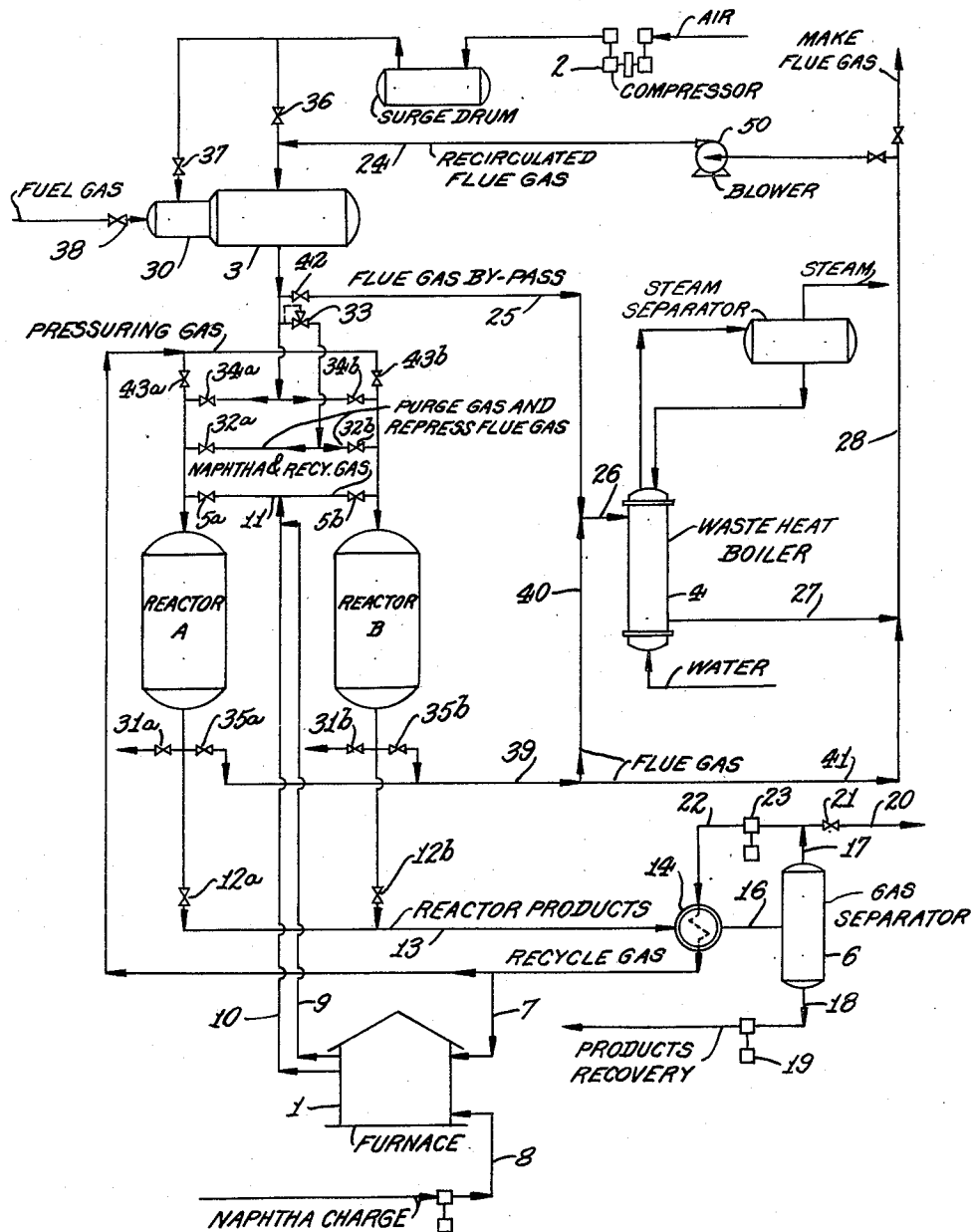


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CATALYTIC REFORMING OF HYDROCARBONS IN
THE PRESENCE OF HYDROGEN
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CATALYTIC REFORMING OF HYDROCARBONS IN THE PRESENCE OF HYDROGEN

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The present invention relates to the conversion of aliphatic hydrocarbons including acyclic and alicyclic hydrocarbons to aromatic hydrocarbons by treatment over a suitable catalyst. In one aspect this invention relates to the conversion of hydrocarbon stocks boiling within, and in some cases within and somewhat above, the gasoline boiling point range to high-grade motor fuel by catalytic aromatization under critically defined conditions. In another aspect the invention relates to a cyclic conversion process wherein the catalyst is employed in successive stages of conversion and regeneration and wherein the spent catalyst is subjected to an improved regeneration procedure.

