

UNITED STATES PATENT OFFICE

2,367,474

CATALYTIC HYDROCARBON CONVERSION PROCESSES

Meredith M. Stewart, Beacon, N. Y., assignor to
The Texas Company, New York, N. Y., a corporation of Delaware

Application December 31, 1942, Serial No. 470,770

8 Claims. (Cl. 196—52)

My invention relates to catalytic hydrocarbon conversion processes, and particularly to an improved method for reactivating spent catalysts in such processes.

In high temperature catalytic hydrocarbon conversion processes, such as cracking and reforming, the catalysts quickly become at least partially deactivated by carbonaceous deposits. The catalysts employed are generally too expensive to discard after this initial deactivation, and are therefore reactivated for further use. The reactivation has been effected in commercial operations by contacting the hot partially spent catalyst with air to burn off the carbonaceous deposits. This procedure, however, has been expensive, and has been disadvantageous for the reactivation of powdered catalysts in view of the difficulty of separating a fine powder from hot combustion gases.

An object of my present invention is to provide an improved method for reactivating hydrocarbon conversion catalysts.

Another object of my invention is to provide a liquid phase process for the removal of carbonaceous deposits from hydrocarbon conversion catalysts.

A further object of my invention is to provide a process for the removal of carbonaceous deposits from hydrocarbon conversion catalysts by hydrogenation in the presence of a liquid phase hydrogen carrier.

An additional object of my invention is to provide an improved cyclic catalytic process for hydrocarbon conversion in which the catalytic reaction is effected in the presence of a liquid hydrocarbon phase, and the carbonaceous deposits are removed from the partially spent catalyst by hydrogenation in the presence of a liquid phase hydrogen carrier.

Other objects and advantages of my invention will be apparent from the following description:

In accordance with my present invention, carbonaceous deposits are removed from hydrocarbon conversion catalysts by hydrogenation in the presence of a liquid phase hydrogen carrier. Any material which is easily dehydrogenated at the temperature and pressure employed for the reactivation will serve as a hydrogen carrier in this process. The material employed should, of course, have no adverse effect on the catalyst itself, even though it is highly reactive with the carbonaceous catalyst deposits. The hydrogen carrier is suitably a compound which may readily be separated from the catalyst, and whose dehydrogenation products may also be separated easily. How-

ever, I prefer to employ as hydrogen carriers compounds which, as such or as their dehydrogenation products, are not undesirable in the catalytic hydrocarbon conversion reaction mixture, and hence do not have to be completely separated from the recycled catalyst. For this purpose, hydrocarbons which are easily dehydrogenated at the reactivation temperature and pressure are the most advantageous hydrogen carriers.

I prefer to employ as hydrogen carriers in my process cyclic hydrocarbons which are at least partially saturated, i. e., less unsaturated than aromatics. Such hydrocarbons may be monocyclic or polycyclic, and may be either partially or completely hydrogenated. The cyclo-paraffins and cyclo-olefins having five or six carbon atom rings are examples of this class of compounds. I generally prefer to employ hydrocarbons having six carbon atom rings, i. e., the hydro-aromatics, and particularly the polycyclic hydro-aromatics. It should be understood, in this connection, that the term "polycyclic" is used herein and in the appended claims to designate bicyclic compounds as well as those having more than two rings. Tetralin and decalin, and analogous polycyclic compounds, with or without alkyl side chains, are examples of my preferred class of hydrogen carriers. Mixtures of such compounds, or hydrocarbon fractions containing substantial amounts of such compounds may be used. Naphthenic petroleum fractions having boiling ranges of the order of 300–600° F. are inexpensive materials well adapted for use as hydrogen carriers in my process.

If the hydrogenation is effected by means of gaseous hydrogen, the hydro-aromatic hydrocarbon will serve primarily as a hydrogen carrier, and will be continuously dehydrogenated and rehydrogenated. In such cases, at the conclusion of the reaction, little if any aromatic hydrocarbons will be present in the reaction mixture. However, any hydrogen carrier may also serve as a hydrogen donor in the reaction, and may constitute the only source of hydrogen for reaction with the carbonaceous catalyst deposits. The use of hydro-aromatic hydrocarbons in this manner is very advantageous, since substantial quantities of valuable aromatic hydrocarbons may thus be produced simultaneously with reactivation of the catalyst.

