July 20, 1943. G. E. LIEDHOLM 2,324,708

PRODUCTION OF GASOLINE

Filed Aug. 25, 1941 2 Sheets-Sheet 1

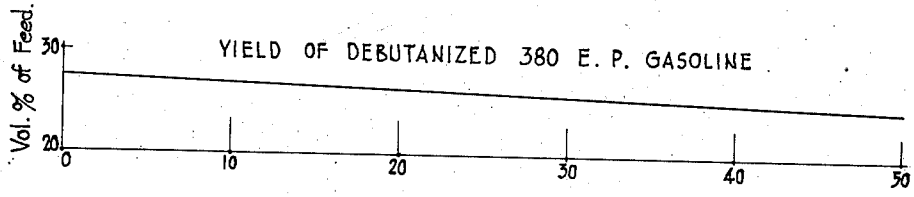

FIG. I

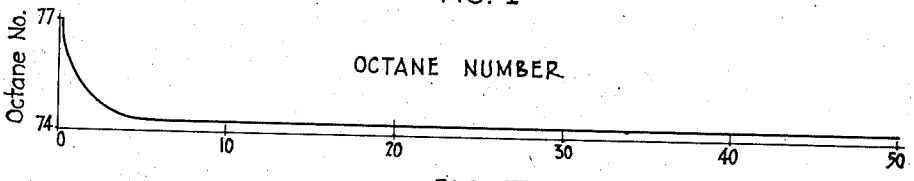

FIG. II

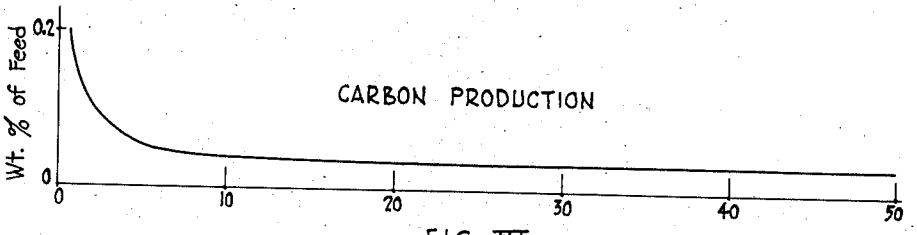

FIG. III

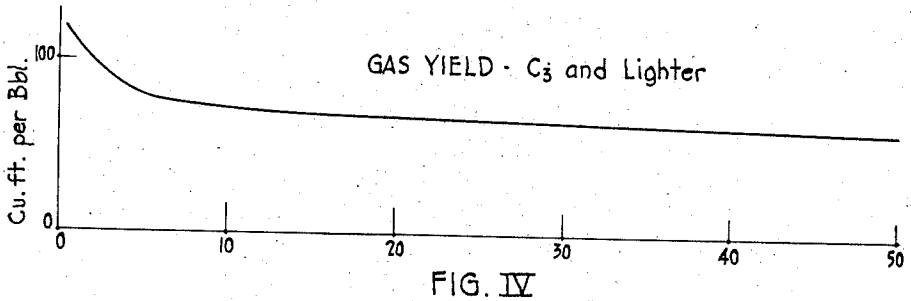