The present application is a continuation-in-part of my prior and co-pending applications, Serial No. 376,783, filed January 31, 1941, in which I am the sole inventor; and Serial No. 440,762, filed April 28, 1942, in which I am a co-inventor, both of said applications now being abandoned. The above-mentioned application Serial No. 440,762 is a division of application Serial No. 294,784, filed September 13, 1939, now Patent No. 2,320,147, issued May 25, 1943. Application Serial No. 440,762 particularly relates to a process for the aromatization of aliphatic hydrocarbons and discloses specific and critical conditions of operation, suitable aromatization catalysts and their composition, and the method of manufacturing the catalyst. Reference may be had, therefore, to application Serial No. 440,762 or to Patent No. 2,320,147 for more specific and detailed discussion of the aromatization reaction conditions and the aromatization catalyst.

In certain of its aspects, the present invention may be regarded as an improvement on the process described in copending application Serial No. 294,784, filed September 13, 1939, now Patent No. 2,320,147 issued May 25, 1943, of which the present applicant is a co-inventor. Pursuant to the process described in said application, aliphatic hydrocarbons, such as a naphtha of low anti-knock rating, is converted into a highly aromatic motor fuel of high anti-knock rating by a catalytic dehydrogenating and cyclicizing reaction. In this process the naphtha is passed in contact with an aromatizing catalyst at a suitable elevated temperature and space velocity to effect the desired conversion, and preferably in the presence of added hydrogen and under a suitable degree of superatmospheric pressure. During the conversion the catalyst is progressively deactivated by reason of the accumulation of a carbonaceous deposit thereon and, accordingly, its activity must be eventually restored by removal of the carbonaceous deposit.

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The usual practice is to regenerate the spent catalyst by removing the carbonaceous deposit by combustion, and since the combustion reaction is strongly exothermic it must be effected under carefully controlled conditions and particularly at a temperature not in excess of the critical temperature at which the activity of the catalyst is destroyed. The complete removal of carbonaceous material is indicated by the appearance of uncombined oxygen in the effluent regeneration gas. Thereafter, the regenerated catalyst may suitably be purged to free it of regeneration gases, and also reheated to a temperature suitable for the following hydrocarbon conversion operation.

It is an object of this invention to provide a process for the conversion of aliphatic hydrocarbons to aromatic hydrocarbons. It is a further object of this invention to provide a process for the conversion of a stock boiling approximately within the gasoline boiling range, and rich in aliphatic hydrocarbons, into high yields of a highly aromatic motor fuel. It is a particularly important object of this invention to provide a catalytic aromatization process to produce extremely small amounts of coke and to give long catalyst life. It is still a further object of this invention to provide a continuous process for the regeneration of spent catalyst used in a process for reforming hydrocarbons. Other and more detailed objects, advantages, and uses of this invention will become apparent as description thereof proceeds.

I have ascertained that the activity of the catalyst is not restored by such regeneration methods to an extent as large as is desirable, and the primary object of my invention is the provision of a method whereby the activity of the catalyst may be more fully restored.

Pursuant to the present invention, regeneration of the catalyst is effected by passing an oxygen-containing gas in contact with the catalyst until complete removal of the carbonaceous material is accomplished, and thereafter continuing to pass an oxygen-containing gas in contact with the catalyst under such conditions as to oxidize the active metallic component of the catalyst. It has been ascertained that a substantial enhancement of the activity of the regenerated catalyst may be accomplished thereby.

The appended drawing illustrates diagrammatically a suitable arrangement of apparatus and process flow for the practice of the invention. The principal elements of the apparatus are a furnace 1 for vaporizing and heating the hydrocarbon charge, a pair of similar reactors or catalyst chambers A and B containing a suitable catalyst and manifolded with fluid inlets and outlets so that each reactor alternately passes through

the successive steps in the complete reaction and regeneration cycle, and auxiliary regeneration equipment including a compressor 2 for supplying an oxygen-containing gas, a flue gas producer and heater 3, and a waste heat boiler 4.

