April 7, 1953 E. J. HOUDRY 2,634,232

PROCESS FOR CATALYTICALLY CRACKING HYDROCARBONS

Filed Sept. 23, 1949 2 SHEETS—SHEET 1

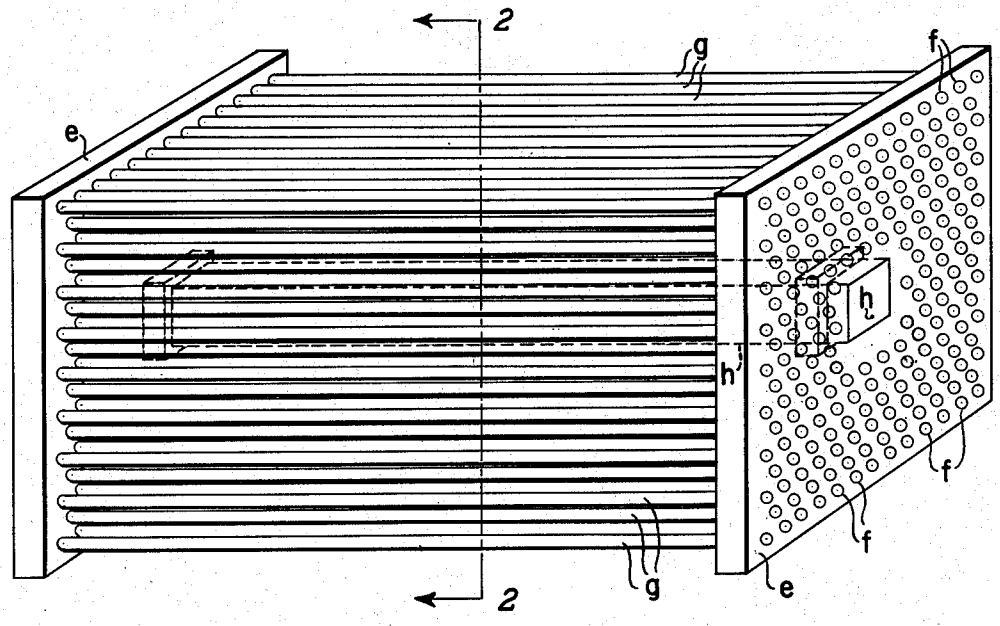


FIG. 1.

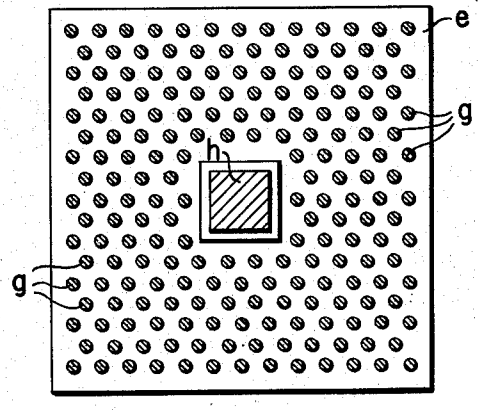


FIG. 2.

