Oct. 12, 1937. J. H. PEW 2,095,265

USE OF CONTACT MASSES

Filed May 27, 1935 2 Sheets-Sheet 1

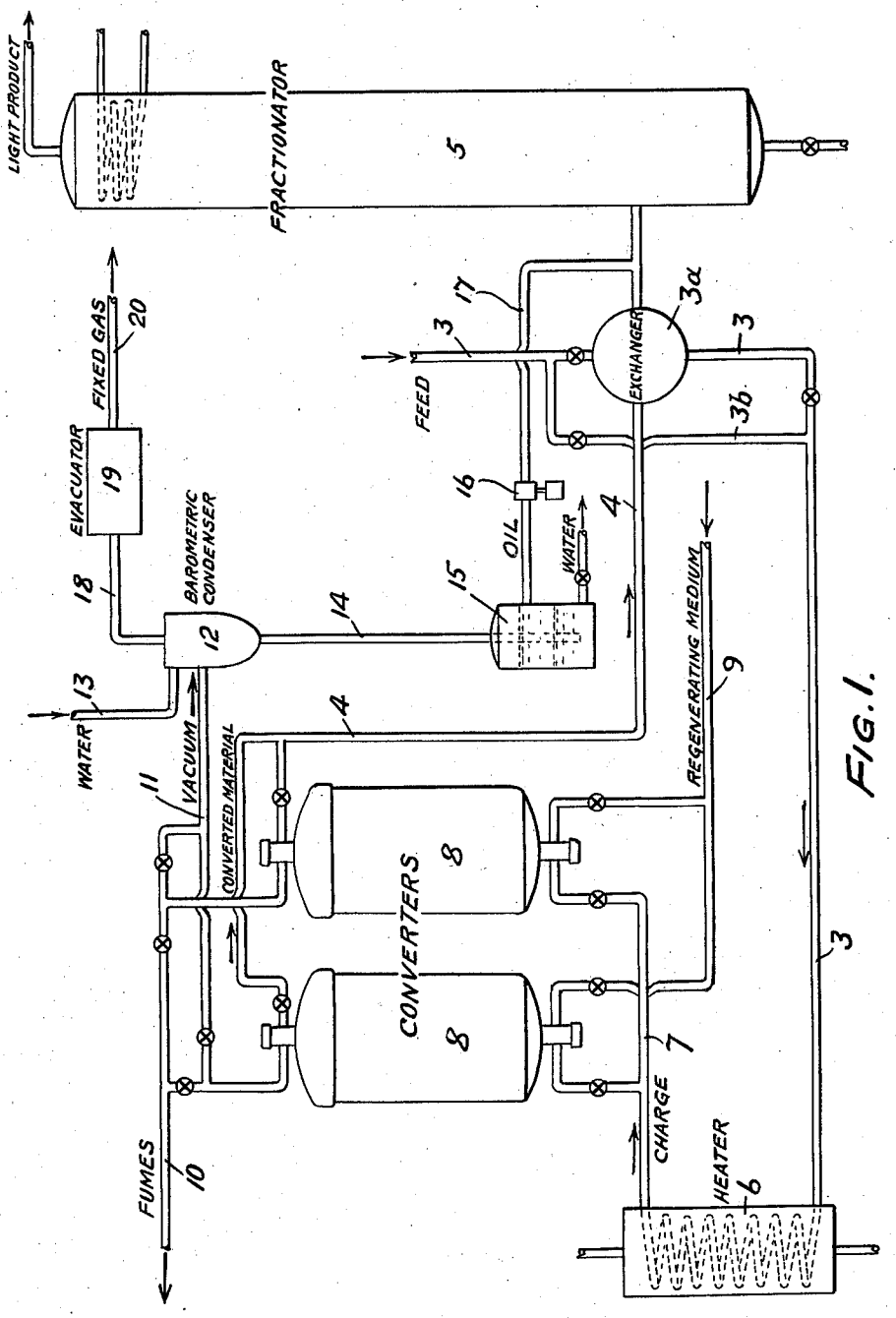


FIG. 1.