Although not limited thereto, the invention is especially well exemplified by its application to the conversion of a low anti-knock rating naphtha into an aromatic motor fuel of high anti-knock rating by a procedure such as that described in application Serial No. 294,784, above mentioned. Pursuant to this process, vapors of the naphtha undergoing treatment are passed in contact with a suitable dehydro-aromatization catalyst under conditions adapted to largely dehydrogenate and cyclize aliphatic compounds present therein to corresponding aromatic compounds. The catalyst comprises about 6 per cent by weight of molybdenum oxide impregnated in or supported on activated alumina. The naphtha charging stock comprises an East Texas heavy naphtha having an A. P. I. gravity of 50.3° containing approximately 14 per cent aromatics, 33 per cent naphthenes, and no olefins, and the remainder being largely paraffin hydrocarbons. This naphtha has an initial boiling point of about 248° F., a 50 per cent boiling point of about 310° F. and an end point of about 396° F. The original octane number measured by the Cooperative Fuel Research Motor Method is 42.3. It is contemplated that the reaction conditions thus maintained will involve the maintenance of an average reaction temperature within the range 875° to 1075° F., for example a temperature of about 975° F., a time factor within the range between 0.1 and 25, preferably between 0.2 and 20, for example a time factor of one, this factor representing the number of hours required to flow one volume of charge measured on a liquid basis through one volume of catalyst space, a superatmospheric reaction pressure within the range of about 30 to 450 pounds per square inch, preferably 50 to 375 pounds per square inch, for example a pressure of 315 pounds, and added hydrogen in amount ranging from 0.5 mol to 8 mols of hydrogen per mol of naphtha charge, for example 3 mols. Passage of the mixture of hydrocarbon vapors and hydrogen over the catalyst under these conditions is continued until a carbonaceous deposit on the catalyst accumulates to an extent where regeneration of the catalyst by removal of the deposit is necessary or economically desirable. By the maintenance of a superatmospheric pressure within the above indicated range and added hydrogen, the feasible length of the conversion period before regeneration is greatly extended.

As to the catalyst used in this process, the oxides of the metals of the left-hand column of group VI of the period table, particularly chromium, molybdenum, and tungsten are preferred, but other metallic oxides and other metallic compounds, particularly oxides of the metals of the left-hand group of columns IV and V of the periodic table, such as titanium, cerium, thorium, and vanadium may be used. Moreover, while these catalytic oxides can be used alone on various supports including magnesia, I find it very highly preferable to utilize them on alumina, particularly an activated alumina or on alumina gel as a support, and in general the catalytic oxides or other catalytic compounds should be the minor constituents, usually from 1 to 40 per cent by weight of the total catalyst including the support, although the optimum

percentage varies, of course, with the catalyst used. It will also be apparent that mixed catalysts can be used, for instance a mixture of chromium oxide and molybdenum oxide alone or preferably on an alumina support, and in this case the active catalytic oxides should be from about 1 to about 25 per cent by weight of the total catalyst. Another catalyst which can be used is magnesium chromite either alone or on a suitable support, preferably alumina. In fact, any aromatization catalyst or metal which promotes dehydrogenation and cyclization of aliphatic hydrocarbons can be used. As those skilled in the art know, the efficiency of a given catalyst is largely determined by its method of preparation, and consequently some catalysts give better results than others under specific conditions. For a detailed description of the method of preparation of the catalyst, reference may be had to my co-pending application, Serial No. 440,762, or my Patent No. 2,320,147, of which the present application is a continuation-in-part. Of all of the catalysts I prefer to use a catalyst comprising molybdenum oxide supported on alumina, particularly activated alumina, and the molybdenum oxide should most advantageously constitute from about 2 to about 10 per cent by weight of the total catalyst since this has been found to include a sharp optimum which gives best results. Larger amounts of molybdenum oxide can, however, be used.

I prefer that the catalyst be substantially free from sulphur since sulphide catalyst as contrasted with oxide catalyst tends to degrade the stock to less valuable paraffin and lead to dominant hydrogenation rather than predominant dehydrogenation, i. e., hydrogen consumption rather than hydrogen production. These hydrogen sulphides also result in increased "production."

As previously indicated the oxide catalysts are preferred but in some cases, such as the preferred molybdenum oxide catalyst, the oxide tends to be reduced in the process and in general instead of using the oxides of the metals of the left-hand columns of groups IV, V, VI, the metals themselves can be used, preferably supported on alumina.