The amount of the cyclic hydrocarbon to be employed as a hydrogen carrier may vary over a considerable range. In any case, there should be sufficient to completely wet the surface of the

catalyst; and if the hydrocarbon is to serve as the sole source of hydrogen for the reaction, it should be present in a concentration such that the amount of hydrogen liberated by its dehydrogenation is at least equivalent to the carbon content of the deposit on the catalyst. Generally, however, the amount of the cyclic hydrocarbon should be much in excess of either of the above minimum requirements. It is preferable to employ sufficient hydrocarbon to obtain a catalyst slurry which may be easily handled and agitated during the hydrogenation reaction. A very large excess of the hydrogen carrier or hydrogen donor may be used, if desired. However, when employing hydro-aromatics as hydrogen donors it is preferable to avoid a large excess, in order that the aromatics produced may be recovered at a relatively high concentration.

The hydrogenation reaction is effected at a temperature in excess of 700° F., and preferably at a temperature of about 750° F. Higher temperatures may be employed if desired, but should not be sufficiently high to cause undue cracking of the hydrogen carrier employed.

The pressure at which the hydrogenation reaction is effected should be sufficient to maintain the hydrogen carrier in liquid phase at the reaction temperature. The minimum pressure will thus vary for different hydrogen carriers, but for hydro-aromatic hydrocarbons having boiling points at least as high as that of tetralin, a pressure of 400 pounds per square inch will usually be sufficient. Much higher pressures, e. g. initial pressures of 1000-3000 lbs. per square inch are usually desirable. If gaseous hydrogen is employed in the reaction, the pressure may be controlled by the introduction of the hydrogen. When hydrogen is not used, pressures higher than the vapor pressure of the hydroaromatic hydrocarbon or other hydrogen carrier may be obtained by the introduction of an inert gas, such as nitrogen, natural gas, or the like.

The contact time employed in the hydrogenation reaction will depend on the temperature used, and the degree of reactivation required. At a temperature of 750° F., contact times of 1-6 hours should generally provide sufficient reactivation of partially spent catalysts. Shorter contact times may be employed if there is thorough agitation of the reaction mixture than is required for a relatively static mixture, and I prefer to provide suitable agitation in all cases.

At the conclusion of the reaction, the reactivated catalyst may be separated from the hydrocarbons by filtration or other suitable means, and may, if desired, be washed or otherwise further treated before recycling. However, it is generally sufficient merely to recover the reactivated catalyst in the form of a concentrated slurry. This may be accomplished by gravity settling and decanting, or by flash vaporizing the bulk of the hydrocarbons from the hot reaction mixture at reduced pressure.

My reactivation process is applicable to the treatment of any hydrocarbon conversion catalysts which have become deactivated due to carbonaceous deposits. Such catalysts are insoluble in hydrocarbons, and are usually entirely inorganic in composition. They are used in fixed bed operations and in "fluid catalyst" operations for relatively high temperature reactions such as cracking, reforming, hydroforming, and the like. My reactivation process is especially applicable to alumina-silica catalysts, such as the clay types of cracking catalysts. The montmorillonite

clays, and especially the highly active forms of these clays, such as "Superfiltrol," are examples of cracking catalyst which may advantageously be reactivated by my process.

A further phase of my present invention comprises controlling the reaction conditions of the catalytic hydrocarbon conversion reaction so that the catalyst deposits obtained are of a nature particularly adapted to my reactivation treatment. This is effected by carrying out the hydrocarbon conversion reaction in the presence of a liquid hydrocarbon phase, so that the carbonaceous deposits formed on the catalyst will be of a more tarry and less coke-like nature. The entire reaction mixture need not be maintained in the liquid phase, but there should be sufficient liquid hydrocarbon to maintain the catalyst surface completely wet during the reaction. This type of operation is best adapted to the catalytic treatment of high boiling petroleum fractions, such as gas oils, reduced crudes, and the like. For the catalytic treatment of lighter fractions, such as naphthas, highly active catalysts are required to effect reactions at the relatively low temperature required to maintain a liquid phase. Such light fractions may, however, be treated at higher temperatures in the presence of a higher boiling fraction to provide a liquid phase.