FIG. IV

LENGTH OF RUN IN HOURS

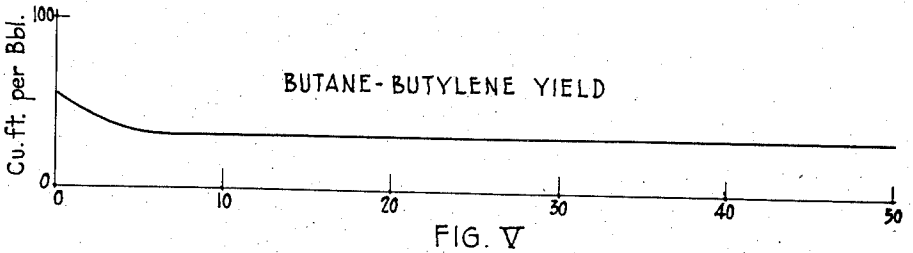

FIG. V

INVENTOR: George E. Liedholm

BY HIS ATTORNEY: L. J. Otte

July 20, 1943. G. E. LIEDHOLM 2,324,708

PRODUCTION OF GASOLINE

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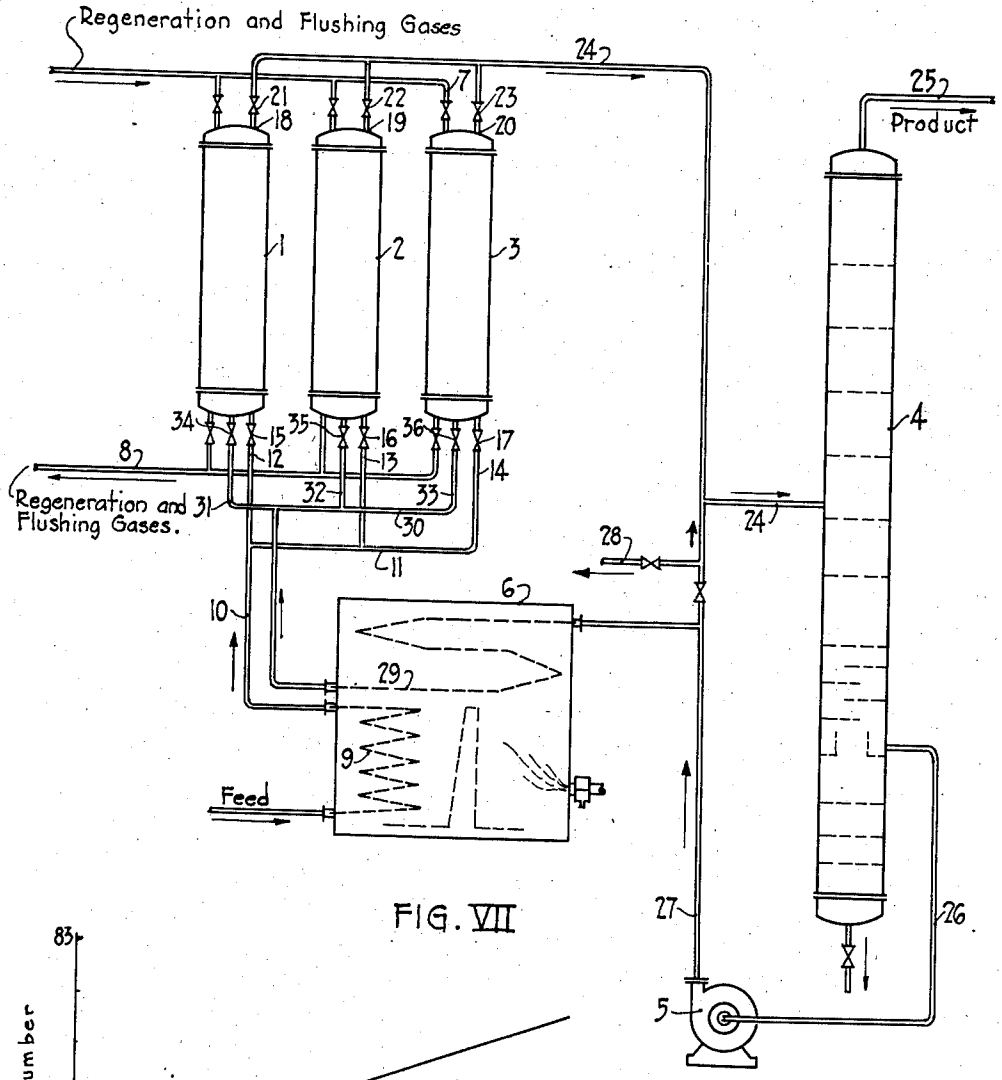