The present process may be applied to various feed stocks, for example a Michigan virgin naphtha having an A. P. I. gravity of 61.5. This naphtha has an initial boiling point of 120° F., a 50 per cent boiling point of 270° F., and an end point of 396° F., and an octane number of 24. Another example of a charging stock is a California virgin naphtha having an A. P. I. gravity of 47.0, containing 1.5 per cent olefins and 13.5 per cent aromatics. This naphtha has an initial boiling point of 258° F., a 50 per cent boiling point of 305° F., and an end point of 398° F., and an octane number of 57.8.

The product of the present invention has a high aromatic content with substantially small amounts of olefins. The A. P. I. gravity of the product is a good measure of its content of aromatic hydrocarbons since aromatics having low A. P. I. gravity or, in other words, high specific gravities. The A. P. I. gravity of the product may vary between 50 and about 40 degrees. With increasing octane number the gravity of the product tends to drop off. The gravity of the stabilized product is less than, and for the preferred operating conditions, at least 3° A. P. I. less than, the gravity of that part of

the original charge stock having the same end point as the end point of the product.

Regeneration of the catalyst is most suitably effected by removing the carbonaceous deposit by combustion. During this operation careful temperature control is necessary in order to burn off the carbonaceous material at a suitable rate and at the same time prevent permanent impairment or destruction of the catalyst's activity which results from excessively high temperatures. Such temperatures may be avoided by removing the exothermic heat of combustion at a suitable rate, effected usually either by indirect heat exchange with cooling coils or similar cooling surfaces embedded in the catalyst, or by the circulation of an inert gas such as flue gas with the oxidizing medium, such as air. Heretofore, the combustion operation has been carried only to the point where the carbonaceous deposit has been completely removed as evidenced, for example, by the appearance of free-oxygen in the effluent gases from the regenerator and the carbon dioxide content of the effluent gases.

Various supplemental and preparatory steps are normally employed both with respect to the conversion and regeneration operation. The regeneration operation normally is preferably carried out under a pressure different from that maintained in the conversion reaction, and hence adjustment of the pressure in the reactor between these steps is normally required. In addition, purging of the residue gases or vapors, and adjustment of the temperature of the catalyst during the periods intervening between the reaction and regeneration operations is usually desirable. The present invention contemplates an additional intervening treatment whereby the activity of the spent catalyst and its suitability for reuse is substantially enhanced compared with the results obtained by removal of the carbonaceous deposit alone. The complete process may suitably involve the steps enumerated below, it being understood that certain of these steps may be omitted and other steps added without departing from the essential features of the invention:

- 1.—Reaction or on-stream operation
- 2.—Depressuring
- 3.—Purging
- 4.—Repressuring
- 5.—Regeneration, or combustion of the deposit
- 6.—Oxidation of the catalyst
- 7.—Reheating
- 8.—Depressuring
- 9.—Purging
- 10.—Repressuring

During the reaction or on-stream period a mixed stream of heated naphtha vapors and hydrogen is supplied to the particular reactor on-stream through reactant's inlet valve 5a or 5b and passed therethrough in intimate contact with the catalyst which is disposed in the reactor in the form of a bed resting on a suitable perforated support or in any other suitable manner. As previously indicated, catalysts comprising an oxide of vanadium or a metal from the group forming the left-hand column of group VI of the periodic table are greatly preferred, particularly molybdenum oxide, preferably supported on activated alumina.

Chromium catalysts can also be used in place of molybdenum catalysts, particularly catalysts containing from 15 to 40 per cent Cr_2O_3 by weight on alumina. A catalyst containing 25 per cent

Cr_2O_3 on 75 per cent of activated alumina is an example. The method of preparation of this catalyst is disclosed in my copending application, Serial No. 440,762, and my Patent No. 2,320,147, above referred to.