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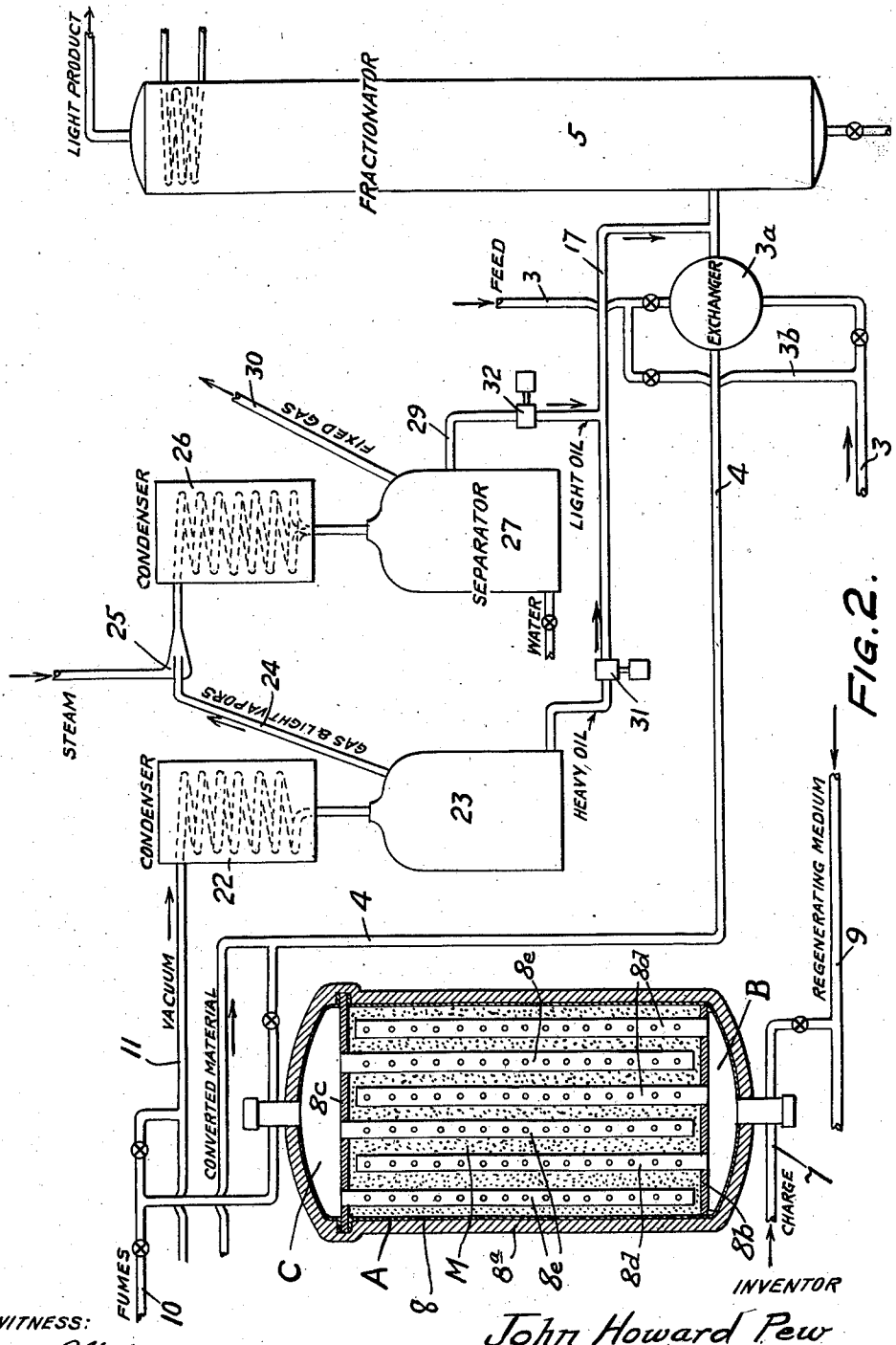


FIG. 2.