FIG. VII

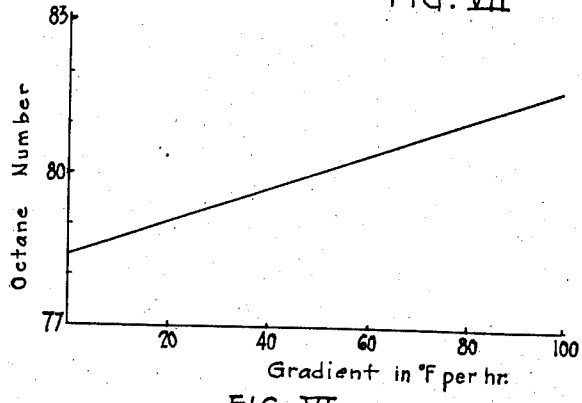

FIG. VI

INVENTOR: George E. Liedholm

BY HIS ATTORNEY: C. J. Ott

Patented July 20, 1943 2,324,708

UNITED STATES PATENT OFFICE

2,324,708.

PRODUCTION OF GASOLINE

George E. Liedholm, Scarsdale, N. Y., assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

Application August 25, 1941, Serial No. 408,192

4 Claims. (Cl. 196—50)

This invention relates to the production of superior grade high anti-knock gasoline by the catalytic treatment of inferior hydrocarbon materials. A particular aspect of the invention relates to an improved process for the conversion of higher boiling hydrocarbon materials which may be vaporized without substantial decomposition into lower boiling high anti-knock hydrocarbons of the gasoline boiling range. Another particular aspect of the invention relates to an improved process for the catalytic conversion of light hydrocarbon oil distillates, such as gasoline, naphtha, and the like, of inferior motor fuel characteristics, particularly with respect to anti-knock value, for the purpose of producing therefrom high yields of high anti-knock gasoline.

In recent years considerable attention has been given to the catalytic cracking of hydrocarbons with clay-type catalysts. The catalytic conversion of hydrocarbons with clay-type catalysts has the advantage that the various reactions taking place may be controlled to a certain extent to produce higher yields of more valuable products while at the same time decreasing the production of less desirable products such as methane, etc. Thus, by the use of suitable clay-type catalysts it is possible to produce equal or better yields of gasoline stocks of superior octane number and lead susceptibility from various hydrocarbon stocks of inferior quality.

The catalytic cracking of hydrocarbons with clay-type catalysts is applicable to the treatment of a wide variety of hydrocarbon feed stocks and may be effected under varied conditions, depending upon the stock treated and the products desired. The process is widely used, for example, for the conversion of higher boiling hydrocarbons into hydrocarbons of the gasoline boiling range. Thus, the process may be employed for the production of gasoline from various heavy hydrocarbon fractions, more particularly heavy distillates which are vaporizable without substantial decomposition, obtained from the distillation of petroleum and various other carbonaceous materials. The process is widely used, for example, for the production of gasoline from gas oils, stove oils, and similar fractions. The process is, however, also applicable for the treatment of lower boiling fractions such, in particular, as thermally cracked gasolines, olefinic naphthas, and the like of inferior motor fuel characteristics, particularly with respect to knocking characteristics and lead susceptibility. This latter type of catalytic cracking operation is referred to sometimes as low temperature cracking and sometimes as isoforming. In this type of catalytic cracking operation, which is hereinafter referred to as isoforming, certain other reactions, many of which are not completely understood, take place in conjunction with the cracking with the result that substantial changes in the character of the distillates treated are obtained with relatively little change in the volatility. Isoforming or low temperature cracking is employed primarily for the purpose of improving the properties and particularly the octane rating and lead susceptibility of inferior olefinic gasoline and naphtha fractions.