The hydrogen gas mixed with the charge may suitably consist of a recycle gas derived from gas separator 6 which contains a large amount of hydrogen in mixture with normally gaseous hydrocarbons. The recycle gas and naphtha charge are supplied to a suitable heating means such as furnace 1 by lines 7 and 8, respectively, and the heated products are withdrawn from the heater by lines 9 and 10, respectively, and passed to the reactor inlet manifold 11. The specific arrangement shown has the advantage of supplying a substantial amount of the heat of reaction by means of the heated recycle gas and the admixture of the recycle gas at a point immediately prior to the introduction into the reactor manifold assists in avoiding undesirable thermal decomposition. The vaporous conversion products are withdrawn through valves 12a or 12b and pass to reactor products transfer line 13 to a condenser 14 wherein normally liquid constituents are condensed, and the cooled mixture passed by line 16 to gas separator 6, wherein a gaseous fraction including the recycle gas is withdrawn overhead through line 17, and the liquid products withdrawn from the bottom through line 18 and pumped by pump 19 to a suitable products recovery system such as a fractionator, rerun tower and the like. Net make hydrogen gas is withdrawn through line 20 controlled by valve 21 which valve controls the pressure imposed on the reaction system. The recycle gas fraction is withdrawn through line 22 and compressed by compressor 23 to the pressure necessary to force it through heater 1 and reintroduced into the reaction system.

The regeneration equipment includes a suitable means such as a waste heat boiler 4 for cooling and recovering energy from the effluent hot regeneration gas and lowering its temperature to that suitable for recirculating to the reactor. In order that steam production in boiler 4 may be suitably constant a flue gas producer and heater 3 is provided from which flue gas may be passed either directly to the reactor or by way of by-pass line 25 to boiler 4. Blower 50 in line 24 is preferably operated in such a manner as to circulate through line 24 flue gas at a constant rate at all times and under a suitable degree of superatmospheric pressure. Dependent upon the requirements of the system, device 3 may be operated merely as a mixer for flue gas and air, or as a hot flue gas producer by admitting air and fuel gas through valves 37 and 38 to the burner 30.

As a starting point in considering the regeneration procedure, reactor A may be regarded as being at the point where it is just completing reaction and is ready for regeneration, the oil inlet and outlet valves 5a, 12a being open and all other valves closed. During this time the flue gas is being recirculated through lines 24, 25, 26, 27 and 28, completely by-passing both reactors, and is heated in the flue gas heater 3 by combustion of fuel gas and air in burner 30 and is thereafter cooled in waste heat boiler 4.

The first step in the regeneration procedure is the preparation for purging by depressuring the reactor to atmospheric pressure. This is effected by closing the oil vapor inlet valve 5a and oil outlet valve 12a and opening valve 31a leading to a blow-down stack (not shown). The oil vapors

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then pass into the blow-down stack in a period of a few minutes, the depressuring rate being controlled in order to prevent damage to the catalyst and supporting structure.

The next operation is to purge residual oil vapors from the reactor by passing an inert gas through the reactor. This may be suitably accomplished by bleeding excess flue gas from the recirculating system into the reactor through valve 32a, the rate preferably being controlled by a back pressure controller 33 to maintain pressure on the recirculating system substantially constant. This operation is continued until a suitable volume of the purging medium, for example about 10 volumes, has been passed through the reactor, at which time valve 31a is closed and the reactor is repressured with flue gas to the pressure of the circulating system, for example about 50 or 100 pounds, by continuing to admit flue gas to the chambers through valve 32a.

When the pressure in the chambers has reached the pressure of the circulating system, valve 32a is closed and valves 34a and 35a are opened, allowing the recirculating flue gas to pass through the reactor. Immediately thereafter valve 36 admitting coke combustion air to the system is opened and valves 37 and 38 are closed thereby cutting off the combustible gas mixture and the heat supply from the flue gas burner 3. The flue gas and air mixture at a relatively low temperature above the ignition temperature, between about 600° F. and about 775° F., for example about 650° F., is now flowing through reactor A causing combustion of coke therein, the resulting heat being removed in waste heat boiler 4, the hot combustion gas passing thereto through lines 39, 40, and 26. The quantity of oxygen or air thus introduced is regulated in such manner that the combustion will proceed at a suitable rate without exceeding the safe maximum regeneration temperature. The oxygen content of the flue gas and air mixture entering the reactor is usually about 1 to about 2 per cent. The burning occurs in a relatively narrow horizontal band or zone which starts at the place of injection of the flue gas and air mixture into the catalyst bed and moves down through the bed as regeneration progresses. The heat liberated by this burning is adsorbed as sensible heat in the flue gas which is heated from its relatively low initial temperature to a temperature of about 1150° F., the latter representing the maximum safe regeneration temperature. After completion of combustion of the carbonaceous deposit or coke the catalyst bed is left at a temperature approximating the temperature of the cooled recirculated flue gas. The completion of this combustion is evidenced by the presence of uncombined oxygen in the effluent gas.

