

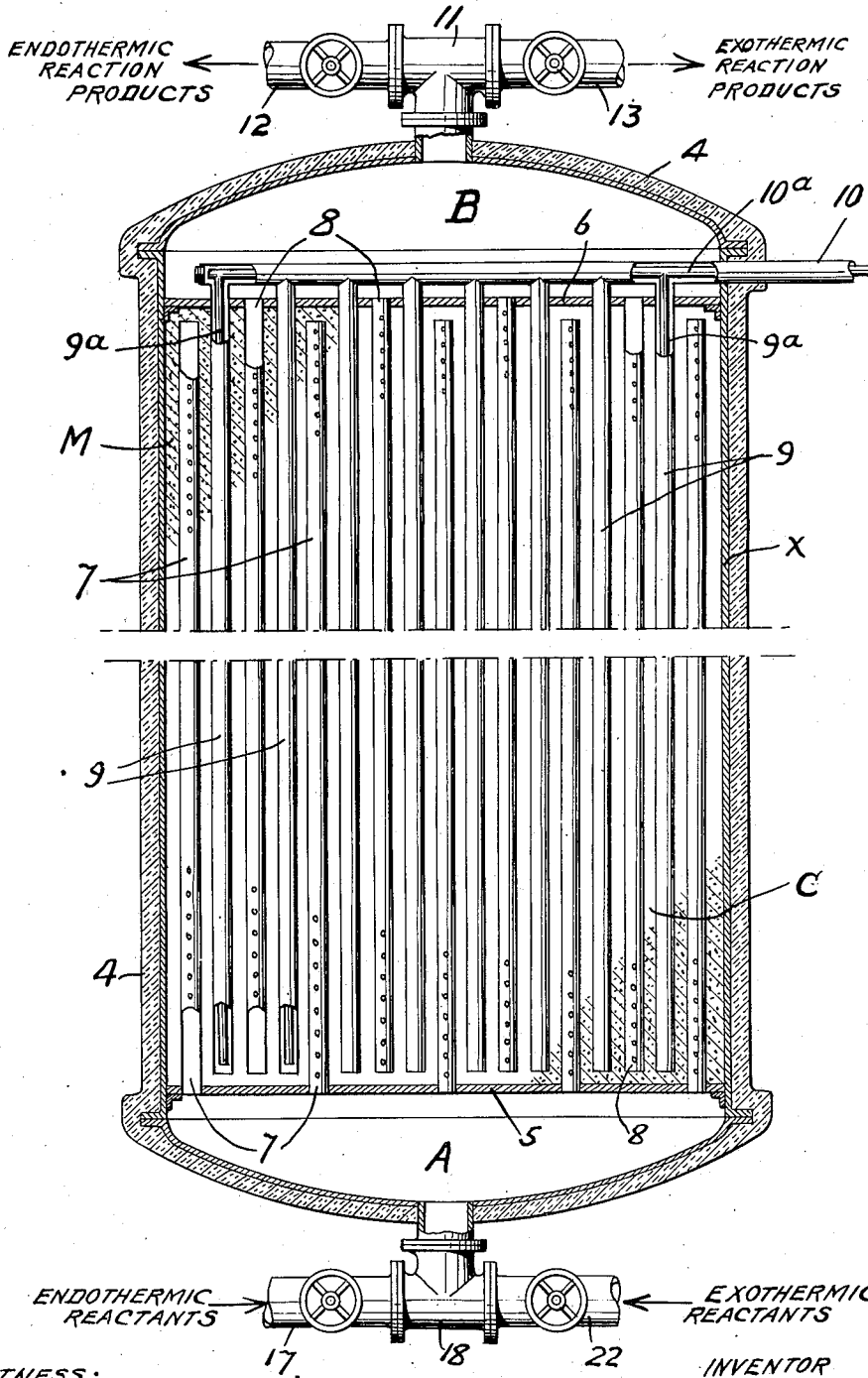
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CATALYTIC OPERATION

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WITNESS:

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CATALYTIC OPERATION

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This invention relates to catalysis and especially to the use of contact or catalytic masses in a cycle of alternate endothermic and exothermic reactions. This cycle of operations is the normal one when the contact mass acquires, during the desired treating or transforming reaction, which may be either endothermic or exothermic but is usually endothermic, a burnable or other deposit which impairs or changes the reaction and which is subsequently removed in the alternate reaction to restore the contact mass to proper condition for resumption of the desired treating operation.