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UNITED STATES PATENT OFFICE

2,095,265

USE OF CONTACT MASSES

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Application May 27, 1935, Serial No. 23,533

9 Claims. (Cl. 196—52)

This invention relates to chemical reactions effected in the presence of or by the aid of contact masses. While possessing features of general application, it is of special importance for contact masses which progressively lose their catalytic or adsorptive power during a transforming operation and must be reactivated or regenerated.

The loss of activity or "poisoning" of the contact mass may be due to a chemical change in the mass, or to the tendency of the latter to retain adsorbed in its pores some of the products of the transforming operation, or to the gradual filling up of the pores by a deposit of contaminating material such as coke, alkali, sulphurous and tarry substances, etc., resulting from the transforming reaction. The present invention is applicable where the loss in activity of the mass is due to the above or other causes. For reactivation, the conventional operation consists in purging the mass of converted and unconverted material, followed, in the case of actual deposition of contaminants, by solvent extraction of the deposits or by burning the same or by both solvents and combustion in sequence and in either order. A second purging operation may follow the removal of deposits.

Heretofore for the purging of large converters containing very substantial amounts of solid contact material, it was deemed essential to use a gaseous purging agent such as steam, for example, since only in this way was it considered possible to insure penetration of the minute pores of the contact mass for the ejection of all charged material therefrom and to avoid pockets tending to retain material which might produce an explosion or other dangerous condition at the beginning of regeneration by combustion or at the start of a subsequent transforming run. There are certain disadvantages to the use of an ejecting agent. In the first place, the operation is expensive due to the quantity of purging agent required to sweep out a large converter. In the second place, unless the temperature of the purging agent is regulated very closely, undesirable temperature changes or variations are often effected throughout the converter or in localized portions of the contact mass. In the third place, the ejecting agent is in most instances extraneous material and provision must be made for its production, storage, separation and removal from the system after it has served its purpose.

One object of the invention is to produce a rapid and thorough removal of material in either gaseous or liquid state from a chamber containing a contact mass without the use of a purging agent. Another object is to minimize or entirely to avoid temperature changes in the mass. Another object is to improve the speed and effectiveness of purging operations. Still another object is to make convenient and inexpensive disposal of the material recovered during the purging operation. Other objects will be apparent from the detailed description which follows.

The invention involves the application of a high vacuum simultaneously at a multiplicity of points within and throughout the depth and cross section of the contact mass so as to be effective at once and to the same extent in every part of the mass. Contrary to expectations it was found that this method of purging was much more efficient in the same or less time than the best previously used purging agent, such as steam, which in most instances is more strongly adsorbed by a catalytic mass than either the charge or the transformed product or both. Taking the best conditions for steam as a basis for comparison, my improved process of vacuum purging, when applied for the same length of time, recovers about 50% more material from the contact mass. This not only involves an important net gain, but there are other advantages: there is substantially no change in the temperature of the mass since no extraneous material is fed thereto; the operation is less expensive even when steam jets are used to produce the vacuum, for much less steam is needed than when the converter is purged with steam; there is no purging agent to be removed from the contact mass at the end of the vacuum purging operation. When the recovered material is wholly or partly in gaseous or vapor state, condensers may be arranged to assist in producing the vacuum. Either surface or barometric condensers may be used. The recovered material is sent back into the system preferably in advance of equipment for separating out the desired product or products. In its preferred form the system is arranged to operate continuously with a plurality of converters connected up in parallel with each converter designed to be alternately on stream and in regeneration.

Illustrative embodiments are shown in the accompanying drawings, in which:

Fig. 1 is a diagrammatic indication of one arrangement of apparatus for practising the invention; and

Fig. 2 is a similar view of part of the apparatus shown in Fig. 1 but disclosing one of the converters in section on an enlarged scale and indicat-

ing different apparatus for the vacuum purging operation.

In the drawings, the feed, which may be any material to be converted or otherwise treated, such as hydrocarbon gases, vapors or liquids, is sent into feed line 3 after heat exchange, if desired, with hot material from any source. The feed in line 3 may be sent through exchanger 3a for heat exchange with transfer line 4 leading to fractionator 5, or it may bypass exchanger 3a in whole or in part by means of bypass 3b. Feed line 3 passes the feed to a heater 6 of any suitable or desired type, such as a pipe still, which raises the feed to the temperature of conversion and sends the same into a charge line 7 having valved connections to a battery of catalytic converters 8.