At this stage pursuant to the present invention, the circulated flue gas is preferably heated to a higher temperature than in the first stage regeneration by burning a mixture of fuel gas and air introduced through valves 37 and 38 to burner 30, and at the same time excess air is introduced through valve 36 into the heated mixture. The resulting temperature of the gaseous mixture is at least 25° F. above the flue gas in the first stage regeneration, generally at a temperature of about 750° F. to about 850° F. or higher. Preferably the temperature of the flue gas in the second stage should be at least 800° F. The hot oxidizing gas thus produced passes through the reactor for a sufficient period to substantially completely oxidize the active metallic

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component of the catalyst and to burn any remaining or embedded carbonaceous deposits. For example, in the case of a catalyst comprising molybdenum, this is oxidized entirely or substantially entirely to the form of the trioxide. The maximum safe temperature during the second regeneration or oxidization step is about 1150° F. similar to the maximum safe regeneration temperature of the first regeneration step in order to prevent injury to the catalyst. The oxygen content of the flue gas and air mixture is controlled to be the same or less than the oxygen content of the flue gas mixture in the first regeneration step in order to prevent the aforesaid maximum safe temperature from being exceeded during the second regeneration or oxidation step. Preferably, the oxygen content of the flue gas mixture in the second stage is held below about 1 per cent by controlling the amount of excess air introduced through valve 36 in order to prevent overheating of the catalyst in the second regeneration step which uses a higher inlet temperature of the hot oxidizing gas.

The advantage of effecting the second stage of the regeneration or oxidization at a higher inlet temperature of the flue gas than in the first stage is not only that the active metallic components may be completely oxidized and embedded carbonaceous deposits burned, but at the higher inlet temperatures the reaction rate is greatly increased; for example, the reaction rate may be increased as much as 2 or 3 times the reaction rate at lower inlet temperatures. Increased reaction rates shorten the time required for regeneration and make for an overall more efficient regeneration system.

Upon completion of the foregoing second regeneration or catalyst oxidation step, the temperature of the catalyst may still be somewhat below the normally desired conversion temperature. In order to reheat the catalyst to this temperature, the supply of heat to the recirculated flue gas is continued by burning fuel gas and air in the burner 30 but the supply of excess oxygen is shut off by closing air valve 35. The temperature of the flue gas supplied from flue gas heater 3 at this time is relatively high, for example about 1075° F. while the temperature of the flue gas from the reactor remains at a relatively low temperature for a substantial portion of the reheating period. This may necessitate by-passing a portion of it around the waste heat boiler by line 41 in order not to reduce the temperature of the flue gas to the flue gas circulating line 24 below the desired minimum, the flow through the by-pass being controlled by a temperature controller (not shown). The reheating operation is continued until sufficient heat has been imparted to the catalyst bed to raise the average temperature thereof to the desired reaction temperature at which time flue gas by-pass valve 42 in line 25 is opened, and valves 34a and 35a are closed.

Depressuring of the reactor is now effected by opening valve 31a conveying the flue gas to the blow-down stack. Valve 31a may then be closed and the reactor is then purged and repressured with recycle gas admitted through valve 43a to the desired reaction pressure, for example about 315 lbs. When the pressure on the reactor reaches the required pressure the flow of the repressuring gas is stopped by closing valve 43a. In a desirable modification of the step, in place of closing valve 31a prior to the admission of recycle gas this valve is permitted to remain open and recycled gas is passed through the reactor there-

by effecting a partial reduction of the catalyst and enhancing its activity as set forth in my copending application Serial No. 294,785, filed on September 13, 1939, now Patent No. 2,270,715. Such a reduction is effected to a certain extent by repressuring alone since this operation is preferably effected over a substantial period of time and at the rate at which make hydrogen gas is available.

Reactor A now contains recycle gas at the required reaction pressure and is ready to be placed in reactor service in place of reactor B which has at this point reached the end of the reaction cycle. Reactor A is now put on reaction by opening valve 5a and 12a and reactor B is removed from reaction by closing the corresponding valves on it, thus completing the regeneration steps in reactor A.