When the catalytic hydrocarbon conversion is effected in the presence of a liquid hydrocarbon phase, the partially spent catalyst may advantageously be extracted with a solvent to remove a portion of the tarry deposit. Any organic liquid which is known to have solvent properties for tarry or resinous petroleum derivatives may be used for this purpose. Petroleum hydrocarbons are suitable for this purpose, and it is generally advantageous to employ the same hydroaromatic hydrocarbon or petroleum fraction containing hydro-aromatics, which is to be used subsequently as the hydrogen carrier in the reactivation process. In such cases, complete separation of the solvent from the catalyst is not necessary prior to effecting the reactivation.

One modification of a preferred procedure employing liquid phase catalytic conversion, extraction of the partially spent catalyst with a hydroaromatic hydrocarbon, and liquid phase hydrogenation in the presence of the same hydroaromatic hydrocarbon is illustrated diagrammatically in the accompanying drawing. As may be seen in this drawing, a suitable hydrocarbon fraction, such as a gas oil, is heated in a conventional tube furnace 1 to a catalytic liquid phase cracking temperature, and is introduced, together with suspended powdered catalyst, into the top of a tower 2 which serves as the cracking reactor.

The mixture of oil and catalyst flows downward through the reactor 2, and is withdrawn from the lower part of the tower, preferably at a point somewhat above the bottom, as shown in the drawing. In this manner, a substantial portion of the catalyst may settle to the bottom of the tower 2, where it can be withdrawn as a slurry and recycled to the top of the tower. This recycling may suitably be effected in the manner shown in the drawing, by injecting the hot charge oil into the catalyst slurry recycle line 3. For this purpose the oil may be heated sufficiently to cause partial vaporization at the pressure maintained in the cracking reactor 2. The resulting vapors formed in the catalyst re-

cycle line 3 may then aid in recycling the catalyst slurry by the "vapor lift" principle.

The mixture of oil and partially deactivated catalyst which is withdrawn from the lower part of the cracking reactor 2 is introduced into a vaporizer 4 at sufficiently reduced pressure to effect flash vaporization of the bulk of the hydrocarbons. The vapors are then fractionated in a conventional manner to recover cracked naphtha and such other fractions as may be desired. Fractionating tower 5 and condenser 6 will serve for simple fractionation to recover naphtha and fuel oil fractions.

The partially deactivated catalyst and a minor proportion of the highest boiling hydrocarbons of the cracked product settle to the bottom of the flash vaporizer 4 in the form of a slurry. This slurry is introduced into an extraction tower 7 at an intermediate level, and the catalyst settles downward, countercurrent to an upflowing stream of a polycyclic hydro-aromatic fraction. The linear velocity of the rising hydrocarbon stream is maintained sufficiently low to prevent substantial amounts of catalyst from reaching the top of the extraction tower 7. The extract is removed from the top of the tower 7 and distilled in fractionator 8. A hydro-aromatic overhead fraction from fractionator 8 is condensed in condenser 9 for recycling to the extraction tower 7.

Any catalyst removed from the extraction tower 7 may be recovered from the extract bottoms by filtration, or other suitable means. Since the tarry material constituting the extract bottoms has little value, it may be burned to recover and simultaneously reactivate its catalyst content, if the amount of catalyst warrants this step. Generally the small amount of catalyst contained in the extract bottoms is not economically recoverable, and is replaced by fresh catalyst charged to the cracking reactor.

The extracted catalyst which settles to the bottom of the extraction tower 7 is withdrawn as a slurry of catalyst and hydro-aromatic hydrocarbon. This slurry passes through a preheater 10 to one of a number of alternately charged high pressure hydrogenation reactors 11—11 prime. These reactors are maintained at a temperature of 750° F., and are preferably equipped with suitable agitating means, not shown in the drawing. Hydrogen or an inert gas is introduced into the reactor 11 at an initial pressure of 1000—3000 lbs. per square inch, and the mixture is agitated for a period of 1—3 hours.

