but normal changes in conditions, the temperature would go either up or down. In those cases where the temperature starts to rise, the ratio of exothermic heat to endothermic heat progressively increases, resulting in the temperature running away in a very few cycles. Thus, in one instance the temperature rose from 920° F. to 1120° F., in a matter of fourteen ten-minute dehydrogenation periods, run alternately with regeneration periods. The increase in the net exotherm is so great that it is impossible to hold the temperature down without some extraneous cooling medium, such as a long air blow.

My present investigations have been in a field heretofore unknown, to wit, the field in which the time of contact is shorter than at perfect

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adiabatic balance at the same temperature of operation. This field can alternately be defined as the field in which the temperature is lower than at adiabatic balance with the same time of contact. I have found that in this field a heat balance between on-stream and regenerating operations is readily obtainable which is not subject to radical changes due to minor variations in conditions of operation. Under these conditions of temperature and time of contact the exothermic heat is less than the endothermic heat. Accordingly, in order to maintain the desired temperature I provide a slight amount of additional heat to the reactor. This may conveniently be done by introducing the inlet materials at an average temperature above the average temperature of the catalyst. Alternatively, if desired, the heat may be introduced by indirect heat exchange. While this would not avoid the use of an indirect heat exchange system, the expense even so would be substantially less than heretofore, due to the much smaller amount of heat which it would be necessary to introduce than the amount which it has been necessary to remove heretofore.

During operation in accordance herewith the catalyst temperature is maintained above 800° F. The temperature is maintained below the temperature of perfect adiabatic balance under the conditions of operation. It should be noted in this connection that the critical temperature and the critical time of contact at which the heat balance changes from producing a net exothermic heat of reaction to a net endothermic heat of reaction are interrelated and, further, are a function of the particular catalyst employed and the particular charge fed to the catalyst for dehydrogenation. Thus, with any particular catalyst and charge, as the temperature for balance increases, the time of contact decreases at which perfect adiabatic balance is attained and as the temperature for balance decreases this time of contact increases. Accordingly, the time of contact must be sufficiently short that, under the conditions of charge and catalyst, perfect adiabatic balance is attained at a temperature above 800° F. In the dehydrogenation of hydrocarbon gases containing between 2 and 5 carbon atoms per molecule it is preferred that the operation be conducted to above 900° F. due to the higher conversions obtained in this range.

The present invention is not limited to dehydrogenation catalysts of any particular composition, or dehydrogenation catalysts prepared by any particular method, or to dehydrogenation catalysts pretreated in any particular manner. It has general application to the field of dehydrogenation of aliphatic materials within which it is intended to include, in addition to normal and iso-aliphatic materials having at least two carbon atoms to the molecule, also cyclo-aliphatic materials and aliphatic derivatives of aromatics having at least two carbon atoms in the alkyl group. This invention does have, however, particular reference to the dehydrogenation of aliphatic hydrocarbon gases with special reference to the dehydrogenation of iso-butane, n-butane, and n-butene, separately or in mixture, for the production of olefins or butadiene, as desired. When it is desired to obtain substantial yields of butadiene, low operating pressures on the order of 3 to 10 inches of mercury absolute are employed. The material charged for the production of butadiene may be either normal butene or a mixed feed of n-butene and n-butane.