It is to be understood that the time required for the various operations is susceptible to substantial variations dependent upon such factors as the character of the charging stock, degree of conversion and the like. As an example of the general magnitude of the time suitably utilized for the various steps reference is made to the conversion by the procedure above described of a heavy virgin East Texas naphtha having an A. P. I. gravity of 51.2 and an octane number of 45.3 to a highly aromatic reformat having a gravity of 49 and an octane number of 80.0. In this instance a twelve hour cycle period was employed, each reactor being on-stream for a period of six hours, and engaged in the various steps of the regeneration procedure for the remaining six hours. In this particular regeneration procedure, a period of about four and a half hours was utilized for combustion of the carbonaceous deposit, a period of about forty minutes for oxidation of the catalyst, a period of about twenty minutes for the reheating step, a period of about twenty minutes for the step of repressuring and treatment with recycle gas, and the remaining time was distributed over the other operations and necessary time for valve changes.

The substantial completion of the coke combustion step is indicated by the oxygen and carbon dioxide content of the effluent gas from this stage. Completion of coke combustion is indicated when no further increase in the carbon dioxide content of the effluent gas occurs and free oxygen appears therein. Completion of the catalyst oxidation or second stage regeneration step is indicated at the point where the free oxygen content of the effluent gases is the same as that of the entering gases and also by the point at which heat evolution due to the exothermic reaction involved ceases. It is to be understood that traces of residual carbonaceous material may be burned off during the catalyst oxidation step.

It will also be apparent that the specific apparatus and process flow above described is merely exemplary of my invention, and various other forms of apparatus and process flow may be advantageously utilized with certain types of charging stock. For example, in the conversion of cracked naphthas containing high amounts of sulphur, apparatus and process flow such as set forth in my copending application Serial No. 358,750, filed September 28, 1940, and abandoned October 29, 1945, may be utilized to advantage. In the latter type of apparatus four or more types of reactor chambers are employed and one chamber is engaged in coke combustion at all times during the reaction, hence it is feasible to dispense with a flue gas heater and producer

except during the starting up period. These and various other possible modifications in applying my invention will be apparent to those skilled in the art and it is to be understood that its scope is not limited otherwise than is required by the claims appended hereto.

I claim:

1. The method of reforming a hydrocarbon in the presence of a catalyst which consists essentially of a reducible metal oxide of group VI of the periodic system carried on an alumina-containing base and added free hydrogen in which operation the reaction takes place under superatmospheric pressure and which operation requires periodic regeneration of the catalyst, the improvement which comprises subjecting the catalyst after regeneration to a purging operation with free hydrogen or free hydrogen-containing gas carried out at pressures substantially less than those employed during the said reforming operation.

2. The method of producing an aromatic from a hydrocarbon fraction containing a naphthene which comprises contacting the said feed stock with a reforming catalyst consisting essentially of a reducible metal oxide selected from the class consisting of molybdenum oxide and chromium oxide carried on an alumina support, in the presence of added free hydrogen and under reforming conditions of temperature and pressure, withdrawing reaction products, discontinuing the flow of feed stock to the catalyst, regenerating the catalyst, purging with inert gas and prior to returning the feed stock to the catalyst, purging the said catalyst with a free hydrogen-containing gas at pressures substantially below those employed during the reforming operation.

3. The method set forth in claim 2 in which catalyst is purged with a flue gas at pressures prevailing during the reforming operation and thereafter purged with a free hydrogen-containing gas at pressures substantially below those employed during the reforming operation.

4. The method set forth in claim 2 in which following purging with a free hydrogen-containing gas at reduced pressures the system is repressured with a gas containing hydrogen.

5. The method of reforming a hydrocarbon which comprises contacting a hydrocarbon feed with a reforming catalyst consisting essentially of a reducible metal oxide selected from the class consisting of molybdenum oxide and chromium oxide carried on an alumina support, in the presence of free hydrogen and under reforming conditions of temperature and pressure, withdrawing reaction products, discontinuing the flow of hydrocarbon feed to the catalyst, regenerating the catalyst, purging with inert gas and prior to returning the hydrocarbon feed to the catalyst, purging the said catalyst with a free hydrogen-containing gas at pressures substantially below those employed during the reforming operation.

6. The method of claim 5 in which said regeneration operation comprises the steps of introducing a mixture of air and flue gas into contact with the catalyst at a temperature above the ignition temperature of the carbonaceous deposits deposited thereon during the reforming operation until substantially complete removal of the carbonaceous deposits is effected and the catalyst is left at a temperature approximating said initial introduction temperature, maintaining a maximum safe regeneration temperature below about 1150° F., subsequently heating an oxygen-containing gas to a temperature at least 25° F. higher than the temperature of the flue gas and

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air in the prior step of regeneration, and introducing the thus heated oxygen-containing gas into contact with the catalyst to substantially completely oxidize the active metallic component of the catalyst and burn any remaining carbonaceous deposits thereon.

