

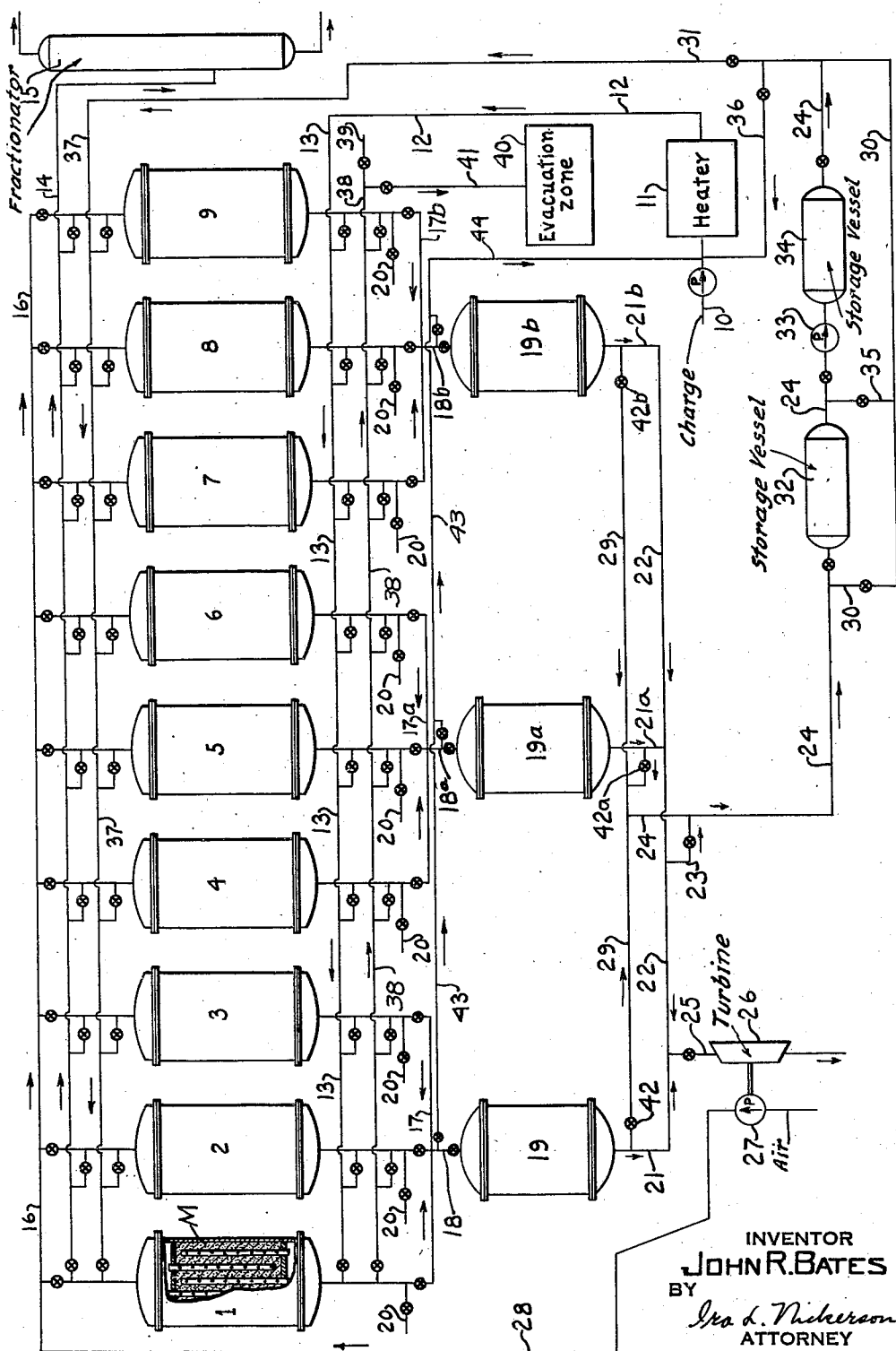
June 9, 1942.

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2,285,401

CONTROLLING ATMOSPHERE WITHIN REACTION EQUIPMENT

Filed April 6, 1939



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UNITED STATES PATENT OFFICE

2,285,401

CONTROLLING ATMOSPHERE WITHIN
REACTION EQUIPMENT

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Application April 6, 1939, Serial No. 266,282

21 Claims. (Cl. 196—105)

The present invention relates to controlling the physical and/or chemical character of fluid contained in reaction equipment by admission on to the latter of fluid of a predetermined and controlled chemical nature. More particularly, it is concerned with processes and apparatus for diluting, displacing or otherwise regulating the nature of reaction fluid within converters containing contact masses which influence desired changes in reactants, such as hydrocarbons and their derivatives, and which, as a result, acquire burnable deposits, especially when the converters are engaged in cyclic operation involving on-stream periods when burnable reactants are fed thereto alternating with regeneration periods when the burnable deposit is removed by controlled combustion. More specifically, it is directed to preparation of fluid useful with respect to both reaction fluid and the contact mass and to admission of controlled amounts of such fluid to the reaction zone at predetermined intervals.

It has become well known practice to utilize selected fluid in operating cycles of the above described type to condition or regulate the nature of the fluid or atmosphere within the converter or converters. One such use is to provide inert or substantially inert atmosphere within reaction zones between on-stream and regeneration periods to prevent mixing of burnable reaction fluid such as reactants or reaction products with air or other free oxygen bearing regenerating medium and the resulting formation of combustible or explosive mixtures. Another use of inert or other suitable fluid is in dilution of vapor phase reactants, as for example, of hydrocarbons, to insure maintenance of desired vapor phase conditions within the reaction zone. Steam, because it can be generated readily and at relatively low cost, has been the diluting or conditioning fluid most commonly employed. In a number of instances it has been found that steam has a deleterious effect upon the catalytic or other activity of certain contact masses with a tendency toward shortening the commercial life of such masses.