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As indicated, no particular catalyst is essential to the present invention. The dehydrogenation catalysts known in the art may be employed. However, with many dehydrogenation catalysts at a temperature within the preferred dehydrogenation range, that is, above 800° F. and at the extremely short times of contact which are necessary with these catalysts, the extent of dehydrogenation is subject to substantial improvement. This improvement in the extent of dehydrogenation is, in accordance with a preferred form of the present invention, effected by pretreating the catalyst under properly controlled conditions with steam. This pretreatment with steam is of general application to dehydrogenation catalysts. Preferred catalysts which are pretreated with steam and are specially adaptable to this invention are those which contain an oxide of chromium supported by a capillary type of carrier, such for example, as dried alumina gel carrying chromium oxide, dried zirconia gel carrying chromium oxide, or dried ceria gel carrying chromium oxide. Alternatively, the support may include mixtures of alumina, zirconia or ceria or mixtures of any two of them. For mechanical reasons in the fabrication of the supported chromium oxide composites it is desirable to calcine the support prior to depositing the chromium compound thereon. It is to be noted that a suitable capillary type alumina is sold on the market under the name of "Activated Alumina." The chromium is deposited upon the support generally in the form of a salt decomposable to oxide upon heating, such as chromium nitrate, and is introduced by dipping the dried or calcined support in a solution of the salt. The salt so deposited is then decomposed by heating. It has heretofore been proposed to effect dehydrogenation of hydrocarbons using a chromium oxide supported by "Activated Alumina." The supported chromium oxide catalyst materials, including those in which Activated Alumina is the support, are subject to very substantial improvement, for use in the present invention, by the steam pretreatment. If desired, molybdenum oxide or vanadium oxide may be substituted for the chromium oxide. It appears that this pretreatment changes the fundamental characteristics of the catalyst to a very substantial extent. To bring about this fundamental change of characteristics of the catalysts, they are subjected to treatment in the presence of steam at a temperature between 1200 and 1600° F. at a partial pressure of steam above 1 lb. per sq. in. and above

$$\frac{400}{T-1160} - 1$$

and a partial pressure of steam below 30 lbs. and below

$$\frac{475}{T-1630} + 32$$

where T equals the temperature of treatment in degrees Fahrenheit. The treatment is continued sufficiently long that the ratio of dehydrogenation effected to coke deposited is increased. This results in an increase of the time of contact for perfect adiabatic balance, all other factors remaining constant. In general it can be said that after one hour of treatment the improvement in the ratio commences and that the improvement continues thereafter during the first 30 hours of treatment. The results effected in this pretreatment are not those which accrue from the deposition of a mono-molecular layer of water upon the catalyst by a pretreatment with steam. These

results from a mono-molecular layer of water, as described in the literature relating thereto, are transitory, and the effect of such a steam treatment is temporary, the catalyst reverting during use. The results of a treatment with steam within the limits stated for an hour or more are permanent. It is apparently impossible to reverse the effect of this steam treatment.

It should be noted, in connection with the mathematical expressions employed to define the treating conditions, that these expressions are purely empirical and define the curved lines BC and EF, respectively, in the accompanying drawing. Thus, along the line BC the partial pressure of steam is equal to

$$\frac{400}{T-1160} - 1$$

and along the line EF the partial pressure is equal to

$$\frac{475}{T-1630} + 32$$

In this drawing the zone of treating is outlined in heavy lines and consists of the zone ABCDEF.

Reference has hereinabove been made to cyclic operation, in one phase of the cycle hydrocarbons being fed to the catalyst for dehydrogenation and in another phase the catalyst being regenerated. This cycle may be employed regardless of whether in situ type of case design is employed in which the catalyst is stationary and alternate periods of on-stream and regeneration are used in each case, or a moving catalyst type of case design is employed in which the catalyst is on-stream for a period in a converter and moves to a regenerator for the regeneration period, from which it is returned to the dehydrogenation case. Regardless of which type of operation is employed, in situ or moving catalyst, it is desirable to employ a heat storage material distributed through the catalyst mass. In either type of operation this heat storage material may be a diluent such as pieces of fused alumina, distributed through the contact material and remaining in intimate mixture therewith, while in the case of an in situ catalyst the heat storage material may be in the form of plates, bars, tubes or the like located in fixed spaced positions. The value of using such a heat storage material is that with the in situ type of catalyst a longer on-stream period may be employed while maintaining a reasonably limited temperature swing between its maximum and minimum; while with the moving type of catalyst a lesser quantity of catalyst needs to be moved for a given amount of conversion.

When a fixed bed of catalyst is employed, the hydrocarbon material and the air for regeneration pass either in the same or in opposite directions through the catalyst bed. The operation may be conducted either with the feed for all cycles being in the same direction, or with the direction of feed of charged materials alternating from cycle to cycle. This alternation of direction from cycle to cycle tends to produce an even temperature throughout the bed. It is, under some special circumstances, desirable to modify this alternating cycle pattern with a limited number of cycles in which all materials charged flow in the same direction.