Heretofore such alternate reactions have been conducted at rather widely different temperatures, the difference being of the order of 200° F. or more. For example, many catalytic treating operations are conducted at 850° F. or below, while the temperature for a good regeneration by combustion of coky, sulphurous, tarry and other burnable deposits in a reasonable length of time has required temperatures of the order of 1050° F. or more. Hence the necessary heating up and cooling down periods in the transition from one reaction to the other have unduly prolonged the regenerative operation as compared with the "on-stream" operation and correspondingly adversely affected the economics of the cycle.

One object of the invention is to improve the operative cycle and to so conduct operations that the contact mass is utilized at high efficiency thereby producing high yields of high quality products. Another object is to maintain a temperature balance between the reactions. Another object is to reduce materially or to obviate entirely both the interim periods between reactions and the supplying of heat from an outside or different source. Another object is to provide for the admission of all reactants at temperatures in or below the reaction range. Another object is to maintain the contact mass at all times and during both reactions within a relatively narrow range of temperature. Still other objects will be apparent from the detailed description which follows.

In one important aspect, the invention contemplates relatively short reaction periods and the supplying of the greater part, if not all, of the heat requisite to the endothermic reaction by the exothermic reaction. During one reaction, such as the endothermic, which is usually the important one from a production standpoint, the contact mass is at a selected temperature or within a selected temperature range. During the subsequent exothermic reaction, which restores to the mass and to the apparatus adjacent thereto the

heat given up during the previous endothermic reaction, the mass is kept substantially at the selected temperature or within or adjacent the selected range of temperature. An important, if not the essential way of regulating the temperature of the contact mass is by controlling the amount of burnable or other deposit laid down on the contact mass during the "on-stream" or treating operation. This in turn is affected, at least in part, by the length of the "on-stream" period and the rate of feed of the charge, i. e., by the quantity of material subjected to the action of the contact mass. In practice, the best operation is to lay down on the contact mass during the "on-stream" period a deposit which is just sufficient to bring the mass back to the selected operating temperature or to the proper end of the selected temperature range. If one reaction is much stronger than its companion reaction, some additional means may be required to maintain the contemplated heat balance, such as a circulated heat exchange or cooling medium to remove the excess heat of a strong exothermic reaction and/or suitable adjustment of the temperature of the entering reactants.

In commercial operations involving the use of large masses of contact material, I have discovered that once the converter is at the proper temperature, all the heat required by the endothermic reaction can be made available from the alternate exothermic reaction. This is accomplished by regulating the reaction periods so as to utilize the contact mass and the metal of the converter as a reservoir for the storage of heat. In a short "on-stream" period, I have found that the reactant fluid can be fed at high rate and in large volume and produce little change in the temperature of the mass, at most a change of only a few degrees. In other words, during the entire "on-stream" period the mass can be kept at optimum reaction temperature, and whatever loss of heat there may be, which loss may be large in terms of calories but scarcely noticeable in degrees due to the heat storage capacity of the contact mass and apparatus, is promptly restored by the succeeding regenerative reaction.

While by no means restricted thereto, concrete examples of the application of the operative cycle may be taken from certain catalytic operations for the conversion, transformation and treating of hydrocarbons including mineral oils in the production of high quality refined and marketable products such as hydrocarbon gases, gasoline, kerosene, naphtha, fuel oils, Diesel oil, etc.

The present invention is adapted to a number

of operations in the temperature range of 700° to 950° F., i. e., a temperature range of the order of 250° F. or less, including the transformation or cracking of heavier hydrocarbons in the gas oil boiling range, for example, to produce lower boiling hydrocarbons as in the gasoline boiling range. Another use is in the so-called "reforming" operation on naphthas, both light and heavy and both straight-run and cracked, to improve their anti-knock rating and better adapt them for use as motor fuel. Still another application is to the viscosity breaking of very heavy hydrocarbons including residual materials containing tars, waxes, asphalt, etc.