One object of the invention is to provide a gaseous medium of controlled composition suitable for admission to converters and other equipment. Another object is to provide such a medium having a variety of uses in assisting and controlling chemical reactions. Another object is to obtain an adequate supply of purging, displacing or diluting fluid which can be mingled with reactants and reaction products. Another object is to improve the purging of reaction chambers

containing solid contact material. Another object is to accomplish the above without interfering with normal operations involving chemical reactions. Other objects will be apparent from the detailed description which follows.

One concrete embodiment of the invention is disclosed in the accompanying drawing which is a somewhat diagrammatic flow chart illustrating a practical arrangement of converters and other equipment for operation of a plant engaged in the transformation or treatment of hydrocarbons.

Referring to the drawing, a suitable number of converters such as 1 to 9 are arranged in a battery to effect continuous transformation of a stream of hydrocarbon charging material, for example, of higher boiling hydrocarbons such as gas oils and crude oil distillation residues into lower boiling products of the gasoline type. Each of the converters contains a suitable contact mass M of silicious or other nature capable of promoting or assisting the desired reaction, such for example, as an active or activated blend or compound of silica and alumina of natural or synthetic origin which is used for on-stream periods, when hydrocarbons are admitted thereto, alternating with regeneration periods when carbonaceous and other burnable deposits resulting from on-stream reactions are removed therefrom by controlled combustion. During on-stream periods the selected hydrocarbon reactants are led by line 10 into heater 11 wherein they are vaporized with or without the aid of a diluting or vaporizing fluid and heated to desired or conversion temperature. The heated reactants are then conducted to the converter battery by line 12 and manifold 13 connected by valved branches to each of the converters 1 to 9 while reaction products are vented from the battery by similar valved branches into manifold 14 and conducted by the latter to suitable further treatment, such as fractionation in fractionator or bubble tower 15. For the regenerating periods, a regenerating medium containing free oxygen, such as air for example, is conducted from manifold 16 through the proper valved branch or branches into the desired one or number of converters while regeneration fumes issuing from the latter discharge into a suitable manifold system such as indicated by manifolds 17, 17a and 17b. In order to maintain continuous flow to the converter battery of reactants for both on-stream and regenerating periods, similar operating periods in individual members of a battery are alternated or staggered so that at the end of an operating

period in one converter another converter in the battery is ready to begin a similar operation. Thus, the feed of reactants is transferred from one converter to another with the result that at least one converter is always on stream while one or more converters are simultaneously in the regeneration phase of the cycle.

Operation of the converters also involves one or more purging steps following on-stream periods, regeneration periods, or both, and preceding admission to the converter of reactants for the succeeding portion of the cycle. Such purging may involve use of suitable, and especially inert, gaseous medium to serve as diluting or displacing agent, in which case a gas having selected properties may be supplied to manifold 37 and from there be admitted in desired quantity and at proper intervals to each of the converters 1 to 9 through the valved branches shown while spent purging medium admixed with purged fluid discharges into manifold 38 from which, if desired, the mixture may be vented from the system, as from valved line 39. The purging step or steps, however, are effected to advantage at subatmospheric pressure in which case vacuum may be applied to the converters, for example, after the manner disclosed in U. S. Patent 2,095,265, issued October 12, 1937 to J. H. Pew or 2,095,264, issued on the same date to A. E. Pew, Jr. As indicated in the drawing, vacuum for such purging may be produced in any known or desired manner in evacuation zone 40, connected to manifold 38 by valved line 41. When vacuum is employed, use of valved line 39 is omitted. Following a vacuum purging step a suitable fluid is admitted to the reaction vessel to raise the pressure in the same toward the level desired for the next step in the operation. Such fluid, which preferably is incapable of forming explosive or other highly reactive mixtures with either the fluid remaining within and near the contact mass after the purging step or with the reactants for the next operating step, may be supplied from any suitable source to manifold 37.

It has now been discovered that a greatly improved purging is effected by admitting to the chamber to which vacuum is being applied a suitable gaseous ejecting or displacing medium. Any gas suitable for admission to the contact mass and for admixture with reactants and reaction products in contact therewith is suitable for this purpose. It supplements and accelerates the action of the vacuum in removing reaction fluid from the chamber whether that fluid be adsorbed and/or absorbed in the contact mass or merely in the free space of the chamber. By continuing feeding of this agent after the vacuum is shut off it serves the additional purpose of adjusting the pressure in the converter toward the level desired for the next operation. Since the ejecting agent mingles with reactants and reaction products of the operation it is preferable that it be inert or substantially so with respect to such material, typical inert fluids being steam, nitrogen, carbon dioxide or any desired mixtures of two or more of these. Such admission of gas to the chamber during its evacuation, in addition to accelerating the purging process has other significant and important process advantages including: (1) more complete removal of reactants and/or reaction products; (2) positive displacement of even the rarified atmosphere of such material from both within and around the contact mass; and (3) provision within the chamber of an atmosphere of fluid

having predetermined and controlled characteristics suitable for admixture with the next fluid to be admitted to the contact mass. These results are obtained inexpensively and without increase in the amount of power necessary to evacuate the chamber within a given time. Moreover, supplementary to the above advantages and contrary to expectation, steam, admitted as purging fluid during evacuation has little if any tendency to shorten the commercial life of contact masses ordinarily adversely affected by it.

In effecting this purging step, vacuum, produced in a vacuum jet, pump or other known or desired evacuating device, is applied to one or more points in the chamber and a predetermined quantity of a suitable purging gas is fed to the chamber at one or more separate points. The selected gaseous medium may be admitted to the chamber and the mass at any time during drawing of the vacuum. Its action is more pronounced, however, and the purging more complete when it is sent into the chamber during at least the latter portion of the evacuation period. For practical purposes in commercial scale operation, a continuous stream of the gas is usually fed for substantially this entire period.