In cases where difficulty is encountered in obtaining a reliable value for the average operating temperature, for example in cases where there is a swing of temperature up and down during the cycle, and where various portions of the catalyst

bed are at different temperatures at the same time, a reliable indication of whether the charged materials are supplying heat to make up for a net endotherm may be obtained from observation of the inlet and outlet temperature. If the average inlet temperature is above the average outlet temperature throughout the cycle, heat is being supplied by the charge and is effectively balancing a net endotherm. This constitutes the most ready indication of whether the inlet materials are at a temperature above the average catalyst temperature since inlet and outlet temperatures are always easy to measure in a plant.

The most advantageous operating conditions considering the extent of conversion are in the range immediately below the point of perfect adiabatic balance. When operations are conducted as close as possible to this point, and reversed in direction of flow from cycle to cycle to even out the temperature, slight but normal variations in conditions, such as slight variation in the exact composition of the charge, may throw the operating conditions above the balance point. In such an event it is possible when operating under these conditions to bring the temperature down by running a plurality of successive cycles in the same direction.

It is to be noted that in operations in the range immediately below the point of perfect adiabatic balance, the average temperature of the feed is often above the critical balance temperature at the time of contact employed.

Example I

A chromium oxide-alumina catalyst was prepared as follows: A solution of chromic acid was prepared by dissolving 18.9 kilograms of chromium oxide (Cr_2O_3) in 23.8 kilograms of water. This solution was absorbed in 34 kilograms of pellets of a capillary type of alumina commonly known as "Activated Alumina." The pellets were then drained and dried at 220° F. in an oven. The dried pellets were then heat treated at 1400° F. for five hours at a partial pressure of water vapor of 0.6 pound per square inch. The pellets contained 21.3% chromium sesqui oxide (Cr_2O_3), based on alumina. There were then added to the catalyst pellets so produced two volumes of alundum grains per volume of catalyst.

Normal butane was then dehydrogenated in the presence of this mixture without the use of indirect heat exchange to control the temperature. The cycle of operation was as follows:

Minutes	Stage
2.5	Evacuation.
2.5	Reduction with H_2 .
1.0	Evacuation.
10.0	Dehydration.
2.5	Evacuation.
7.5	Regeneration with air.

The dehydrogenation was effected at an absolute pressure of 7 inches of mercury, feeding the butane at 8 grams per liter of catalyst per minute. With the catalyst bed initially heated to 1100° F. and with the inlet temperature being maintained at 1050° F. the case came to equilibrium at a catalyst temperature of 1000° F. in about 20 cycles. When the temperature of the bed was dropped to 890° F., other operating conditions being the same, the temperature again came to equilibrium at 1000° F. in 20 cycles. The specific gravity of the outlet mixture, after

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equilibrium was attained, was 1.48 based on air equal to 1. This shows that extensive dehydrogenation had occurred, inasmuch as the specific gravity of butane is equal to 2.14.

However when the temperature of the catalyst bed was increased to 1130° F. by preheating, the temperature, after going on-stream, continued to rise. Accordingly under these operating conditions, with this catalyst, the maximum temperature at which thermal balance is obtained lies between 1100° F. and 1130° F.

Example II

Normal butane was again dehydrogenated under the same conditions stated in Example I with the exception that the time of contact was decreased by increasing the rate from 8 to 12 grams per liter per minute. With the bed at an initial temperature of 840° F. the temperature rose in 28 cycles to an equilibrium temperature of 985° F. When the initial bed temperature was increased to 1150° F., equilibrium of 985° F. was attained in 24 cycles. By comparison with Example I it is to be seen that the decreased time of contact increased the maximum temperature at which thermal balance is obtained to above 1150° F. The specific gravity at equilibrium was 1.64.

Example III

A catalyst was prepared by dipping 10 kilograms of "Activated Alumina" in a solution of 7.62 kilograms of chromic oxide (CrO₃) in 9.6 kilograms of water. After standing in the solution for one-half hour, the pellets were drained and then dried in an oven, in which air was circulated, at a temperature of 200° to 210° F. The pellets were then heat treated at 1400° F. for ten hours at a partial pressure of water vapor of 3.25 pounds per square inch, and were found to contain 20% Cr₂O₃. There were then added to the catalyst pellets so produced two volumes of alundum grains per volume of catalyst.