The slurry is then withdrawn from the hydrogenation reactor 11 and introduced into a flash vaporizer 12 where the bulk of the hydrocarbons are vaporized. The vapors may then be fractionated in fractionating tower 13. An overhead fraction from tower 13 comprising low boiling aromatics resulting from the hydrogenation and cleavage of polycyclic aromatics in the catalyst deposit and from hydrogenation and cleavage of polycyclic aromatics resulting from dehydrogenation of the polycyclic hydro-aromatics employed as hydrogen carriers is recovered as a condensate from condenser 14. The fractionator bottoms comprise unreacted hydrocarbons of the polycyclic hydro-aromatic fraction employed as the hydrogen carrier, together with any hydrocarbons of the same boiling range produced in the hydrogenation reaction. This fraction may suitably be recycled to the extraction tower 7, as shown in the drawing.

The reactivated catalyst and unvaporized hydrocarbons are withdrawn as a slurry from the

bottom of the flash vaporizer 12. The catalyst may be recovered from this slurry by filtration or other suitable means, if desired. However, I prefer to recycle the slurry directly to the cracking reactor 2, as shown in the drawing.

My invention will be further illustrated by the following specific examples:

Example I

A gas oil of about 38.5 A. P. I. gravity is cracked in the liquid phase at a temperature of about 700° F. and a pressure of approximately 500 lbs. per square inch, with a residence time of about one hour, employing approximately 20% of a powdered silica-alumina cracking catalyst, based on the weight of the oil charged. On a once-through basis, a yield of about 30% cracked naphtha of 400° F. end-point is obtainable, with the carbon content of the partially deactivated catalyst about 5% by weight of the catalyst, or 1% by weight of the charge.

The partially spent catalyst is charged to a high pressure reactor with a highly naphthenic distillate fraction of 350—500° F. boiling range, in a weight ratio of oil to catalyst of about 2/1. The mixture is agitated and heated to a temperature of about 750° F., at the vapor pressure of the hydrocarbons, for a period of 2 hours. The pressure is then released and the bulk of the hydrocarbons are flash vaporized from the catalyst, leaving a concentrated slurry for recycling. The carbon content of the catalyst suspended in this slurry may be reduced to 0.8% by weight, or lower, on an oil-free basis; and the cracking activity of the regenerated catalyst should equal, and may exceed the activity obtainable by burning off the catalyst deposits.

Example II

An alumina-molybdena hydroforming catalyst is employed in fixed bed operation for hydroforming a heavy straight run naphtha of about 50° API gravity 250—400° F. boiling range, and a CFR octane number of 44. Using a catalyst temperature of about 950° F., a pressure of 200 lbs. per square inch, an oil feed rate of 1 volume of oil per volume of catalyst per hour, and a gas recycle rate of 2500 cubic feet per bbl. of feed, a yield of 85—90% gasoline and 84 CFR octane number is obtainable with a coke production of about 1% by weight of the charge. The process is operated in 6 hour cycles, and the reactivation of the catalyst is effected by reaction with tetralin at a temperature of 750° F., using the hydroforming recycle gas to obtain an initial pressure of 2000 lbs. per square inch. When employing two reactors alternately on stream, and using all of the off-stream period for the reactivation reaction, less only the time required for charging and discharging, the coke deposits on the catalyst may be substantially completely removed, and the catalyst activity restored to a value as high, or higher, than can be obtained by burning off the coke deposits.

It is to be understood, of course, that the above examples are merely illustrative, and do not limit the scope of my invention. Catalysts used in other types of hydrocarbon conversion processes may be reactivated in a similar manner, and other hydro-aromatic hydrocarbons, or other types of liquid phase hydrogen carriers may be substituted for the particular materials employed in these examples. Other catalytic hydrocarbon conversion processes may also be operated at least partially in the liquid phase in order to obtain catalyst deposits of a nature particularly adapted for

removal by my liquid phase hydrogenation process. In general, it may be said that the use of any equivalents or modifications of procedure which would naturally occur to those skilled in the art, is included in the scope of my invention. Only such limitations should be imposed on the scope of my invention as are indicated in the appended claims.