The amount of gaseous agent that need be used is small and is but a fraction of the amount necessary to effect, if used at normal pressure, a reasonably good purging and is below amounts which affect to substantial extent the temperature of the converter and its contents. The quantity fed and the rate of its admission to the chamber are preferably below the pulling capacity of the jet or the like so that substantial vacuum within the chamber is obtained and maintained. In fact, in many if not most instances, the most complete removal of reaction fluid from the contact mass and the chamber is realized when the flow of gas into the chamber is so limited as to have very little if any effect on the absolute pressure within the latter, as for example, to restrict the pressure increase caused by such gas to less than 6 or 8 inches of mercury, and preferably to below 4 inches of mercury. Moreover, the effect of small and even practically negligible quantities of purging gas on the completeness of removal of reaction fluid from the mass and its container becomes more pronounced with decreasing absolute pressures and especially at pressures below 15 inches of mercury. The effect on the absolute pressure of the added gas may be reduced to substantial extent or even practically eliminated by use of a condensible purging gas such as steam, and condensation of that portion of it which is drawn from the chamber with the purged gases in a barometric or other suitable condenser disposed between the evacuator and the container for the contact mass, for example, after the manner disclosed in the aforesaid Patent 2,095,265.

The startling and pronounced effect of adding only small quantities of selected purging gas to the contact mass undergoing evacuation will be appreciated from the fact that the addition to a highly adsorptive contact mass saturated with reaction fluid of less than six volumes of suitable purging gas (measured at standard conditions) for each volume of contact mass usually reduces by 50% and often by 90% or more the quantity of residual reaction fluid remaining on or within the mass over that remaining if no gas is admitted. This volume of purging medium is

equivalent, in many cases, to less than the volume of reaction fluid released as gas from the chamber during the entire purging step. In many instances, less than half or a third of this quantity of purging gas reduces the amount of residual reaction fluid by as much as 95%. In removing some types of reaction fluid, for example, heavy and high boiling hydrocarbons from adsorptive materials, the combined use of vacuum and a purging gas often ejects from the mass strongly held deposits which, heretofore, could not be removed by a practical purging process. As a result of the quantity of deposit to be removed by burning is reduced reflecting in a tendency to shorten the burning or regeneration period itself.

In the interests of effecting efficient and complete purging in a minimum of time, the vacuum is preferably applied simultaneously to a multiplicity of points within the contact mass as described in the aforesaid U. S. Patent 2,095,265, as for example, through use of a plurality of perforated conduits embedded in the mass, as indicated in converter 1 of the drawing. By preference, and to further accelerate the purging step, as also indicated in converter 1, the gaseous purging medium is admitted to the mass at a separate multiplicity of points thereby to provide uniform movement of fluid through substantially all portions of the mass.

The pronounced advantages of the novel purging operation are indicated by the following typical use. In effecting catalytic transformation of a long residuum from a Mid-Continent crude oil three runs were made in each of which substantially all portions of the entire crude boiling above the motor fuel range, except approximately 6% of tar which was practically incapable of vaporization, was fed in vapor phase, at a rate of about one volume of liquid charge per hour for each volume of contact mass to and through a highly adsorptive blend of silica and alumina maintained at about 850° F. for operating periods of about 10 minutes. These runs were made under conditions as nearly identical as could be obtained. After each run was terminated the contact mass was subjected to a three minute purging operation, that conducted after the first run being admission of steam to the converter at a rate of about two volumes per minute (standard conditions) for each volume of mass. Following the second run vacuum was applied for three minutes, reducing the absolute pressure within the converter to about 3 inches of mercury. For the third purging step, vacuum was applied to the mass while simultaneously admitting steam to the converter at a rate of about $\frac{2}{3}$ volume per minute (standard conditions) for each volume of mass. In this three minute period an absolute pressure of about 7 inches of mercury was reached. A representative sample of this contact mass was analyzed for content of burnable deposit following each of the purging operations, and the remainder of the mass was subjected to regeneration by controlled combustion. The regeneration fumes were cooled to condense any oil vapor carried over with them and the resulting condensate separated from the flue gases and measured. The analyses of the contact mass showed coky deposits to the amount of about the order of 6 grams for each liter of mass following the steam purging and vacuum purging steps, respectively. The coky deposit remaining after the use of steam and vacuum simultaneously was, however, about 4.8 grams per liter, a reduction of

at least 20%. The condensate separated from the regeneration fumes amounted to somewhat more than one gram per liter of contact mass following steam purging, about 0.9 gram per liter of mass following the vacuum purging operation, but was of the order of 0.05 gram per liter when obtained after the purging operation using both steam and vacuum, representing a reduction of about 95% of the quantity of reaction fluid left adsorbed in the mass over each of the other two purging steps. In fact, the contact mass and the converter were so free of hydrocarbon components following the third purging step that it was not necessary to utilize an inert repressuring medium to raise the pressure within the converter toward the level desired for the next step in the process, regeneration. Air was safely used for this purpose without danger of uncontrolled burning or explosion. Likewise, following a similarly conducted purging step after the regeneration period, highly flammable hydrocarbon gas or vapor, for example, vaporized fresh charge for the on-stream period, or vapors or fixed gas resulting from this transforming operation were safely utilized for this purpose.