The catalyst-alundum mixture was used for a two stage dehydrogenation procedure in which the charge in one stage was a normal butane, and the charge in the other stage was a mixed feed of normal butane and normal butene. The analysis of the two feeds, by weight, was as follows:

	N-Butane	Mixed Feed
Iso-butane.....	3.6	0
N-butane.....	94.8	34
Iso-butene.....	0	1.2
N-butene.....	0.6	61.4
Butadiene.....	1	1.5
C ₄ +.....	0	1.9
	100	100

The cycle of operation was as follows:

Minutes	Stage
2.5.....	Evacuation.
2.5.....	Reduction with H ₂ .
1.....	Evacuation.
5.0.....	Dehydrogenation of N-Butane.
1.....	Evacuation.
10.....	Dehydrogenation of mixed feed.
2.5.....	Evacuation.
10.....	Regeneration with air.

The charged materials were maintained at about 1100° F. The normal butane was charged at a rate of 10 grams per liter of catalyst per minute, under a pressure of 7 inches of mercury

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absolute, whereas the mixed feed was charged at a rate of 20 grams on the same basis, under a pressure of 5 inches of mercury absolute. Starting at a catalyst temperature in the range of 1000° to 1100° F. equilibrium was established with average temperatures during dehydrogenation of normal butane of 1080° F. and during dehydrogenation of mixed feed of 1060° F. The average temperature when going on-stream was 1090° F.

The product analysis, by weight, from the two stages was as follows:

	From Butane	From Mixed Feed
	Per cent	Per cent
Hydrogen.....	1.9	1.2
Methane.....	0.6	0.5
C ₂	1.2	0.6
C ₃	0.8	0.5
Iso-butane.....	4.5	0
N-butane.....	40.8	27.7
Iso-butene.....	2.9	0.3
N-butene.....	38.8	49.8
Butadiene.....	4.6	16.7
C ₄ +.....	2.9	1.0
Coke.....	1.0	1.7
	100.0	100.0

C₄ materials are separated from the product from both feeds separately, and the butadiene then removed from that from the mixed feed. Enough C₄ mixture from the butane dehydrogenation is added to the C₄ materials from the mixed feed dehydrogenation after separation of butadiene to make up for materials removed from the mixed feed product. The composition is substantially identical to the original composition of the mixed feed. This represents a desirable process for the preparation of butadiene from butane. Alternatively, the necessary amount of make up C₄ from butane dehydrogenation may be added to C₄ from the mixed feed dehydrogenation and the butadiene recovered from the mixture which then contains 14.1% butadiene.

Example IV

The same catalyst-alundum mixture as in Example III was employed for the dehydrogenation of a mixed feed of the following analysis by weight:

	Mixed feed
Iso-butane.....per cent.....	5.0
N-butane.....do.....	68.0
Iso-butene.....do.....	0.0
N-butene.....do.....	26.7
Butadiene.....do.....	0.2
C ₅ +.....do.....	0.1
	100.0

The cycle was as follows:

Minutes	Stage
2.5.....	Evacuation.
2.5.....	Reduction with H ₂ .
1.....	Evacuation.
5.....	Dehydrogenation of mixed feed.
2.5.....	Evacuation.
10.....	Regeneration.

The inlet temperature of mixed feed was maintained at about 1100° F. and of regeneration air at 1050° F. The rate of charging the mixed feed was 20 grams per minute per liter of catalyst and the pressure was maintained at 5 inches of mercury absolute. Equilibrium was attained at about 1030° F. average catalyst temperature with

a temperature of about 1050° F. at the beginning of each dehydrogenation run.

The product analysis, by weight, was as follows:

	Product
Hydrogen -----per cent--	0.9
Methane -----do-----	0.5
C ₂ -----do-----	0.1
C ₃ -----do-----	0.2
Iso-butane -----do-----	2.7
N-butane -----do-----	40.3
Iso-butene -----do-----	2.8
N-butene -----do-----	39.7
Butadiene -----do-----	11.4
C ₅ + -----do-----	0.3
Coke -----do-----	1.1
	100.0

After removal of the butadiene, normal butane may be added to the residual C₄ gas to make up to substantially the composition of the original feed. This may therefore be employed as a single stage process for the production of butadiene from normal butane.