The catalytic transforming or cracking of hydrocarbons in the gas oil boiling range is advantageously effected in the temperature range of the order of 750° to 900° F., i. e., a temperature range of about 150° F. The still more limited and preferred range is 800° to 860° F. for virgin material, which range may be carried somewhat higher for recharged material. For naphtha reforming, an advantageous temperature range is 850° to 950° F., for example with the more limited preferential range lying between 875° and 925° F. For viscosity breaking, a suitable temperature range is 700° to 900° F., with the more restricted preferential range lying between 790° and 850° F.

Any catalyst capable of effecting the desired transformation, conversion or treatment of the starting material may be used, but, inasmuch as the present invention contemplates relatively short reaction periods and regeneration of the contact mass in situ, the catalytic material should be in the form of lumps, fragments or molded pieces, as indicated, for example, in my copending application Serial No. 600,581, filed Mar. 23, 1932, which issued as Patent No. 2,078,945 on May 4, 1937. Any metals or metallic compounds having the desired selective or adsorptive activity may be used and, if desired, these may be incorporated in finely divided form into or upon porous carriers which are themselves either catalytically active or inert. If the carriers are intended to be inert or relatively inert, they may be formed of china clay, pumice, fuller's earth, diatomaceous earth, and like clayey materials. On the other hand, the catalytic mass may be active or activated and comprise blends of silica and alumina produced by suitable acid or other chemical treatment of naturally occurring clays or blends of clays. A good silica to alumina ratio is of the order of 3½:1, and the ratio may be carried as high as 4 or 4½:1. For certain operations, metals or metallic compounds may be combined with catalysts of the selected silica to alumina ratio, as, for example, for naphtha reforming, small percentages of vanadium, chromium, tungsten or molybdenum may be used. For mere viscosity breaking, a silica-alumina catalyst may be utilized of very low activity and made especially porous by incorporation of vegetable matter which is later removed by oxidation, as disclosed and claimed in U. S. Patent No. 1,818,403, issued August 11, 1931, to Alfred Joseph. When viscosity breaking is to be combined with a certain degree of transforming or cracking, one method of preparing the contact material is to make a highly active blend of silica and alumina and then reduce the activity of the mass to the desired extent by suitable heat or other treatment.

In commercial apparatus adaptable to the practice of the invention such as large converters containing several tons of catalyst wherein

provision is made for distribution of reactants all through the mass and removal of products from a multiplicity of points within the mass, a large number of conduits, certain of which are usually provided with fins, are embedded in the contact mass, with the result that the catalyst, with the metallic conduits and shell of the converter, provide a large reservoir for the storage of heat. Converters of this general type are disclosed in Patents Nos. 1,987,905 and 1,987,911 issued to me and to T. B. Prickett, respectively, on Jan. 15, 1935. The metallic parts form good conductors of heat, but the catalytic mass, especially when composed of hydrosilicates of alumina, is a poor conductor of heat. By utilizing the converter for the storage of heat and suitably controlling the duration and extent of the alternate endothermic and exothermic reactions, it is possible to supply all the heat for the endothermic reactions by the exothermic reactions, and to keep the contact mass at or close to the optimum temperature or range of temperatures for the productive reaction which, in the instance of the operations on hydrocarbons heretofore referred to, is an endothermic reaction. For example, in the transformation or cracking of a virgin gas oil by a suitable silica-alumina catalyst at a temperature of 840° F. and at a feed rate of 1/1 (one liter of oil per hour to one liter of catalyst), the charge entering the mass at 830° F., for example, it is possible to operate for ten minutes with a drop of only 6 to 8 degrees in the temperature of the mass, and up to 30 minutes with a drop of only 25 degrees. The period of the "on-stream" run is determined by the amount of coky or other burnable deposit left on the catalyst, which deposit should not be allowed to accumulate appreciably in excess of, for example, 1% by weight of the contact mass. Hence, while it is possible, under the given conditions, to operate for approximately 30 minutes with the catalyst still in the optimum range of temperature, in most instances this produces too large a deposit of coke, and the usual operation is from 5 to 15 minutes. The catalyst is then regenerated by sending into the mass an oxidizing medium in large volume such as air mixed or not with other gases as flue gas, steam, etc., preferably under pressure, and at a temperature not above 800° F., but preferably considerably lower in order that the oxidizing medium may be utilized to carry off some or all of the excess heat of the exothermic reaction. If desired, other means, such as the circulation of a cooling medium, after the manner disclosed in copending application of myself and R. C. Lassiat, Serial No. 728,544, filed June 1, 1934, (which issued on May 4, 1937, as Patent No. 2,078,947), and in my copending application, Serial No. 6,291, filed February 13, 1935 (which issued on May 4, 1937, as Patent No. 2,078,948), may be utilized to keep the temperature of the mass from going much above the optimum "on-stream" range, and to bring the temperature back quickly, if this range is exceeded. Thus regeneration can be effected in approximately the period of the "on-stream" operation, and all of the heat lost in the preceding "on-stream" operation is restored, the cycle being continued as described. Since the heat for the "on-stream" or endothermic reaction is supplied by the alternate exothermic reaction, no heat need be given to the mass by the entering stream of reactants. Hence the charge to be converted is sent into the mass at a temperature not exceeding the optimum range and, if desired, 75