According to certain aspects of the invention, regeneration fumes issuing from one or more converters in the battery are utilized as a supply or source of suitable, and especially inert, gas valuable for use as conditioning fluid to effect or assist in purging and/or repressuring of converters, for addition to on-stream reactants, and for other purposes where gaseous fluid having controlled composition and properties is necessary or desirable for plant operation. Regeneration fumes, however, are not constant in composition for the entire course of a regeneration period. In most instances, a substantial and often the major portion of those produced in a regeneration period contain such high concentrations of free oxygen that they are unfit for admission into converters or other reaction equipment which contains or is about to contain burnable fluid. Consequently, the invention involves segregation from regeneration fumes of a quantity having controlled composition, preferably containing less than 6% by volume of free oxygen. In many, if not most, regeneration procedures, the fumes change progressively in nature during the course of a single regeneration period, from a fluid free or substantially so of oxygen but containing substantial quantities of burnable components, to a combustion supporting medium containing as high as 15% by volume of oxygen. In such instances, it is fumes formed early in the regeneration period that are segregated from the balance and utilized as process fluid.

In some instances and for some purposes, as for example, when the conditioning fluid is to be added to burnable reactants which are within or are entering the reaction equipment the selected portion of the products of the regenerating reaction may be conducted directly to the desired point or points of use as conditioning fluid. For example, in the specific embodiment of the invention disclosed in the drawing, the desired quantity of oxygen free fumes entering manifolds 17, 17a and 17b may be conducted by lines 18, 18a and/or 18b by manifold 43 and by line 44 to feed line 10 for addition to fresh feed therein. Excess regeneration fumes including those containing undesirably high quantities of oxygen may, if desired, be vented from the system, as through valved lines 20. By preference, however, the quantity of fumes made early in the regen-

eration and desired for ultimate use as conditioning fluid is subjected to purification, usually controlled combustion, capable of reducing the amount or concentration of active fluid such as burnable components and/or free oxygen present in the fumes to yield a fluid consisting essentially of inert gases, for example, of carbon dioxide and nitrogen, as when air is utilized as regenerating medium.

The controlled combustion is effected to best advantage with the aid of a combustion promoter. To this end, the desired portion of regeneration fumes leaving the battery of converters may be conducted through a suitable manifolding and conduit system to a catalytic combustion zone comprising one or any desired number of converters, as for example and as indicated in the drawing, by manifolds 17, 17a and 17b, lines 18, 18a and 18b to converters 19, 19a and 19b containing any known or desired combustion promoter. Suitable combustion promoters include metals and metal oxides selected, for example, from the group copper, nickel, chromium, iron. The promoter may or may not be supported by active or inert material such as silica or alumina or naturally occurring or artificially prepared blends or compounds of these materials. When this aspect of the invention is followed, excess fumes may be vented from the system at any desired point before the combustion zone, as by use of valved lines 20. Then, any desired quantity of the inert fluid discharged from any or all the converters 19, 19a and 19b into lines 21, 21a and 21b may be conducted through manifold 22, valved connection 23 and into line 24 to be led to the desired point of its use. Since, however, the regeneration fumes provide an abundant source of heat or other energy, flue gases produced during the entire regeneration period may be and preferably are continuously conducted through converters 19, 19a and 19b and the bulk of the fluid issuing from these converters used to supply such energy, as indicated for example in the copending application of Eugene J. Houdry and Richard S. Vose, Serial No. 58,858, filed January 13, 1936 which issued August 1, 1939 as U. S. Patent 2,167,655. In such a case, valved line 23 will be closed off and the fluid in manifold 22 conducted under pressure through valved line 25 to the desired energy recovery equipment, for example, to operate turbine 26 driving blower or compressor 27 to force regenerating medium through line 28 and into manifold 16. Then, purified fumes in lines 21, 21a, and 21b desired for use to assist the cyclic operation will be admitted to manifold 29 and line 24 in response to change in the concentration of free oxygen in the fumes traversing lines 21, 21a and 21b and during periods when this concentration is below a predetermined amount, as for example not in excess of 5% by volume.

As stated above one valuable use for inert fluid is conditioning interiors of converters in the battery especially to assist process steps effected between combustion or regeneration periods. To this end, desired amounts of the inert fluid entering line 24 under suitable pressure may be conducted to line 36 to be admitted to reactants in line 10 and/or to manifold 37, as desired or required in the latter, for purging and/or repressuring purposes. When the purified inert fumes are drawn into line 24 under pressure suitable for the desired use and at rates and times correlated with the rates and times at which such fluid is needed or desired in the oper-

ation of the converter battery, they may be conducted directly from line 24 to the desired point of their admission into the conversion system as process fluid, as by use of valved conduits 30 and 31. When these rates and times do not coincide, use may be made of a surge tank or storage vessel such as 32 located in line 24 and necessary or desired pressure adjustment of the conditioning fluid may be made in compressor 33 which may or may not be followed by a storage vessel such as tank 34. Either storage vessel 32 or compressor 33 may be by-passed by use of valved line 35. Storage and/or compressing means similar to those shown in line 24 may, if desired, be disposed in line 44.

The time intervals during which the fumes resulting from regeneration contain 6% or less of unused oxygen depend upon the nature and amount of the deposit on the contact mass and to some extent upon the rate at which the selected regeneration procedure removes that deposit. In commercially practicable reactivation processes following treatment or conversion of hydrocarbons, for example, the free oxygen content of the combustion products usually remains below 6% for from a third to a half of the regeneration period and, in most instances, remains below 5% and often below 2% or 3% for the entire or substantially the entire first third of the reactivation. The fumes resulting from the early portion of the regeneration step are often sufficient in quantity to supply all inert process fluid desired in conducting the cyclic operations. For effecting or assisting in purging steps, half and often a quarter of the fumes made during this third are more than ample; in fact, in many commercial operations involving vacuum purging, below 10%, and even 5% or less, of this portion of the regeneration fumes are all that need to be purified and conducted to the battery of converters for admission thereto during and/or after application of vacuum for purging and repressuring purposes. When the oxygen free regeneration fumes, with or without being subjected to catalytic combustion, are to be added to on-stream reactants to assist in vaporizing the same or to insure their maintenance in vapor phase condition, as for example by addition to fresh feed in line 10, as indicated in the drawing or to the reactants during their passage through heating and/or separating zones, as indicated in the copending applications of Albert G. Peterkin, Serial No. 65,013, filed February 21, 1936 which issued July 18, 1939 as U. S. Patent 2,166,176, and Serial No. 65,955, filed February 27, 1936 which issued July 18, 1939 as U. S. Patent 2,166,177, and in the copending application of Eugene J. Houdry, Serial No. 51,770, filed November 27, 1935, replaced by substitute application, Serial No. 287,972 filed August 2, 1939, which issued September 9, 1941, as Patent No. 2,255,060, quite large proportions as up to 75% of the oxygen free or 25% of the total quantity of regeneration fumes may be necessary, depending upon the volume, boiling range characteristics, and other properties of the reactant material. When such large quantities of the regeneration fumes are used as process fluid in producing the preferred aspect of the invention, it is sometimes desirable to supplement the output of energy recovery equipment such as turbine 26 with power obtained from another suitable source. The actual control of the times and/or rates of admission of the desired conditioning fluid into manifold 29 and/or into manifold 43 may be