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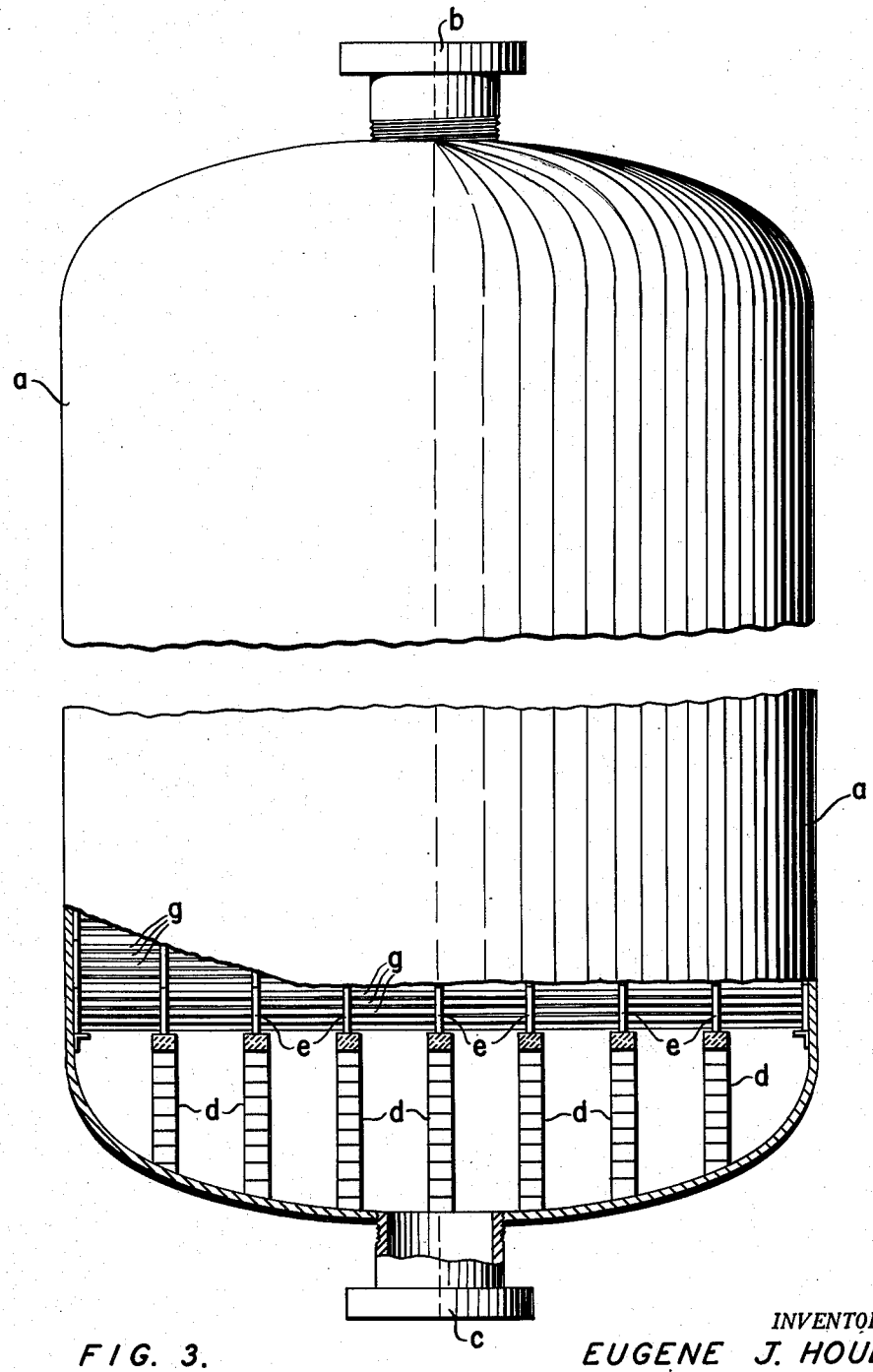


FIG. 3.

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2,634,232

PROCESS FOR CATALYTICALLY CRACKING HYDROCARBONS

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2 Claims. (Cl. 196—52)

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Processes for converting a relatively high-boiling hydrocarbon fraction to a relatively low boiling hydrocarbon fraction by catalytic cracking have been used extensively on a large commercial scale for a number of years, particularly as applied to the cracking of crude petroleum or, more usually, the cracking of a gas oil fraction of petroleum. The first commercial cracking plant was of the fixed bed type, which was followed by the so-called moving bed type and the fluid-catalyst type. These processes are now well known in the art. All of them are in extensive commercial use. All have certain advantages and certain disadvantages.

The first named two types of catalytic cracking processes have many features and advantages in common. The fixed bed type has distinct advantages, such as good control of catalyst temperature while on stream or in regeneration and with relatively small catalyst losses due to attrition, which means low consumption of catalyst and consequently permits the industry to use catalysts of high quality and high activity. On the other hand, the disadvantages of the fixed bed unit are (1) high cost due to the large amount of steel used for the fin tubes and the so-called "salt system" for temperature control; (2) the impossibility of charging sour crude to the units; and (3) the high cost of discharging and replacing the catalyst.