Any desired number of converters may be provided in the battery, but only two are shown, these being sufficient to indicate that the system can operate continuously with the converters alternately on stream and in regeneration. If more than two converters are provided, they may be arranged singly or in parallel, as desired, for the transforming operation, and singly or in parallel for the regenerating operation. One method of handling such a battery of converters is disclosed in the copending application of James W. Harrison and Thomas B. Prickett, Serial No. 612,086, filed May 18, 1932 which issued on February 25, 1936 as Patent No. 2,031,600. As indicated in Fig. 2, each converter is provided with a series of perforated outlet conduits which are uniformly distributed throughout the contact mass for the withdrawal of converted material which is discharged from the converters through valved connections to transfer line 4. For the best operation, it is preferable to distribute the charge uniformly all through the mass, and such preferred arrangement is illustrated in the sectional view of one of the converters in Fig. 2. As illustrated, each converter 8 is entirely enclosed by a thick layer of heat insulating material 8a for the conservation of the desired temperature or temperatures, and the interior is divided, by flue sheets or partitions 8b and 8c adjacent the ends thereof, into end manifolding chambers B and C and a central reaction chamber A which is filled with a catalytic or other contact mass M capable of effecting the desired transformation or treatment of the charge. For the conversion or modification of hydrocarbon gases, vapors and liquids, contact mass M may be activated hydrosilicate of alumina with or without other active materials such as finely divided metals or metallic oxides, the mass being made up of bits, fragments or molded pieces, such as disclosed in the copending application of Eugene J. Houdry, Serial No. 600,581, filed March 23, 1932. Perforated distributing conduits 8d, symmetrically disposed within the contact mass M, extend through flue sheet 8b to establish communication between manifolding chamber B and reaction chamber A. Similarly, a second series of perforated outlet conduits 8e is provided, the conduits being embedded in contact mass M in uniform and symmetrical arrangement relative to each other and to conduits 8d and extending through the opposite flue sheet 8c to establish communication between reaction chamber A and manifolding chamber C after the manner disclosed in the co-pending application of Eugene J. Houdry, Serial No. 611,362, filed May 14, 1932 which issued on June 2, 1936 as Patent No. 2,042,468.

For the regeneration of the contact mass after its activity has been impaired by "poisoning", as by the deposit therein and thereon of contaminants resulting from the transforming operation, the regenerating medium, such as an oxidizing agent when the regeneration is to be by combustion, is sent from line 9 through valved connections to one end of each of converters 8, and the fumes are withdrawn from the opposite ends of the converters through suitable valved connections to line 10. Prior to regeneration, it is advisable or necessary to purge the converters of material left therein at the close of the transforming operation, both to avoid the danger of explosion when the regenerating medium is sent in, and also to avoid loss and destruction of the material still in the converters, which is partly converted and partly unconverted charge. In accordance with the present invention, this purging is effected by subjecting the converters to a high vacuum through suitable valved connections from each converter to vacuum line 11. By reason of the series of perforated outlet conduits 8e extending to all parts of the contact mass, the vacuum becomes available at once throughout the mass to substantially the same extent, producing a substantially complete removal of all of the charge remaining within the converters, whether converted or unconverted and whether absorbed or adsorbed within the pores of the catalystic mass M.

In Fig. 1, vacuum line 11 connects to a barometric condenser 12, water admitted by an inlet pipe 13 being utilized to condense the evacuated vapors which are washed down through barometric leg 14 into a well 15 where separation of oil and water is effected. The oil, substantially at atmospheric pressure, is removed from chamber 15 by suitable pumping means 16 and forced through line 17 into transfer line 4 in advance of fractionator 5 but beyond heat exchanger 3a. The uncondensable or fixed gases are removed from the top of condenser 12 through line 18 by an evacuator 19 of any known or desired type, the gases being discharged thence through line 20 to be used as fuel or for other purposes.