effected in direct response to analysis for oxygen of a continuous sample of the fumes passing through lines 21, 21a and 21b, or, with a little experience in conducting the regeneration, simply by manipulation of valves 42, 42a and 42b at predetermined times.

One of the specific operations to which the invention finds valuable application is the use of an active contact mass comprising, for example, a selectively adsorptive blend of silica and alumina containing these two components in the weight ratio of at least 3½:1, such as described in the United States Patents 2,078,945 and 2,078,951, issued May 4, 1937, to Eugene J. Houdry, alternately on stream in the transformation of higher boiling hydrocarbons into high anti-knock motor fuel, effected for example, in the temperature range of 750° to 1000° F. and in regeneration in situ by combustion effected under such controlled conditions that the temperature of the mass does not exceed a predetermined maximum, say 1100° F. For such an operation, a suitable high boiling charge, for example, a long gas oil cut or viscosity broken bottoms from Mid-Continent crude may be vaporized with the aid of a small amount of vaporizing fluid and fed to the contact mass at a rate of about 4 volumes of liquid charge per hour to each 5 volumes of contact mass for an operating period while maintaining the mass at a temperature of the order of 825° to 880° F. and the reaction zone at a pressure of the order of 15 pounds per square inch gauge. In the succeeding regenerating periods a suitable oxygen bearing regenerating medium, for example air, may be passed through the contact mass under a pressure of 50 to 60 pounds per square inch gauge at a rate of about 680 volumes of air, measured at standard conditions, to each volume of contact mass per hour. The exothermic heat of the regeneration reactions may be removed at controlled rate in any known or desired manner, as for example by heat exchange members (not shown) embedded in the contact mass as indicated in United States Patents #2,078,947, issued May 4, 1937 to Eugene J. Houdry et al., #2,078,948, issued May 4, 1937 to Eugene J. Houdry and #2,078,949, issued the same date to Eugene J. Houdry and the copending application of Eugene J. Houdry and Thomas B. Prickett, Serial No. 261,728, filed March 14, 1939, so as to maintain the temperature of the mass within a predetermined range, preferably below a maximum of 1050° or of 1000° F. This process may conveniently be effected in a 45 minute cycle in a plant wherein the contact mass is disposed in nine converters as shown in the drawing. In this cycle, periods of about 15 minutes each for feeding the hydrocarbon charge and regenerating medium, respectively, may be utilized. The remaining 15 minutes may then be divided into about 7 minute and 4 minute vacuum purging periods following on-stream and reactivation reactions, respectively, and four intervals of about 1 minute each for effecting the necessary valve changes at the end of each step in the cycle. One method of operating a plant is to start individual members of the battery of converters in the cycle successively and at 5 minute intervals, thus to provide three converters on stream, three in regeneration and three in various stages of the purging operation at any given time. In this or similar operations the catalytic combustion equipment is preferably so arranged and connected to the converters that fumes produced

early in the regeneration conducted within one converter do not mingle with fumes containing relatively high concentrations of oxygen and made during later portions of the regeneration in another converter. This may be realized by providing three combustion converters, such as indicated at 19, 19a and 19b, respectively, manifolded to successive groups of three of the converters 1 to 9, as indicated, and starting converters 1, 4, 7, 2, 5, 8, 3, 6 and 9 on stream in the sequence named. Thus, each combustion zone will at all times be receiving the fumes from only one converter in the battery. For example, following the regenerating period in converter 1, the stream of regenerating medium is transferred from it to converter 2 to start regeneration in the latter; then, at the end of regeneration in converter 2, the regenerating medium is transferred from it to converter 3 to be again returned to converter 1 at the end of this third regenerating period. Thus, manifold 17 and converter 19 receive a continuous stream of regeneration fumes under superatmospheric pressure coming successively from converters 1, 2 and 3. Similarly, manifolds 17a, 17b and converters 19a and 19b each receive continuous flow of combustion gases coming successively from converters in the groups 4, 5 and 6, and 7, 8 and 9, respectively. When this preferred arrangement is employed, the combustion step is advantageously one involving the use of a contact mass capable of supplying the oxygen necessary to burn the hydrocarbon fluid, for example, one comprising or containing copper oxide maintained at a temperature of 800° F. or higher, as disclosed, for example, in the copending application of Eugene J. Houdry, Serial No. 78,542, filed May 8, 1936 and replaced by substitute application, Serial No. 266,010, filed April 14, 1939 which issued July 15, 1941 as Patent No. 2,248,994. As indicated in the last mentioned applications, it is not ordinarily necessary to employ a separate regenerating step to return to oxide form metals which have supplied oxygen to the combustion processes effected in converters 19, 19a and 19b. Oxidation of the combustion promoters takes place automatically when the regeneration fumes entering these converters contain excess or unused oxygen, as is usually the case during the latter portions of a regeneration period. At suitable intervals, usually infrequent, a reducing medium containing hydrogen, for example, may be admitted to the combustion catalyst to restore to active metallic or oxide form portions of it which have been converted into inactive sulphates by sulphurous components of the regeneration fumes.