Example V

With the same catalyst mixture as in Example III, a feed of the following composition was dehydrogenated:

Iso-butane -----	1.9
N-butane -----	96.4
Iso-butene -----	1.2
N-butene -----	0.4
Butadiene -----	0
C ₅ + -----	0.1
	100.0

The feed temperature was about 1100° to 1110° F. At a feed rate of 20 grams per liter of catalyst per minute, thermal equilibrium was attained at 1080° to 1085° F. average temperature when operating at atmospheric pressure, and at 1095° F. when operating at 5 lbs. gauge pressure (20 lbs. absolute). The product analysis was as follows:

	At atmospheric	At 5# Gauge
Hydrogen -----	1.1	1.9
Methane -----	1.0	1.7
C ₂ -----	3.2	4.3
C ₃ -----	3.1	4.1
Iso-butane -----	2.1	3.4
N-butane -----	36.6	38.3
Iso-butene -----	3.7	3.2
N-butene -----	44.1	36.5
Butadiene -----	2.0	2.4
C ₅ -----	0	0.2
Coke -----	3.1	4.1
	100.0	100.0

The lower pressure of the atmospheric run is preferable since there is greater selectivity under these conditions. This type of operation is desirable when the production of olefins is desired.

I claim as my invention:

1. In effecting catalytic dehydrogenation of aliphatic hydrocarbon material in a cyclic operation involving use of dehydrogenation catalyst alternately, to promote dehydrogenation while supplying endothermic reaction heat and declining within a predetermined range of temperatures, and in regeneration when carbonaceous deposit resulting from the dehydrogenating reaction is burned and resulting heat of combustion

is stored in the catalyst for subsequent release to the dehydrogenating reaction with resultant increase in catalyst temperature substantially equal to said decline during dehydrogenation, the

- 5 process of maintaining the catalyst within the desired range of temperatures without use of extraneous heat exchange fluid which comprises effecting the dehydrogenating reactions at such conditions of temperature and time of contact that the carbonaceous deposit produced stores within the catalyst upon burning a portion only of the endothermic heat released thereby during dehydrogenation, and supplying the balance of said endothermic heat by admitting reactants to the catalyst at temperature above the average of said range of catalyst temperatures, said catalyst being an oxide active in promoting dehydrogenations selected from the group consisting of chromium oxide, molybdenum oxide and vanadium oxide supported by a carrier having a capillary structure substantially free of silica which has been subjected substantially in the absence of carbonaceous deposit to steam treatment at temperature between 1200° F. and 1600° F. at a partial pressure of steam above one pound per square inch and above

$$\frac{400}{T-1160}-1$$

- 30 and below thirty pounds per square inch and below

$$\frac{475}{T-1630}+32$$

- 35 (where T equals treating temperatures in degrees Fahrenheit) for time sufficient permanently to reduce the coke making characteristics of the catalyst with respect to its dehydrogenating activity.

- 40 2. In effecting catalytic dehydrogenation of aliphatic hydrocarbon material in a cyclic operation involving use of dehydrogenation catalyst alternately, to promote dehydrogenation while supplying endothermic reaction heat and declining within a predetermined range of temperatures, and in regeneration when carbonaceous deposit resulting from the dehydrogenating reaction is burned and resulting heat of combustion is stored in the catalyst for subsequent release to the dehydrogenating reaction with resultant increase in catalyst temperature substantially equal to said decline during dehydrogenation, the process of maintaining the catalyst within the desired range of temperatures without use of extraneous heat exchange fluid which comprises effecting the dehydrogenating reaction at such conditions of temperature and time of contact that the carbonaceous deposit produced stores within the catalyst upon burning a portion only of the endothermic heat released thereby during dehydrogenation, and supplying the balance of said endothermic heat by admitting reactants to the catalyst at temperature above the average of said range of catalyst temperatures, said catalyst comprising chromium oxide and active alumina which has been subjected substantially in the absence of carbonaceous deposit to steam treatment at temperature between 1200° F. and 1600° F. at a partial pressure of steam above one pound per square inch and above

$$\frac{400}{T-1160}-1$$

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and below thirty pounds per square inch and below

$$\frac{475}{T-1630} + 32$$

(where T equals treating temperatures in degrees Fahrenheit) for time sufficient permanently to reduce the coke making characteristics of the catalyst with respect to its dehydrogenating activity.