I claim:

1. In a catalytic hydrocarbon conversion process in which the catalyst becomes at least partially deactivated by carbonaceous deposits and is reactivated and reused in the conversion operation, the steps which comprise subjecting deactivated catalyst to hydrogenation at a temperature in excess of 700° F. in the presence of a liquid phase hydrocarbon which is capable of substantial dehydrogenation under the catalyst reactivation conditions, and separating the resulting liquid phase from the catalyst.
2. In a catalytic hydrocarbon conversion process in which the catalyst becomes at least partially deactivated by carbonaceous deposits and is reactivated and reused in the conversion operation, the steps which comprise subjecting deactivated catalyst to hydrogenation in the presence of an at least partially saturated cyclic hydrocarbon at a temperature in excess of 700° F., and at a pressure sufficient to provide a liquid hydrocarbon phase, and separating the resulting hydrocarbon mixture from the catalyst.
3. In a cyclic catalytic hydrocarbon conversion process in which the catalyst becomes at least partially deactivated by carbonaceous deposits and is reactivated and recycled to the conversion operation, the steps which comprise subjecting deactivated catalyst to the action of a hydroaromatic hydrocarbon at a temperature of 700-900° F., and at a pressure sufficient to provide a liquid hydrocarbon phase, separating the resulting catalyst and hydrocarbon phases, and recycling the catalyst to the catalytic hydrocarbon conversion process.
4. In a process for the catalytic cracking of petroleum hydrocarbons in the presence of an alumina-silica catalyst in which the catalyst becomes at least partially deactivated by carbonaceous deposits and is reactivated and recycled to the cracking operation, the steps which comprise subjecting deactivated catalyst to the action of a hydrocarbon fraction comprising polycyclic hydroaromatic hydrocarbons at a temperature of about 750° F., and at a pressure sufficient to provide a liquid hydrocarbon phase, separating the resulting catalyst and hydrocarbon phases, and recycling the separated catalyst to the cracking operation.
5. In a cyclic catalytic hydrocarbon conversion process, in which the catalyst becomes at least partially deactivated by carbonaceous deposits and is reactivated and recycled to the conversion operation, the steps which comprise effecting the catalytic conversion in the presence of a liquid hydrocarbon phase, subjecting deactivated catalyst to hydrogenation at a temperature in excess of 700° F., and in the presence of a liquid phase hydrocarbon which is capable of substantial dehydrogenation under the catalyst reactivation conditions, separating the resulting catalyst and hydrocarbon phases, and recycling the separated catalyst to the hydrocarbon conversion operation.
6. In a cyclic catalytic hydrocarbon conversion process, in which the catalyst becomes at least partially deactivated by carbonaceous deposits and is reactivated and recycled to the conversion operation, the steps which comprise effecting the catalytic conversion in the presence of a liquid hydrocarbon phase, subjecting deactivated catalyst to solvent extraction, subjecting the extracted catalyst to the action of an at least partially saturated cyclic hydrocarbon at a temperature in excess of 700° F., and at a pressure sufficient to provide a liquid hydrocarbon phase, separating the resulting catalyst and hydrocarbon phases, and recycling the separated catalyst to the hydrocarbon conversion operation.
7. In a cyclic catalytic process for cracking petroleum hydrocarbons, in which the catalyst becomes at least partially deactivated by carbonaceous deposits and is reactivated and recycled to the cracking operation, the steps which comprise effecting the cracking reaction in the presence of a liquid hydrocarbon phase, subjecting deactivated catalyst to extraction by a petroleum hydrocarbon fraction, subjecting the extracted catalyst to the action of a hydroaromatic hydrocarbon at a temperature of 700-900° F., and at a pressure sufficient to provide a liquid hydrocarbon phase, separating the resulting catalyst and hydrocarbon phases, and recycling the separated catalyst to the cracking operation.
8. In a cyclic process for the cracking of petroleum hydrocarbons in the presence of a silica-alumina catalyst, in which the catalyst becomes at least partially deactivated by carbonaceous deposits and is reactivated and recycled to the cracking operation, the steps which comprise subjecting deactivated catalyst to extraction by a petroleum fraction comprising polycyclic hydroaromatic hydrocarbons, subjecting the extracted catalyst to the action of said hydrocarbon fraction at a temperature of about 750° F., and at a pressure sufficient to provide a liquid hydrocarbon phase, separating the resulting catalyst and hydrocarbon phases, and recycling the separated catalyst to the cracking operation.

MEREDITH M. STEWART.

CERTIFICATE OF CORRECTION.

Patent No. 2,367,474.

January 16, 1945.

MEREDITH M. STEWART.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, lines 43 and 48, Example II, for "CFR" read --CFRR--; 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 5th day of June, A. D. 1945.

Leslie Frazer

(Seal)

Acting Commissioner of Patents.