The fumes made in each converter for about the first 5 minutes of each regeneration therein, following catalytic combustion, are substantially free of oxygen, at no time containing more than 4% by volume of this material, and are valuable for use as conditioning fluid. Upon further analysis of the above described specific operation, it is evident that, since every 5 minutes one of the converters in the battery starts in regeneration, there is a continuous flow from the battery of desired fluid having a low oxygen content and under pressure suitable for use in desired portions of the operation cycle. Thus, this fluid may be conducted directly and without intervening storage to the desired point or points of its use as process fluid in the conversion system. In operating, for example, according to the preferred aspect of the invention wherein burned

regeneration fumes issuing from catalytic combustion zones 19, 19a and 19b are continuously utilized to supply motive or other energy, as by running a turbine such as 26, the desired quantity of gases consisting of substantially pure carbon dioxide and nitrogen may be continuously withdrawn from lines 21, 21a and 21b into manifold 29 and thus conducted directly through lines 24, 30 and 31 to lines 37 and/or 36 by opening the valves 42, 42a and 42b for successive 5 minute intervals. Thus, valve 42 will be open during the first 5 minutes of regeneration in converter 1, valve 42a open for the next 5 minutes during the early stages of regeneration in converter 4, etc.

In the particular and specific operation described 10% of the fluid leaving converters 19, 19a and 19b and so conducted to line 37 is more than adequate for admission into converters during and following application of vacuum thereto to assist in the purging operation and to raise the pressure in the reaction zones to substantially the desired operating level. For example, when utilizing a preferred type of converter, namely, one containing substantial quantities of so-called free space and having a plurality of conduits embedded in the contact mass for admission of reactant fluid thereto at a multiplicity of points and simultaneous withdrawal of reaction products therefrom at a separate multiplicity of points as in converters of the general type and design disclosed in United States Patent #2,042,468 issued June 2, 1936, to Eugene J. Houdry, the aforesaid Patent #2,078,947, and in the aforesaid copending application of Eugene J. Houdry and Thomas B. Prickett, Serial No. 261,728, filed March 14, 1939, about 7.5% of the quantity of regeneration fumes produced during the first 5 minutes of regeneration in converter 1 or about 2.5% of the total flow from the battery are usually sufficient to raise the pressure in converters 3 and 4 from 3 to 5 inches of mercury (absolute pressure) to their respective operating levels for on stream and regeneration steps in repressuring steps occurring in this 5 minute interval. A further quantity of fumes having the desired composition representing about 5% of the flow from the battery is sufficient for admission to the converters during each evacuation to assist and accelerate the purging process. The remaining 92.5% of the total fumes produced in the battery contain sufficient energy recoverable in a turbine such as 26 to compress substantially all the regenerating medium supplied to the converter battery.

In the practice of its various aspects, the invention finds application in many processes of industrial significance. Although being of particular value in connection with cyclic operations wherein a contact mass is used alternately on stream to promote reactions and in regeneration to remove contaminating deposits, purging effected with simultaneous use of vacuum and a selected purging gas is valuable also to provide for complete and rapid removal of desired recoverable product from contact masses utilized to remove, by selective adsorption, one or more components from gaseous mixtures containing the same. By selecting a purging medium having a boiling point different from the boiling point or range of the ejected adsorbed material any small quantity of purging gas that may be discharged from the chamber under evacuation may, if desirable or necessary, be separated from the desired material by simple condensation or

by fractionation. Regeneration fumes obtained normally from cyclic operations provide a prolific source of process fluid having predetermined and desired properties suitable and valuable for use in effecting this novel and efficient purging step and for other uses as process fluid.

This fluid being free or substantially free of oxygen is incapable of providing dangerous or explosive mixtures when admitted to converters or other portions of a plant containing organic reaction fluid. When the conditioning fluid results from controlled combustion it consists substantially of inert material such as carbon dioxide and nitrogen and is particularly valuable for admission to any desired point in a conversion system for any desired portion of a cyclic process conducted therein. Whether or not this fluid has been subjected to controlled combustion to destroy its content of burnable components it chemically resembles regeneration fumes formed as an integral part of the operation cycle, and, for this reason, it cannot, through poisoning or other action, shorten the commercially useful life of the catalytic or other contact mass. Moreover, it is made available from what is normally excess or waste material in a simple operation which is coordinated with the cyclic process and which in no way interferes with even very complicated cyclic operations.

Some typical cyclic operations, other than the transformation of higher boiling hydrocarbons into lower boiling motor fuel described above, to which the various aspects of the invention find application, are, refining of distillate and residual hydrocarbons within the boiling ranges of motor fuels and lubricating oils with the aid of adsorptive masses, catalytic dehydrogenation and/or aromatization of, saturated hydrocarbons, catalytic polymerization of unsaturated hydrocarbons to yield higher boiling products, catalytic hydrogenation of polymers or of other distillate or residual hydrocarbons, refining of gases involving use of contact masses capable of removing sulphurous or other undesirable components, contact viscosity breaking or vaporization of heavy bottoms to yield marketable fuel oils or cracking stocks, and catalytic oxidations and condensations of hydrocarbons and their derivatives.

I claim as my invention:

1. In effecting chemical reactions involving the use of solid contact material disposed in a reaction zone alternately on stream to assist reactions which form contaminating deposits thereon and in regeneration to remove said deposits, the steps of segregating from the products of regeneration after their withdrawal from said reaction zone a portion containing less than 6% free oxygen capable of use as inert process fluid with reactant charge and as purging medium before and after on stream periods of operation, and utilizing said segregated material for at least one of said purposes.