The moving bed type of catalytic cracking process is advantageous in eliminating certain disadvantageous features of the fixed bed type, more particularly in that the cost of construction is substantially reduced. Its advantages, however, over the fixed bed type are neutralized by recognized comparative disadvantages, particularly in that there are large losses due to attrition, which requires the catalyst to be extremely cheap or made extremely resistant to attrition in order to reduce the cost of operation. This requirement has not been met.

The object of my invention is to provide a process that will secure the advantages, and avoid the disadvantages, of both processes.

A cracking catalyst that gives an ideal result is one that gives a good distribution of the cracked products, that is, a high yield of the main product sought to be produced, usually gasoline, and low formation of carbon and high quality gas. I am convinced that no such catalyst is available if, as in the traveling bed type of catalytic cracking plant, it is rolled over and over again or subjected to sand blasting. The solution of the problem must, therefore, be found in the fixed bed type. The present invention discloses a fixed bed apparatus in which the principle of the cracking reaction remains the same, but which is adapted to carry out a process that is so far improved over the commercial process as to secure, in maximum degree, the desirable results above specified while avoiding all the disadvantages characterizing the fixed bed process as heretofore developed and at the same time not only retaining, but enhancing, its recognized advantages.

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An essential feature of the invention is the catalyst structure itself, which, as hereinafter described, embodies certain necessary features and also preferred features more especially adapting it to the cracking of hydrocarbons. It may have the specific structure disclosed in my application Serial No. 95,031, filed May 24, 1949, or that disclosed in my application Serial No. 109,288, filed August 9, 1949, or other specific structures that have been and are being developed by me and those associated with me in such developments and which may form the subject matter of an application or applications to be filed later. But all such catalyst structures will have the essential features of the specific catalyst which I will now proceed to describe.

Briefly, such catalyst comprises a support or assembly of porcelain which is chemically inert under operating conditions; such porcelain material being obtained at temperature above 2300° F., which is far superior to the destruction temperature of an alumina-silica cracking catalyst. It is well known that cracking catalyst activity, whether of activated clay type or synthetic type, becomes nil when such catalyst is submitted to a temperature above 1800° F. Upon the porcelain assembly is distributed the active catalyst, which should be one known in the art, such as silica-zirconia, silica-beryllia, silica-magnesia, or (preferably) silica-alumina. This may be effected in different ways. The porcelain assembly may be dipped into an alumina-silica solution, or into an alumina salt solution to which finely ground active silica-alumina powder is added. The porcelain assembly should comprise the above mentioned materials in such proportion that the expansion coefficients of the porcelain assembly and the active silica-alumina are of the same order.

The porcelain assembly is then dried slowly and brought to the decomposition temperature of the alumina salt solution. At this time a film of active silica-alumina catalyst is deposited on the porcelain assembly. The operation is repeated as many times as may be necessary to obtain the desired film thickness.

It should be understood that a silica-alumina catalyst, and its adaptation to the cracking of

petroleum hydrocarbons, is well known. Various means of building up such a cracking catalyst are known. It has been customary to do this either by coprecipitation of silica and alumina, or by the addition of alumina to silica gel, the best proportion being eleven parts of alumina and 89 parts of silica for maximum activity of the catalyst. For instance, the addition of alumina over silica gel such as can be effected by dipping silica gel in aluminum nitrate, with consequent decomposition of aluminum nitrate at 900° F., shows that the activity index of the catalyst so obtained increases from 30 to 50 when the added alumina increases from one per cent. to eleven per cent. Addition of more alumina does not increase the activity of the catalyst.

Recently I made a series of experiments which consisted of addition of silica to active alumina pellets such as are sold commercially by dipping the pellets in ethyl silicate, and found that the catalytic activity would increase from 5 A. I. up to 45 A. I. when the proportion of silica reached 35 per cent. of the weight of the alumina.

