

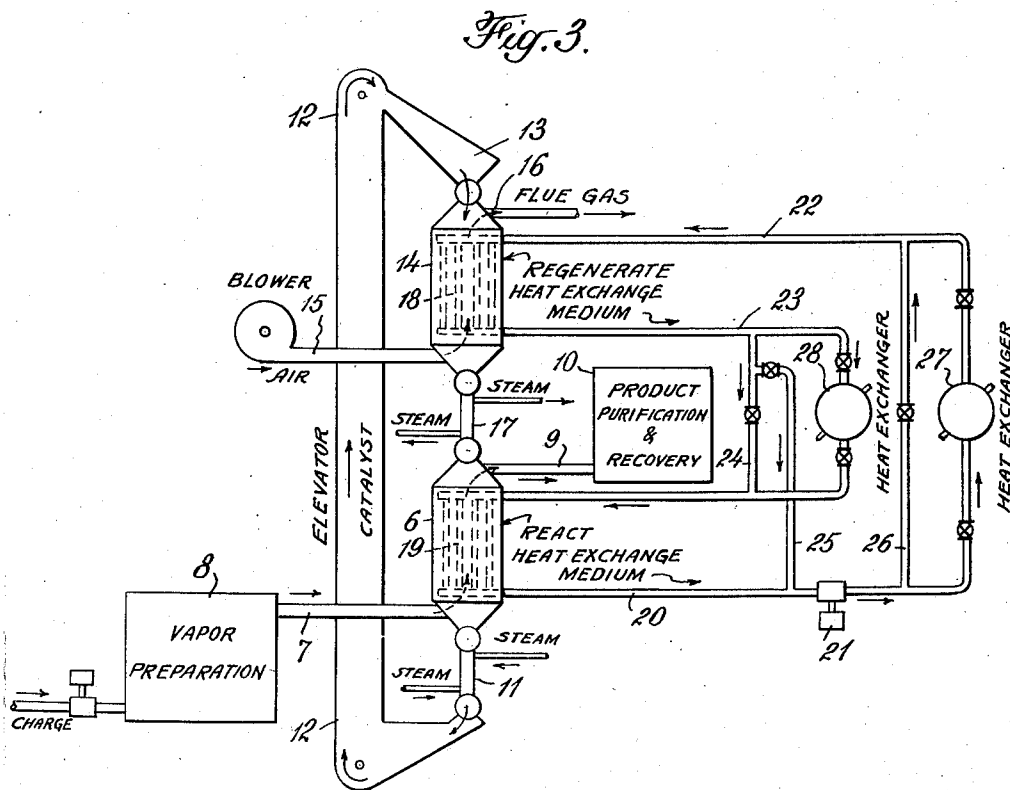
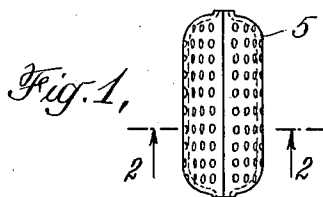
Aug. 14, 1945.

E. UTTERBACK

2,382,371

HYDROCARBON CONVERSION PROCESS

Filed May 3, 1941



Ernest Utterback  
INVENTOR

BY  
Myron Bushard  
ATTORNEY

## UNITED STATES PATENT OFFICE

2,382,371

## HYDROCARBON CONVERSION PROCESS

Ernest Utterback, Upper Darby, Pa., assignor to  
Socony-Vacuum Oil Company, Incorporated,  
New York, N. Y., a corporation of New York

Application May 3, 1941, Serial No. 391,619

4 Claims. (Cl. 196—52)

This invention is a continuation in part of my previously filed application Serial No. 247,464, filed December 23, 1938, and relates to hydrocarbon conversions in operations involving alternate reaction of materials in the presence of a contact mass and regeneration of the contact mass. It is specifically concerned with contact masses which catalyze, promote, enter into, or assist in the treatment of materials, such as for example in the conversion by cracking, polymerization, controlled combustion, molecular rearrangement, chemical treatment, and the like of hydrocarbons and hydrocarbon derivatives. Such contact masses consist in the usual case of particles, pellets, or granules of a material of more or less refractory and adsorptive nature, which of itself may be capable of catalytically entering into or assisting in the desired reaction, or which may have other material of catalytic nature, such as metals or metal derivatives distributed upon or within the particles, etc., or which may promote the desired reaction by providing physical conditions suitable for its accomplishment.

As is well known, such contact masses for the most part are used in operations wherein the desired reaction is accompanied by the deposition of a combustible carbonaceous material upon and within the contact mass, which is removed by a regenerative combustion. The main reaction may be and usually is endothermic to some extent. The regeneration is highly exothermic. The main reaction is usually conducted at a temperature different from that of regeneration. Regeneration temperatures must be high to bring about complete regeneration, but must be below the limit at which the contact mass suffers degradation due to temperature. Such temperature alternations which in the usual case are about 200° F. or more, impose physical strain upon the contact mass particles, resulting in physical degradation. Further, such contact mass particles suffer physical degradation in normal handling even though that handling consists only of charging and discharging a contact mass container at infrequent intervals. The processes in which such contact masses are used are uniformly of the batch type insofar as a given volume of contact mass is concerned, for while processes exist and have been proposed wherein contact mass materials may be passed continuously through separate zones in which reaction and regeneration occur, no contact mass material promises to be capable of economically surviving the rather severe handling incident to such processes.