7. The method according to claim 6 in which the temperature of the air and flue gas in the primary regeneration step is between about 600° F. and about 775° F. and the temperature of the oxygen-containing gas of the subsequent step is at least 800° F.

8. The method of claim 7 in which following purging with a free hydrogen-containing gas at reduced pressures the system is repressured with a gas containing hydrogen.

9. The method of claim 7 in which catalyst is purged with a flue gas at pressures prevailing during the reforming operation and thereafter purged with a free hydrogen-containing gas at pressures substantially below those employed during the reforming operation.

10. In the method of reforming a hydrocarbon in the presence of a catalyst which consists essentially of a reducible metal oxide of group VI of the periodic system carried on an alumina-containing base and added free hydrogen in which operation the reaction takes place under superatmospheric pressure accompanied by the deposition of carbonaceous deposits on the catalyst and which operation requires periodic regeneration of the catalyst at a temperature substantially lower than the maximum safe regeneration temperature by introducing a mixture of air and flue gas into contact with the catalyst at a temperature above the ignition temperature of the carbonaceous deposits until substantially complete removal of the carbonaceous deposits is effected, the improvement which comprises heating an oxygen-containing gas after regeneration of said catalyst to a temperature higher than the temperature of the oxygen-containing gas used in the aforesaid regeneration and introducing said thus heated oxygen-containing gas into contact with the catalyst to substantially completely oxidize the active metallic components of the catalyst and to burn any remaining carbonaceous deposits, and subsequently subjecting the catalyst after the aforesaid oxidation treatment to a purging operation with free hydrogen or free hydrogen-containing gas carried out at pressure substantially less than those employed during said reforming operation.

11. In the method of reforming a normally liquid hydrocarbon oil containing naphthenic components in which such a hydrocarbon oil is reformed under superatmospheric pressure and elevated temperatures and in the presence of added free hydrogen and a reforming catalyst consisting essentially of a reducible metal oxide selected from the class consisting of molybdenum oxide and chromium oxide carried on an alumina support, and in which the catalyst is regenerated by introducing an oxygen-containing gas into contact with said catalyst at a temperature within the range of about 600° F. to about 775° F. until substantially complete removal of carbonaceous material deposited thereon during the reforming operation is effected at a temperature below the maximum safe regeneration temperature, the improvement which

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comprises following said regeneration heating an oxygen-containing gas to a temperature in excess of about 800° F. and introducing the thus heated oxygen-containing gas into contact with the catalyst to substantially completely oxidize the active metallic component of the catalyst and burn any remaining carbonaceous material thereon, subsequently purging the catalyst following the aforesaid catalyst oxidation treatment with a free hydrogen-containing gas at pressures substantially below those employed during the reforming operation.

12. In a process for the conversion of aliphatic hydrocarbons to aromatic hydrocarbons involving passing vapors of aliphatic hydrocarbons into contact with a metallic oxide aromatizing contact catalyst at an elevated temperature of about 875° F. to about 1075° F. in the presence of about 0.4 to about 8 mols of hydrogen per mol of hydrocarbon feed and at a pressure of about 30 to about 450 pounds per square inch, continuing the passage of said vapors until activity of the catalyst is substantially decreased by the accumulation of carbonaceous deposits thereon, regenerating the catalyst by introducing a gas containing between about 1 and about 2 per cent oxygen in contact with said catalyst at a temperature within the range of 600 to about 775° F. until substantially complete removal of the carbonaceous deposits is effected, maintaining the temperature of regeneration below the maximum safe regeneration temperature of about 1150° F., and reusing the regenerated catalyst for the conversion of further quantities of aliphatic hydrocarbons, the improved method of reconditioning said regenerated catalyst prior to reuse thereof for further conversion which comprises heating an oxygen-containing gas containing less than 1 per cent oxygen to a temperature in excess of about 800° F. and introducing the thus heated oxygen-containing gas into contact with the regenerated catalyst to substantially completely oxidize the active metallic component thereof and to burn any remaining carbonaceous deposits thereon at a temperature below the aforesaid maximum safe regeneration temperature, subsequently purging the catalyst with free hydrogen or free hydrogen-containing gas at a pressure substantially less than those employed during said conversion operation.

EDWIN T. LAYNG.

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