it may be below the optimum range. This is an important feature of the invention, since there is no longer any necessity for heating the charge in excess of desired reaction temperatures. In many catalytic operations, including the transforming or cracking of hydrocarbons, superheating causes thermal cracking, which has an adverse effect upon a catalytic operation, since the thermally cracked material is of very poor anti-knock value and produces an unduly large deposit of coke on the catalyst, thereby reducing the yield and impairing the quality of the products.

For the reforming of straight run or cracked naphtha showing undesirable detonating characteristics, the reforming to improve the anti-knock rating is effected through the use of metals or metallic compounds, preferably of vanadium, chromium, tungsten and molybdenum, individually or combined, and supported upon inert or active carriers, as specified above. The temperature operating range is of the order of 850° to 950° F., and preferably between 875° and 925° F. Due to storage of heat in the converter, during the exothermic regenerating reaction, as heretofore described, an ample quantity of heat for the endothermic or reforming reaction is provided, and the material to be reformed can be sent into the mass at temperatures of 850° F. and below, particularly if the selected optimum temperature for the reaction is set at the middle of the preferential range, as at about 900° F. Short runs will be made to keep the carbon deposit low.

The viscosity breaking operation to convert hydrocarbon residues into domestic fuel oils, Diesel oils and cracking stock in the gas oil boiling range is catalytically effected in a temperature range of 700° to 900° F. and in the preferential range of 790° to 850° F. Virgin charging stock is readily transformed at the lower end of the preferential range, while bottoms from cracking and other operations, wherein the stock has been subjected previously to high temperatures, require treatment toward the upper end of the preferential range. The contact masses, as previously described, are formed with large pores, and, as compared with cracking catalysts, are relatively inert or of considerably reduced activity, dependent upon the amount of light products which it is desired to produce during the viscosity breaking operation. Here again substantially the entire heat for the viscosity breaking or endothermic reaction can be stored in the mass for "on-stream" runs of short or moderate duration, and the charging material can be brought into the reaction zone at the lower end of the preferential range, as between 790° and 830° F. If the charge is brought into the converter at any higher temperature, it will be for the sole purpose of keeping the charge in vapor phase and more than 50% of the heat of the reaction will still be supplied by the stored-up heat in the contact mass. The operation is conducted so as to produce a small burnable deposit on the catalyst to avoid difficulties in taking care of the excess heat of the strong exothermic regenerative reaction.

The ability to bring the charging material into the reaction zone at temperatures in or below the reaction range is one of the important features of the present invention. Since no excessive superheating of the charge is needed to supply any of the heat of the reaction, it is possible not only to minimize but entirely to avoid all

thermal cracking, which is highly deleterious to a catalytic operation. Thermal cracking, even in small degree, has a very adverse effect upon the yield and quality of the products. Since this can now be entirely avoided, it is possible to conduct a truly catalytic reaction. The permissive low temperature of the charge leads to wide latitude in other operating conditions. Almost any feed rate can be selected, for example, as low as $\frac{1}{10}$ (one liter of oil per hour to 10 liters of catalyst) or as high as $10\frac{1}{2}$. Also, any pressure condition can be utilized,—sub-atmospheric, atmospheric, or superatmospheric. Hence the best operating conditions can be selected for the production of both high yield and high quality.