This invention has for its subject the provision

of a process using an adequately protected contact mass particle capable of withstanding severe handling and temperature stresses without undue degradation. Another object is the provision of contact mass particles of enhanced heat adsorptive capacity and of enhanced heat conductivity.

The principal objects of this invention are accomplished by the provision of a process using a pellet or particle of contact mass material enclosed within a foraminated or porous metal sheath. For the contact mass material, there may be used any of those materials already proposed and found practicable for such uses. For example, fire clays, kieselguhr, diatomaceous earth, fuller's earth, specially blended and specially treated clays and other material of similar nature may be used. As a specific example of this class of material, which forms an excellent catalyst for cracking of petroleum hydrocarbons, there may be described a mixture of silica and alumina in the proportions 3½:1 or 4:1 which is substantially free of the oxides of magnesium, calcium, and iron. Such materials are usually prepared for use as contact masses by molding a plastic or fluid mass of the material, wet with water or other treating agent, into particles of desired size. For various purposes, such as, for example, desulphurization of hydrocarbon gases, these materials may be impregnated, before or after molding, with metals or metal oxides. For other purposes they may be impregnated, before or after molding, with other materials, such as various inorganic salts, etc. All such contact mass material may be used in this invention.

Such contact masses, as indicated, are utilized in the form of particles, granules, or pellets of small size. For example, a popular form of contact mass particle consists of cylindrical pellets or about 2.5 millimeters diameter and about 2.5 millimeters long. Where the term "particle" is used herein, it denotes such pellets, or granules, or particles.

For the metal sheath there may be used any metal which does not undergo serious degradation under the conditions of reaction and which may be readily worked. It is possible to use a metal which may enter into the reaction catalytically or otherwise to some extent provided it is not physically altered thereby. It is preferable to use a metal of relatively high strength which is also possessed of relatively high heat capacity per unit of volume and has good heat conductivity. Iron and aluminum are exemplary metals which combine such properties with attractive cost and also appear to be applicable to most of

the reactions in which such contact masses are used.

The metal is most conveniently and preferably used in the form of relatively thin strip material which is foraminate in nature, although any method of applying metal capable of accomplishing the purposes and objects herein desired and pointed out may be used. In any event, the metallic material is one which enters into the operation as a homogeneous metallic material and which after being applied is possessed of a similar metallic form not substantially dependent upon the catalytic particle with which it is associated.

In order to understand this invention reference is now made to the drawing attached to this specification in which Figures 1 and 2 show a sheathed catalyst pellet of the type herein referred to and Figure 3 shows in diagrammatic form a process in which the pellet form protected catalytic particle is highly useful.

In Figures 1 and 2 the metal sheathed pellet is shown in one modification in which the sheath is formed of perforated thin metal. In the pellet here shown the central core of catalytic material is surrounded by a sheath of perforated metal. Details of the various methods useful in making such sheathed catalyst pellets are disclosed in my copending application Serial No. 247,464 above mentioned.

In Figure 3 there is shown, in diagram form a continuously moving catalyst form of catalytic hydrocarbon conversion process using the sheathed pellet form of contact mass particle. In this process the pellets moving under the influence of gravity flow down through vessel 5 in contact with reactant vapors introduced therein by pipe 7, which vapors have previously been heated to reaction temperature in heater 3. Reaction products depart through pipe 9 to product purification and recovery steps indicated at 10. Catalyst pellets leaving the reaction zone are preferably steamed or otherwise purged in zone 11 and are then elevated by elevator 12 to flow into hopper 13 from which they pass into vessel 14 wherein they are regenerated, as by combustion in the presence of a regeneration medium, e. g., air, introduced by a blower 15. Fumes from this regeneration leave vessel 14 through pipe 16. Catalyst undergoing regeneration flows through vessel 14 under the influence of gravity and, upon leaving the vessel 14, may be purged, as by steam in passage 17 before re-entry to vessel 5 where reaction takes place. In case it is desirable to add or extract heat from either vessel 5 or vessel 14 during reaction or regeneration, a suitable fluid heat exchange medium, as, for example, a molten inorganic salt may be circulated as desirable through the coil 18 in vessel 14 or through the coil 19 in vessel 5 utilizing the external circuit indicated by items 20, 21, 22, 23, 24, 25, 26, 27, 28 which together comprise a flexible heat control system. It is obvious that the superimposition of regeneration on reaction may be reversed, that is that the vessel 14 with its function may appear physically below vessel 5 with its function, since this implies no reversal of process steps.

While the sheathed pellet form of catalyst is most highly useful in operations of the sort shown, the structural strength and other advantages of this pellet are also highly useful in bed-in-place catalytic operations of the more usual type, as will be seen from the following remarks as to the properties of the sheathed pellet form.