Consequently, for good catalytic cracking activity, it is simply necessary to have in close contact finely divided alumina and finely divided silica. Whether alumina or silica is deposited first on the porcelain assembly or whether a fine powder of coprecipitate of alumina and silica is added in suspension to an aluminum salt solution in order to obtain the active silica-alumina cracking catalyst, or whether the active silica-alumina is otherwise deposited on the porcelain assembly, is not material. However, for good distribution of the products, and especially low coke formation, the proportion of silica to alumina is of great importance, as more particularly disclosed in an application filed by James W. Harrison and myself of even date herewith, Serial No. 117,489, now U. S. Patent No. 2,580,429 issued January 1, 1952. This patent discloses the coating of the catalytically inactive porcelain base with active alumina and impregnating this coating with silica in a proportion between 1 to 5 silica to 10 alumina, an example of which is given in the preceding paragraph. An important feature of novelty of my improved process is the use of a support or assembly, such as porcelain, catalytically inactive and having substantially the same coefficient of expansion as the active silica-alumina catalyst.

The adaptation of such a catalyst structure to the fixed bed process presents a secondary problem which I have solved by the arrangement shown in Figs. 1 and 2, in which—

Fig. 1 is a perspective view of one unit of the catalyst structure that is contained within the reaction chamber.

Fig. 2 is a section on the line 2—2 of Fig. 1.

Fig. 3 is a side elevation, partly in section, of the reaction chamber with a multiplicity of catalytic units contained therein.

I have assumed that the cracking chamber *a* is one having a diameter of twelve feet and which, for the greater part of its height, say for about thirty feet, is of cylindrical form. The top of the chamber may be rounded to form a dome of about three feet in height while the bottom is of similar rounded form and of the same height. The overall height of the chamber may then be assumed to be thirty-six feet. An inlet *b* for the higher boiling fraction to be cracked is provided at the top, while at the bottom is an outlet *c* for the cracked products, including the desired lower boiling fraction, with some light gas and some heavier material, which are fractionated, in any manner known in the art, to separate the desired product.

Erected on the bottom of the chamber are a number of arches *d* of refractory brick upon which the assembly, hereinbefore described in general terms, is supported.

The specific porcelain assembly shown comprises a series of pairs of rectangular plates *e* of porcelain which may be each nine inches square and of a thickness of ¾ of an inch. These porcelain plates are each drilled through with a multitude of holes *f* of a diameter of $\frac{3}{16}$ of an inch in which are inserted the ends of porcelain rods *g* of corresponding diameter. Such rods extend between the plates of a pair, the arrangement being quite similar to that shown in my said application Ser. No. 109,288. Between the two plates of a pair extends a spacer bar *h*, preferably square in cross-section, having shoulders abutting against the respective plates *e*. The plates and spacer are cemented together to present a fixed assembly. The porcelain rods *g* are preferably inserted after the plates *e* are secured together by the spacer *h*. To the described assembly is then applied the active catalyst, preferably in one of the ways hereinbefore described, and is then, also as hereinbefore described, after drying, mounted on the supporting arches *d*. Or, preferably, as hereinafter described, the active catalyst may be applied to the supporting assembly after the latter is positioned in the converter.

Instead of arranging the plates *e* in pairs as described each of the spaced-apart plates (except the end plates) may be connected, by rods *g*, with both of the more nearly adjacent plates.

The complete porcelain assembly is so designed that the oil vapors and the regenerating medium contact the catalyst with no appreciable pressure drop, so as to permit the recirculation of the regenerating medium in the desired quantity for maintaining heat balance of the operation with a low pressure blower such as used in recirculating the fumes in a pipe still furnace.

A zone of oxidation catalyst may be added in the stream of regeneration fumes so as to oxidize the carbon monoxide and hydrocarbons contained in the regeneration fumes. This zone may be of the type described in one of my said copending applications so that no appreciable pressure drop will occur. A waste heat boiler is interposed in the circuit so as to recover the heat of regeneration.

Adverting now to the disadvantages characterizing the conventional fixed bed catalytic cracking process, all these objections are overcome by my invention.