When regeneration of the contact mass is by oxidation, it is essential that the deposit burn freely within the selected temperature range. To insure this, it is desirable that the contact mass contain an oxidation promoter, such as manganese in small amount as disclosed in my copending application Serial No. 35,101, filed August 7, 1935 (which issued on May 4, 1937, as Patent No. 2,078,951), unless some other material capable of producing this effect is already present.

Apparatus in which the improved cycle of the present invention may be practised has already been disclosed in my copending application Serial No. 604,997, filed April 13, 1932 (which issued on March 16, 1937, as Patent No. 2,073,638), in the previously identified patents to T. B. Prickett and myself, and in the aforesaid copending applications Serial Nos. 728,544 (Patent No. 2,078,947) and 6,291 (Patent No. 2,078,948), also in my copending application Serial No. 12,564, filed March 23, 1935 (which issued on May 4, 1937, as Patent No. 2,078,949). However, the invention is not primarily a matter of apparatus but rather a process of controlling certain operations. It is applicable to many forms of apparatus in addition to those mentioned above, but not to the same extent. For example, the more efficient the heat exchange between entering reactants and the contact mass, the lower the temperature at which the reactants may be fed to the converter. Moreover, if the converter provides for the circulation of an independent heat exchange medium adapted to carry away heat, a larger burnable deposit can be laid down in the mass during the "on-stream" reaction, since there is provision for removing the excess heat of a more intense regenerating reaction.

For one specific illustration of apparatus, reference may be had to the accompanying drawing, the single figure of which is a vertical sectional view of a catalytic converter with certain parts shown in elevation or partly in elevation and partly broken away. The converter X, of any desired shape and size, is preferably covered with suitable heat insulating material, such as lagging 4, and is divided into end manifolding chambers A and B and a centrally located reaction chamber C by perforated partitions or flue sheets 5 and 6. Fluid reactants for either endothermic or exothermic reactions supplied selectively by valved lines 17 or 22 may pass through T18 to enter manifolding chamber A and be distributed uniformly throughout the depth and cross section of contact mass or catalyst M, disposed in reaction chamber C, by means of a series of distributing members or perforated conduits 7 (which may or may not be of nested construction) while fluid reaction products are simultaneously vented from a plurality of points in mass M into a series of perforated outlet con-

duits 8. The fluid reaction products are discharged into manifolding chamber B and thence into T11 to pass out through valved line 12 (or valved line 13). Nested conduits 9 and 9a embedded in mass M serve to conduct a plurality of streams of an extraneous heat exchange fluid, in reverse flow, in heat exchange relation with mass M to regulate the temperature of the mass, e. g. to compensate for differences between endothermic and exothermic heats of reaction, and especially to remove heat therefrom during exothermic reaction periods or during a portion of each or all thereof. Manifolds 10 and 10a in nested relation supply the heat exchange fluid to and remove this fluid from conduits 9 and 9a. A continuously fresh supply of the heat exchange fluid may be used, or the fluid may be recirculated through conduits 9 and 9a and a suitable cooling system, as, for example, the circuits described in the aforesaid Patent No. 2,078,947, may be employed, as desired.

While the present invention contemplates a cycle wherein the contact mass is kept at all times within a selected temperature range, it is to be understood that it is not to be limited strictly to this condition. To insure adequate storage of heat in the contact mass and adjacent apparatus, especially when the productive reaction is to be continued for a rather long period, it is at times desirable to carry the regeneration temperatures for a part of the regenerative reaction outside or above the specified range. This may also be done from time to time, if desired, to effect a very complete or thorough regeneration of the contact mass. All such variations and temporary modifications are within the spirit and scope of the present invention.