Contact mass particles so formed have high

structural strength and a corresponding degree of resistivity to physical degradation resulting from handling and thermal expansion, even when the clay or other contact mass material has little intrinsic strength. This is of great advantage in that it permits the use of catalytic materials heretofore impractical because of structural weakness. Many materials not heretofore useful because of inability to retain a particle, pellet, or granule form under conditions of use may be taken advantage of.

Certain further advantages reside in the metallic sheath besides those arising from increased structural strength. These advantages arise from the increased heat absorption capacity of the entire contact mass and the increased heat conductivity of the entire contact mass when metal sheathed particles are used. These advantages are highly useful in types of operation when the contact mass is retained in fixed position as in a contact mass container wherein reaction and regeneration are alternately accomplished by passing appropriate material through the contact mass.

In such operations the use of a contact mass of high heat absorptive capacity permits of a more accurate control of temperature during reaction, since much heat may be handled in the form of sensible heat changes in the contact mass and need not be added or removed by other agencies. It is obvious that the combination of catalytic material and a metallic sheath presents a packing material of higher heat absorptive capacity.

As is well known, the usual means of control of exothermic reaction temperatures is by removing heat through the agency of a fluid heat transfer medium circulated in heat exchange relationship with the contact mass, usually through tubes embedded therein. Porous refractory absorption contact mass materials of the types usually used are low in heat conductivity. Hence, in order to permit efficient heat extraction, the usual catalyst container is provided with heat transfer medium tubes in which are attached highly ramified metallic fin structures to bring all portion of the contact mass within efficient heat transfer distance of the tubes. Such construction is expensive to build and expensive to maintain. With a metal sheathed catalyst particle, the heat conductivity of the entire contact mass is so increased that these finned tube structures may be minimized and in some cases dispensed with.

Similarly, in both bed-in-place and continuously-moving-catalyst types of operations where control of regeneration temperatures and rate of regeneration control may be desired to be accomplished by recirculation of regeneration flue gases to dilute incoming regeneration medium, important and significant advantages will arise from the use of the sheathed pellet here disclosed. These advantages arise variously from the greater density of the combined metal and clay pellet, from its increased conductivity, and from the possibility of control of the porosity of the mass which may be accomplished by proportioning of the metal sheath.

As indicated hereinbefore the usefulness of this process is broadly directed to any process of cracking, reforming, hydrogenation, dehydrogenation, isomerization, polymerization, aromatization, or any other process making use of a contact mass of generally refractory and/or absorptive nature and may be so used, under conditions of temperature and pressure and with proper hydrocarbon

reaction mixtures, all of which are well known, in such processes.

I claim:

1. That method for the conversion of hydrocarbons comprising the steps of flowing hydrocarbon reactants at reaction temperature in contact with a moving confined stream of contact mass particles of relatively small size, each of which composite particles comprises a core particle of refractory adsorptive material and a metal sheath closely engaged thereto in supporting relationship therewith while permitting access of reactants thereto.

2. That method for the conversion of hydrocarbons comprising the steps of flowing hydrocarbon reactants at reaction temperature in contact with a moving confined stream of contact mass particles of relatively small size, each of which composite particles comprises a core particle of refractory adsorptive material and a metal sheath closely engaged thereto in supporting relationship therewith while permitting access of reactants thereto and subsequently regenerating said contact mass particles by flowing a regeneration medium, at regeneration temperatures, in contact with a moving confined stream of said particles.

3. That method for the conversion of hydrocarbons in the presence of a particle-form contact mass cyclically subjected to hydrocarbon reaction and to regeneration at a temperature level differing from that of reaction while preventing degradation of particle size of contact mass due

to thermal and other operative stresses which comprises the steps of passing hydrocarbons at conversion conditions into contact with a contact mass comprising a large number of individual composite particles of relatively small size, each of which composite particles comprises a core particle of refractory adsorptive material and a metal sheath closely engaged to said core in supporting relationship therewith while permitting access of reactants to said core, followed by regeneration of said contact mass material at a temperature level different from that of reaction.

4. That method for the conversion of hydrocarbons in the presence of a particle-form contact mass cyclically subjected to hydrocarbon reaction and to regeneration at a temperature level differing from that of reaction while preventing degradation of particle size of contact mass due to thermal and other operative stresses which comprises the steps of passing hydrocarbons at conversion conditions into contact with a contact mass comprising a large number of individual composite particles of relatively small size, each of which composite particles comprises a core particle of catalytic material and a foraminiferous metallic sheath closely encasing and supporting said core while permitting access of reactant thereto, followed by regeneration of said contact mass material at a temperature level different from that of reaction.

ERNEST UTTERBACK.

---

CERTIFICATE OF CORRECTION.

Patent No. 2,382,371.

August 14, 1945.

ERNEST UTTERBACK.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 39, for "absorption" read --adsorption--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of December, A. D. 1945.

Leslie Frazer

First Assistant Commissioner of Patents.

(Seal)