2. In effecting chemical reactions involving the use of solid contact mass disposed in a reaction zone alternately on stream to assist reactions which form contaminating deposits thereon and in regeneration to remove said deposit by means of an oxidizing regenerating medium, the process of obtaining from products of regeneration valuable and substantially inert process fluid of controlled composition for admission to the contact mass to assist in controlling the physical and chemical properties of the fluid content of said zone, comprising the steps of puri-

ifying of active components regeneration products withdrawn from said reaction zone during a portion of a regeneration period when the oxygen content of said products is low, and of said withdrawn products admitting to the mass only resulting purified product.

3. In effecting chemical reactions involving the use of solid contact mass alternately on stream to assist reactions which form burnable deposits thereon and in regeneration by controlled combustion to remove such deposit, the process comprising the steps of subjecting to catalytic combustion products of said regeneration containing burnable fluid and no more than 6% of free oxygen to yield a substantially inert fluid, and admitting inert fluid so produced and segregated from regeneration products of higher concentration of oxygen to a reaction zone containing said mass.

4. In controlling cyclic operations wherein a contact mass is used alternately in the treatment of hydrocarbons which form contaminating deposit thereon and in regeneration in place to remove said deposit by controlled combustion, the process steps comprising purging said mass of reaction fluid between on stream and regeneration steps, subjecting to controlled combustion five gases issuing from said mass during a regeneration period and having low content of components capable of entering into combustion to yield a fluid substantially free of such components, and utilizing said last-named fluid segregated from the portions of said five gases having comparatively high content of the aforesaid components to assist in said purging operation.

5. In controlling cyclic operations wherein a contact mass is used alternately on stream to assist reactions which form burnable deposit thereon and in regeneration by burning to remove said deposit, the process steps comprising subjecting said mass to vacuum between on stream and regeneration periods to remove adherent reaction fluid therefrom, segregating from combustion products of regeneration a quantity of fluid produced early in a regeneration period containing less than 6% free oxygen, and admitting said fluid into contact with said mass while the latter is under vacuum.

6. In preparing for reuse a contact mass which has become contaminated with burnable deposit as a result of its use on stream in assisting chemical reactions, the process steps comprising admitting an oxygen bearing regenerating medium to said mass for a regenerating period while maintaining the temperature of the latter below a predetermined maximum to remove said deposit by controlled combustion, purging said mass of absorbed and adsorbed reaction fluid in an interval between on stream and regeneration periods with the aid of substantial subatmospheric pressure applied to said mass, obtaining from combustion products formed during a regeneration period a segregated quantity of five gases substantially free of components capable of reacting with the fluid being purged from said mass, and admitting a small quantity of five gases so obtained to said mass while simultaneously maintaining substantial sub-atmospheric pressure to cooperate with the low pressure in removing reaction fluid from the mass.

7. In controlling operations wherein a contact mass is used alternately on stream to assist reactions which form contaminating deposit thereon and in regeneration to remove said de-

posit, the process of removing fluid reactants and reaction products from the mass and the vessel containing the same in at least one interval between on stream and regeneration periods with the aid of vacuum applied to said vessel, simultaneously and while maintaining absolute pressure in said vessel not in excess of about 15 inches of mercury admitting to the same a quantity of gaseous purging fluid substantially less than enough to effect by itself efficient purging of said mass to cooperate with the vacuum and accelerate removal of said reaction fluid, and subsequently admitting reactants for the next operating period into contact with said mass.

8. In controlling operations wherein a contact mass is used alternately on stream to assist reactions which form contaminating deposit thereon and in regeneration to remove said deposit, the process of purging reaction fluid from said mass comprising the steps of applying vacuum to a multiplicity of points within the vessel containing said mass to remove reactants and reaction products therefrom during at least one interval between on stream and reaction periods, simultaneously with application of said vacuum admitting an amount of an inert gaseous purging agent insufficient in itself to effect said purging to at least one other point in said vessel to increase the rate and completeness of removal of said reactants and reaction products from the same, and restricting the rate of admission of said purging agent to said vessel to such a low value that subatmospheric pressure below 15 inches of mercury is obtained within said vessel during application of said vacuum.

9. In controlling operations wherein an adsorptive contact mass is used alternately on stream to assist reactions which form burnable contaminating deposits thereon and in regeneration by combustion to remove said deposit and involving purging of fluid reactants and reaction products from said mass between on stream and regeneration periods, the process of effecting such purging comprising the steps of applying vacuum to at least one point in said mass during at least one interval between on stream and regeneration periods, simultaneously with application of vacuum admitting a gaseous purging medium to at least one other point in said mass, and limiting the volume of gaseous fluid so admitted to no more than the volume of adsorbed fluid removed from the mass during the purging period.

10. In purging an adsorptive contact mass of reaction fluid adsorbed therein, the process of pulling substantial vacuum on the mass and simultaneously and while maintaining the mass at substantial sub-atmospheric pressure, flowing a small amount of a purging fluid through said mass insufficient to affect substantially the temperature of the latter, thereby to accelerate removal of reaction fluid from the same and to increase completeness of said removal.

11. In purging an adsorptive contact mass of reaction fluid adsorbed therein, the process of pulling substantial vacuum on the mass through a multiplicity of points distributed within and throughout the same, and simultaneously admitting to said mass at a multiplicity of points a quantity of purging gas restricted to less than 6 volumes of such gas for each volume of said mass, thereby to provide substantially uniform and positive flow of fluid across and out of said mass.

12. In preparing a contact mass for further use in a cyclic process involving alternating op-

erating periods, the process of purging the mass of absorbed and adsorbed fluid in the interval between alternating periods by subjecting it to evacuation while admitting thereto a restricted quantity of gaseous purging medium, stopping the evacuation and continuing flow of said gaseous medium to the purged mass to raise its pressure toward reaction level.