I claim as my invention:

1. In the conversion of high boiling hydrocarbon fluids to produce lower boiling hydrocarbons including gasoline, involving the use of a converter containing a solid adsorptive contact material or catalytic mass in alternate periods of endothermic reaction, during which combustible deposits accumulate on or within said mass, and of regeneration in place by combustion of said deposits, the steps of process which comprise maintaining the catalytic mass or contact material within a predetermined and optimum temperature range of not more than 250° F. which lies below 950° F. throughout each cycle of operation; during an on-stream or reaction period passing hydrocarbon reactants, heated to within the aforesaid temperature range, into said converter and in contact with said catalytic mass, so that said catalytic mass drops within the aforesaid range during the on-stream period due to heat absorbed by the endothermic conversion of hydrocarbons; during an alternate period of regeneration passing an oxygen-containing regenerating fluid into said converter and in contact with said catalytic mass to remove contaminants therefrom so that the said mass rises within the aforesaid range during the regenerating period due to heat evolved by the exothermic regeneration; limiting the duration of said on-stream or reaction period so that the accumulated combustible deposits on the said catalytic mass do not exceed substantially 1% by weight of the mass; said catalytic mass being maintained within the aforesaid range throughout the entirety of the on-stream period and of the period of regeneration, thereby to provide an efficient cyclic operation for the conversion of hydrocarbons in the

presence of a contact material and for regeneration of said contact material in place.

2. In processes for utilizing a converter containing an adsorptive catalytic mass alternately for the endothermic conversion of carbonaceous fluids which leave combustible contaminants on or within the mass and for regeneration of the mass in place by combustion of such contaminants, the steps of maintaining the converter and catalytic mass within a predetermined temperature range of not more than 150° F. which is mainly below 950° F. during both conversion and regeneration periods, during the conversion periods passing heated fluid reactants into said converter and into contact with said catalytic mass, said fluid reactants being heated so as to avoid thermal cracking prior to introduction into said converter to such temperature adjacent the lower end of said range that the catalytic mass and converter substantially supply the endothermic heat of reaction and their temperatures fall within the aforesaid range, during each alternate exothermic regeneration period passing a regenerating medium into said converter and into contact with said mass so as to burn away combustible deposits and to cause the temperatures of said converter and of said mass to rise within the aforesaid range, and limiting the duration of the conversion periods so as to control the combustible contaminants deposited on or within said mass to an amount, which when burned during said regeneration periods, will produce enough heat to raise the temperatures of said mass within the aforesaid range, this amount of said deposit being of the order of 1% by weight of the mass, thereby to provide a cyclic catalytic operation in which temperatures of the catalytic mass increase during one period of the cycle and decrease during the other period thereof.

3. In the cracking of reactant hydrocarbons boiling to substantial extent above the gasoline boiling range to produce therefrom high antiknock low boiling motor fuels including gasoline involving the use of a converter containing an adsorptive silicious contact material or catalyst in recurring cycles, each of alternate periods of endothermic transformation or cracking of hydrocarbons and of regeneration of the contact material in place by combustion of burnable contaminants deposited thereon during a preceding transformation period, the steps of process which comprise maintaining the contact material during a predominant proportion of each cycle of operation within a predetermined temperature range which is above 750° and below 950° F.; during each on-stream or transformation period admitting reactant hydrocarbons into contact with the catalyst or contact material at such a temperature approximating the aforesaid range that thermal cracking is avoided prior to contact with the catalyst and that the said catalyst and converter supply endothermic heat of reaction and their temperatures fall within the aforesaid range and limiting the duration of individual on-stream periods so the combustible deposits which accumulate on said catalyst do not exceed an amount of the order of 1% by weight of said catalyst; during each alternate period of regeneration passing a combustion-supporting regenerating medium into contact with said catalyst so that the temperature of the latter rises within said range and even slightly above the top temperature thereof; the temperatures of said contact material or catalyst being decreasing temperatures which are completely within the aforesaid

range throughout substantially the entirety of respective individual on-stream periods and temperatures during regeneration being rising temperatures which are within the aforesaid range throughout the predominant proportion of the duration of respective individual regeneration periods, and circulating a heat exchange fluid in heat exchange relation with but out of contact with said catalyst or contact material particu-

larly during any portion of each regeneration period when the temperature of the catalyst is above the aforesaid range so as to control the temperature of said catalyst and quickly to restore it to a temperature within the aforesaid range, thereby to provide an efficient cyclic operation for the transformation of hydrocarbons in the presence of a contact material.

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