First.—It is obvious, without explanation, that the cost of the converter is small relative to the cost of the conventional converter, there being no complicated and expensive interior arrangement of steel pipes and no need for any cooling media such as salt or water. The proportion of active material to inactive material may be determined exactly, so that the catalyst temperatures during the on-stream period and the regenerating period may be determined almost at will, which permits of the complete elimination of salt-cooling or water-cooling.

Exclusive of the catalytic assembly itself and of the relatively inexpensive brick supporting arches, the converter may be an empty shell, preferably calorized inside.

Second.—The converter embodying my invention can handle sour crudes, for the reason that the simplicity of the converter construction eases the problem of converter corrosion, the catalyst and its porcelain support presenting no problem due to charging of sour crudes. If occasion should arise for protecting the inside of the converter from contact by the charged hydrocarbons, means for so doing are known in the art.

Third.—There is no problem of charging or discharging the catalyst for the reason that after the supporting assembly is in position, the chamber may be filled with the described catalyst solution to a level above that of the supporting assembly. After withdrawal of the solution a stream of hot air or flue gas may be charged to the chamber to thereby dry slowly the alumina-silica deposit and thereafter bring the material to the decomposition temperature of the salt solution. The catalyst may be then cooled slowly by air or flue gas. As many coatings as desired may be made so as to obtain the desired proportion of active catalyst relative to the porcelain supporting assembly, which proportion may vary from 10% to 50% by volume. When the catalyst has lost activity to a degree that makes it desirable to renew it, the catalyst coating may be removed, say by a caustic soda solution that does not react with the material of the porcelain assembly, and a new coating is made, following the procedure above explained.

Fourth.—Not only does my improved process retain the advantage, characteristic of the fixed bed process as compared with the traveling bed process, but any attrition losses are reduced close to zero, which even the conventional fixed bed process does not accomplish. That is, even in the fixed bed process the steel pipes and fins have a shearing effect upon the catalyst grain due to expansion and contraction occurring with the changes of temperature incidental to the steps of on-stream and regeneration. In my improved process the catalyst is disposed in a great number of individual units independent of one another, so that there is no factor contributing to attrition.

Fifth.—Far from being least in importance is that the catalytic mass presents no resistance to the flow and, consequently, permits the use of a very low pressure blower. This is another factor that contributes in high degree to low investment cost.

Sixth.—The addition of an oxidation catalyst on the stream of regeneration fumes with no pressure drop permits the recovery of all the heat or energy contained in those fumes. The use of a waste heat boiler permits the recovery of this extra heat in the form of steam, and also control of the regeneration step.

In specifying catalytic cracking I mean also

to include any operation, such as the catalytic treating of the product of catalytic cracking, that is in use in modern catalytic cracking plants. Indeed, it is not intented to exclude the use of the described catalyst structure for any use, such, for example, as the refining of lubricating oils, to which it may be found adapted.

What is claimed is:

1. In a process for cracking hydrocarbons in a fixed catalytic bed in the presence of a cracking catalyst which gradually undergoes loss of activity, and thus requires periodic replacement, an improved method for the installation and removal of the cracking catalyst which comprises depositing from a liquid media an initially wet film of cracking catalyst upon a plurality of catalytically inactive porcelain supports arranged in spaced-apart relation within a reaction chamber, flowing a hot gas through said reaction chamber to effect drying of said wet film of cracking catalyst upon said supports to thereby leave an adherent film of active catalyst thereon, alternately flowing hydrocarbons under cracking conditions, and regenerating fluid under regenerating conditions, through said reaction chamber over said porcelain supports in contact with the film of cracking catalyst deposited thereon until the activity of said catalyst is reduced below a predetermined limit, and then, without removing said supports from said reaction chamber, removing the relatively inactive catalyst from said porcelain supports by means of a reagent which is capable of attacking said film of cracking catalyst but which is substantially inactive with respect to said porcelain supports, and then redepositing a new film of active cracking catalyst upon said supports, thus preparing said reaction chamber for further cracking operations.

2. A method in accordance with claim 1 in which the cracking catalyst is a silica-alumina catalyst.

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