Another method of applying vacuum to purge the reaction chambers of the converters and of handling the recovered material is disclosed in Fig. 2, in which vacuum line 11 leads to a surface condenser 22 which is preferably operated at a temperature of 225° to 250° F., with the result that the heavier oils boiling above 250° F. are condensed and collected in vessel 23, while the vapors and gases are withdrawn from vessel 23 through line 24 by the action of suitable evacuating equipment as, for example, a single or multi-stage steam jet 25. The mixed gases and vapors pass thence into a second and final condenser 26 which discharges into a separator 27 having an outlet 28 at the bottom for water, an outlet 29 at a higher level for the light oils, and a discharge conduit 30 near the top of 27 for the fixed gases. The heavy oils from the bottom of vessel 23 and the light oils from connection 29 may be removed separately or together. By preference, they are both pumped into line 17 which returns this material, as in Fig. 1, to transfer line 4 in advance of fractionator 5 but beyond exhanger 3a. Two pumps will be required, inasmuch as one of them, namely, 31 in the heavy oil line from vessel 23, must withdraw the oils against the high vacuum produced by jet 25 and step the same up to whatever pressure exists in transfer line 4, while pump 32 in light oil line 29 is merely required to raise the pressure of the withdrawn material from sub-

stantially atmospheric in separator 27 to that of transfer line 4.

When the converted material withdrawn by vacuum line 11 during the purging operation is of a nature not to form undesirable and persistent mixtures, such as emulsions, with the cooling liquid used in the barometric condenser, this type of condensing equipment as illustrated in Fig. 1 may be utilized. This is the case, for example, when the converters are utilized for polymerization of hydrocarbon gases into liquid material in the gasoline boiling range, or for the reforming of heavy naphtha to improve its antiknock characteristics, or for the refining and stabilizing of motor fuels of the gasoline type, since such light oils do not readily emulsify with water. When the material withdrawn by vacuum line 11 comprises or contains heavier oils, as when converters 8 are used for the transformation of hydrocarbon distillates and residues of gas oil boiling range and higher, it is preferable to utilize separating equipment of the type disclosed in Fig. 2, since the heavier oils are first separated out from the recovered material, while any water which was originally in the feed or which has been added to the feed as steam for the purpose of assisting in the transformation, is still kept in vapor phase. In this way, only the vapors of the very light oils and steam (if present) are conducted, still in vapor phase, from vessel 23, and a steam jet may be utilized for evacuation, since the light oils may then be separated out from the water in separator 27 without the formation of undesirable emulsions.

The composite stream of converted, partly converted and perhaps some unconverted material in transfer line 4, with the addition by line 17 of material recovered by the purging operation, is shown in the drawings as sent directly into fractionator 5 for division of the same into fractions by overhead, bottom, and side streams as may be desired, which fractions may be finished products or intended for further treatment. It is to be understood, however, that any other type of separating or subsequent treating equipment may be provided, or that the composite stream may go directly to storage.

I claim as my invention:

1. In chemical reactions effected by or in the presence of a contact mass, the process of freeing the mass of liquid or gaseous material contained therein or retained thereby after a period of operation which comprises subjecting the mass to a vacuum and making the vacuum effective simultaneously and to substantially the same extent at a multiplicity of points distributed uniformly within and throughout the depth and cross section of the mass.

2. In chemical reactions effected by or in the presence of a contact mass, the process of recovering charged material from the mass at the end of a period of operation which comprises subjecting the mass to a high vacuum effective simultaneously and to substantially the same extent at a multiplicity of points throughout the interior of the mass and creating the vacuum partly by condensation of the material removed from the mass and partly by rapid removal of the uncondensed material.

3. In a process of treatment or conversion of a fluid material substantially in vapor phase by the action of a body of contact mass capable of periodically being regenerated by passing a regeneration fluid therethrough wherein the mass is alternately on-stream to effect the desired treatment or conversion and in regeneration to restore the mass to a state of increased activity, the step which comprises, intermediate the on-stream and regeneration steps, applying a vacuum to the said body of mass simultaneously at points throughout the same, so as to effect a rapid and substantially complete purging therefrom of fluids contained within the said body of mass, in the absence of inert purging fluid to any substantial extent.