3. In effecting catalytic dehydrogenation of aliphatic hydrocarbon material in a cyclic operation involving use of the catalyst alternately to promote dehydrogenation and in regeneration by burning of coky deposit thereon, the process comprising subjecting such material to dehydrogenation conditions in the presence of dehydrogenating catalyst comprising an oxide active in promoting dehydrogenations selected from the group consisting of chromium oxide, molybdenum oxide and vanadium oxide supported by a carrier having a capillary structure substantially free of silica which has been subjected substantially in the absence of carbonaceous deposit to steam treatment at temperature between 1200° F. and 1600° F. at a partial pressure of steam above one pound per square inch and above

$$\frac{400}{T-1160} - 1$$

and below thirty pounds per square inch and below

$$\frac{475}{T-1630} + 32$$

(where T equals treating temperatures in degrees Fahrenheit) for time sufficient permanently to reduce the coke making characteristics of the catalyst with respect to its dehydrogenating activity, said conditions including temperature within the range of 800° F. to 1200° F. and contact time of hydrocarbons with said catalyst sufficiently short that the endothermic heat of dehydrogenation exceeds the exothermic heat of burning of said coky deposit, storing said exothermic heat within the catalyst during regeneration periods and releasing heat so stored to the dehydrogenating reaction, and supplying sufficient additional heat to the catalyst during the operating cycle to maintain temperature of the catalyst within a predetermined range and at substantially constant average for successive and repeated operating cycles.

4. In effecting catalytic dehydrogenation of aliphatic hydrocarbon material in a cyclic operation involving use of the catalyst alternately to promote dehydrogenation and in regeneration by burning of coky deposit thereon, the process comprising subjecting such material

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to dehydrogenation conditions in the presence of dehydrogenating catalyst comprising chromium oxide and active alumina which has been subjected substantially in the absence of carbonaceous deposit to steam treatment at temperature between 1200° F. and 1600° F. at a partial pressure of steam above one pound per square inch and above

$$\frac{400}{T-1160} - 1$$

and below thirty pounds per square inch and below

$$\frac{475}{T-1630} + 32$$

(where T equals treating temperature in degrees Fahrenheit) for time sufficient permanently to reduce the coke making characteristics of the catalyst with respect to its dehydrogenating activity, said conditions including temperatures within the range of 800° F. to 1200° F. and contact time of hydrocarbons with said catalyst sufficiently short that the endothermic heat of dehydrogenation exceeds the exothermic heat of burning of said coky deposit, storing said exothermic heat within the catalyst during regeneration periods and releasing heat so stored to the dehydrogenating reactions, and supplying sufficient additional heat to the catalyst during the operating cycle to maintain temperature of the catalyst within a predetermined range and at substantially constant average for successive and repeated operating cycles.

EUGENE J. HOUDRY.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,279,703	Bradley et al.	Apr. 14, 1942
2,284,603	Belchetz et al.	May 26, 1942
2,312,006	Thiele	Feb. 23, 1943
2,322,366	Kassel	June 22, 1943
2,324,708	Liedholm	July 20, 1943
2,274,988	Matuszak	Mar. 3, 1942
2,271,751	Visser et al.	Feb. 3, 1942
2,231,446	Grosse	Feb. 11, 1941
2,307,240	Ruthruff	Jan. 5, 1943
2,209,215	Gaylor et al.	July 23, 1940
2,161,676	Houdry	June 6, 1939
2,263,363	Menshih	Nov. 18, 1941
2,327,746	Shultz	Aug. 24, 1943
2,290,845	Voorhees	July 21, 1942
2,325,516	Holt et al.	July 27, 1943
2,356,697	Rial	Aug. 22, 1944
2,367,622	Schulze et al.	Jan. 16, 1945