13. In controlling cyclic operations wherein a contact mass is used alternately on stream to assist reactions which form burnable deposit thereon and in regeneration by burning to remove said deposit, the process steps comprising subjecting said mass to vacuum between on stream and regeneration periods to remove adherent reaction fluid therefrom, segregating from combustion products of regeneration a quantity of fluid produced early in a regeneration period and containing less than 6% free oxygen, admitting said fluid into contact with said mass while maintaining the latter under substantial vacuum and later discontinuing evacuation to terminate the purging step, but continuing flow of said fluid to raise the pressure of the mass toward the level of the next period of the operating cycle.

14. In effecting chemical reactions involving the use of solid contact material alternately on stream to assist reactions which form contaminating deposit thereon and in regeneration to remove said deposit by combustion, the process steps of purging said contact material of reaction fluid between alternating operations at reduced pressure, segregating from products of regeneration which have issued from contact material early in a regeneration period a portion of such products having controlled and low oxidizing potential and consisting essentially of inert components, and admitting products so segregated to the purged contact material to raise the pressure toward that of the next operating period.

15. In the treatment of organic reaction fluid with the aid of solid contact material which accumulates burnable deposit as a result of said treatment and is periodically regenerated by combustion, the process comprising segregating from the combustion products formed early in a regeneration period a quantity of flue gas containing not in excess of about 3% by volume of free oxygen, and feeding said segregated flue gas together with on stream reaction fluid to said contact material.

16. In the operation of a battery of converters containing contact mass used alternately but at spaced intervals to assist vapor phase changes in organic fluids which leave burnable contaminating deposit thereon and therein and in regeneration in place by controlled combustion of said deposit, members of said battery being successively in regeneration so that there is substantially continuous flow of regenerating medium to and regeneration fumes from the battery, the process comprising effecting catalytic combustion of regeneration fumes issuing from said battery to destroy burnable components and increase the energy content of said fumes, utilizing burned fumes to supply industrial energy, separating a small portion of the burned fumes from the stream of the same issuing from said battery, effecting said separation in response to concentration of oxygen in said fumes and while the burned fumes contain less than 5% oxygen, and admitting fumes so separated to a converter as a process fluid for said operation cycle.

17. In the operation of a battery of converters containing contact mass used alternately on stream to assist hydrocarbon reactions and in regeneration in place by controlled combustion of deposit formed on or in said mass as a result of said reactions, regenerating medium being flowed through at least one converter in the battery for a regenerating period and at the end of that period being transferred to another converter for a successive regeneration period in the latter to provide continuous flow of regenerating medium through the battery, the process comprising sending a continuous stream of regeneration fumes issuing from the battery through a single combustion zone containing a combustion catalyst maintained at combustion conditions, segregating from the stream of burned fumes issuing from said combustion zone a portion of those of low oxygen content formed during the first third of at least one of the successive regeneration periods, and returning fumes so segregated to said battery of converters and into contact with contact mass contained therein to serve as a process fluid in conducting the cyclic operation.

18. In apparatus for effecting changes in organic fluids, in combination, a converter providing a reaction chamber for containing a contact mass, valved conduits connected to said converter for selectively admitting organic fluid and regenerating medium thereto, valved outlet conduits for selectively receiving and conducting organic reaction products and regeneration fumes from said converter, means providing a catalytic combustion chamber connected with the outlet conduit for regeneration fumes for burning burnable components of said fumes, and means including a valved conduit for conducting combustion products from said combustion chamber to said converter, for admission to the latter as desired or required therein.

19. In apparatus for treating hydrocarbons, in combination, a converter providing a reaction chamber for containing a contact mass, said converter being arranged and adapted for use alternately in the treatment of hydrocarbons and in regeneration in place and being selectively connected to sources of hydrocarbon reactants and oxygen bearing regenerating medium, a valved conduit for conducting hydrocarbon reaction products from said converter, a second converter providing a reaction zone containing a contact mass capable of promoting combustion of burnable components in a stream of fluid containing the same, a conduit interconnecting said converters for conducting regeneration fumes from the first named to the second named converter, means adapted and arranged to utilize energy content of said fumes, a conduit interconnecting said last named converter and said means for conducting burned fumes from the former to the latter, and valved conduit means interconnecting said first and last named converters for periodically conducting to the former burned and inert fumes issuing from the latter.

20. In apparatus for treating hydrocarbons, in combination, a plurality of converters, each providing a reaction chamber for containing a contact mass and arranged and adapted for use alternately on stream in the treatment of hydrocarbons and in regeneration of the mass in place, means for producing vacuum selectively connected to each of said converters, a vessel providing inlet and outlet connections and enclosing a reaction chamber for containing a com-

bustion catalyst, valved conduits selectively connecting said converters with said inlet connection for conducting regeneration fumes from the former to said vessel, and conduit means including a manifold and valved branches selectively connecting said outlet connection and each of said converters for periodically conducting regeneration fumes issuing from said vessel to each of said converters to serve as purging fluid therein.

21. In apparatus for the treatment of hydrocarbons, in combination, a battery of converters, each providing a reaction chamber for containing a contact mass and being arranged and adapted for use alternately on stream in the treatment of hydrocarbon charge and in regeneration of said mass in place, a reaction vessel

5 providing a combustion zone, valved conduit means selectively connecting said converters with said reaction vessel for conducting regeneration fumes to the latter, a compressor selectively connected to said converters for forcing regenerating medium into the latter, a turbine for driving said compressor, a conduit interconnecting said reaction vessel and said turbine for discharging burned regeneration fumes into the
10 latter, a manifold selectively connected to each of said converters for periodically supplying process fluid to each, and valved conduit means for conducting to said manifold selected portions
15 of the burned fumes issuing from said reaction vessel.

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