4. In the continuous transformation or treatment of material by the action of a contact mass disposed in a plurality of zones, the operating process which comprises feeding the charge to said zones in sequence under reaction conditions to produce a continuous stream of transformed material, purging the contact mass in each zone at the end of the transforming period by subjecting the mass to a vacuum and making the vacuum effective simultaneously and to substantially the same extent at a multiplicity of points distributed uniformly within and throughout the depth and cross section of the mass, and adding the material recovered by the purging operation to the continuous stream of transformed material.

5. In the continuous transformation or treatment of material by the action of a contact mass disposed in a plurality of zones, the operating process which comprises feeding the charge to said zones in sequence under reaction conditions to produce a continuous stream of transformed material, purging the contact mass in each zone at the end of the transforming period by subjecting the mass to a vacuum and making the vacuum effective simultaneously and to substantially the same extent at a multiplicity of points distributed uniformly within and throughout the depth and cross section of the mass, adding the material recovered by the purging operation to the continuous stream of transformed material, and regenerating the contact mass in each zone after the purging operation in preparation for another transforming period by freeing the mass of contaminating deposits not removed by the purging operation.

6. In a process of treatment or conversion of a combustible or explosive fluid material substantially in vapor phase by the action of a body of contact mass capable of periodically being regenerated by passing a combustion-supporting fluid therethrough, wherein the mass is alternately in conversion and in regeneration, the step which comprises, intermediate the conversion and regeneration steps, applying a vacuum to the said body of mass at a plurality of points therewithin so as to effect a rapid and substantially complete purging therefrom of fluids contained within the said body of mass, in the absence of an inert purging fluid to any substantial extent.

7. In a process of treatment or conversion of a combustible hydrocarbon fluid material substantially in vapor phase by the action of a body of contact mass capable of periodically being regenerated by passing a combustion-supporting regeneration fluid therethrough, wherein the mass is alternately in treatment or conversion and in regeneration, the step which comprises, intermediate the conversion and regeneration steps, applying a vacuum to the said body of contact mass at a plurality of distributed points so as to effect a rapid and at least substantially complete purging therefrom of fluids contained within said body of mass, in the absence of an inert purging fluid to any substantial extent.

8. In a process of treatment or conversion of a combustible hydrocarbon fluid material by the action of a body of adsorptive contact mass capable of periodically being regenerated by passing a combustion-supporting regeneration fluid therethrough, wherein the mass is alternately in treatment or conversion and in regeneration, the steps which comprise, following the conversion or treating step, applying a high vacuum simultaneously to a plurality of points throughout said body of mass so as to effect a rapid and an at least substantially complete purging therefrom of hydrocarbon fluid contained therein, in the absence of inert purging fluid to any substantial extent, then regenerating said mass by passing a combustion-supporting regenerating fluid thereinto, and when combustible deposits are substantially eliminated, interrupting the passage of said combustion-supporting fluid and applying a high vacuum to said body of mass, in the absence of inert purging fluid to any substantial extent so as to effect an at least substantially complete purging therefrom of regenerating fluid contained therein, preliminary to another on-stream treating or conversion step, and repeating the above operations.

9. Apparatus for effecting chemical transformations comprising a battery of converters, each containing a contact mass capable of effecting the desired transformation and of regeneration, connections and controls for operating each of said converters alternately on stream and in regeneration and for selective control of the entire battery so that the apparatus may be operated continuously, a transfer line for the converted material to which certain of said connections and controls extend from all of said converters, means for effecting a rapid evacuation of liquid and gaseous contents of said converters including condensers connected in series and adapted to operate at different temperatures, one of said condensers being connected to at least one of said converters, means for separately collecting the condensate from said condensers, an evacuator intervening in circuit between said condensers for withdrawing the uncondensed material from one and discharging it into another of said condensers, and means for discharging said condensates into said transfer line.

JOHN HOWARD PEW.