It is the object of this invention to provide an improved method for executing catalytic cracking processes of the above general types. A particular object of the invention is to provide a method whereby vaporizable higher boiling hydrocarbon fractions may be catalytically cracked with clay-type catalysts to produce equal or better yields of gasoline stocks having superior octane numbers and lead susceptibilities. A further particular object of the invention is to provide an improved method for isoforming light hydrocarbon fractions such as gasoline and naphtha with clay-type catalysts.

In the above-described type of catalytic cracking processes the most common procedure is to pass vapors of the hydrocarbon to be treated through a fixed bed of a clay-type cracking catalyst in a so-called catalyst case or converter. During the conversion, carbonaceous matter is deposited upon the catalyst and this causes a gradual decline in the catalyst activity. The catalyst is therefore periodically regenerated by burning off such materials in situ with a stream of combustion supporting gas. In general, several catalyst cases are employed in parallel, one or more being regenerated while the remainder are on-stream. The total time between similar conditions of any given catalyst case, for example, from the beginning of one regeneration to the beginning of the next regeneration, is called a process cycle. The process cycle is in turn subdivided into the process period (also sometimes called "make period" and "on-stream period"), the regeneration period, and such flushing, heating, cooling, etc. periods as may be necessary. When the process period is longer than about 3–6 hours, the process is considered to be a long-cycle operation. On the other hand, when the process period is short, such as less

than 1–3 hours, the process is considered to be a short cycle operation. A typical short cycle operation, for instance, comprises two cycles per hour, each consisting of a 10-minute conversion period, a 5-minute flushing period, a 10-minute regeneration period, and a 5-minute flushing period. The present invention relates to the so-called short cycle operation. The distinction between long and short cycle operations will be more fully appreciated from the following considerations.

As stated above, during the process period, carbonaceous materials are deposited upon the catalyst and there is a gradual falling off of the catalyst activity. This is illustrated in the attached drawings, Figure I, wherein there is shown the change in the activity of a typical clay-type cracking catalyst (as expressed in terms of the yield of 380° end point gasoline obtained therewith) with time when catalytically cracking a typical cracked stove oil from low level operation, under typical conditions (temperature of 950° F.; liquid hourly space velocity, 4.5; molal steam-hydrocarbons ratio, 1:1; catalyst bed outlet pressure, 15 p. s. i.) in once-through operation. It is seen that the yield of gasoline produced under typical cracking conditions declines quite slowly. When the purpose of the process is primarily to produce the highest yields of gasoline at the lowest cost, the process is therefore effected with long cycle operation. However, as explained above, one of the chief advantages of the use of catalytic processes employing clay-type catalysts is in the quality of the products that may be obtained. Such processes are therefore not usually operated with the aim of producing the highest yields of gasoline at the lowest cost but with the aim of economically producing gasolines of superior quality, even at the expense of somewhat increased operating costs. When the quality of the products is considered, an entirely different situation is presented. It is found that, although the cracking activity of the catalyst declines quite slowly, a considerable change in the quality of the products takes place during use and that after a few minutes on-stream, products of much inferior quality are produced. The remarkable changes in the type of reaction taking place during the process period are illustrated in Figures II, III, IV and V wherein there is shown graphically the change in the octane number, carbon production, gas yield and yield of butane-butylene with the length of the process period under typical treating conditions. The curves again refer to operation at 950° F. It is seen that in all cases there is a very decided change in the function of the catalyst during the initial stages of the process period and that after about three hours of use the curves all flatten out corresponding to the normally expected slow decline in the cracking activity of the catalyst. The gasoline produced in the initial stages of the conversion, as can be seen by the octane number, is much superior to that produced during later stages of the process period. Besides having superior octane numbers, the gasolines produced during about the first three hours on-stream are superior with respect to lead susceptibility and storage stability. Thus, the bromine numbers of the gasolines likewise increase rapidly in the first stages of the conversion. When the primary object of the process is to produce superior quality gasolines, use is made of this fact and the process is effected by a short cycle operation. In order to obtain the benefit of short cycle operation it is necessary to maintain the process periods below about three hours. Thus, short cycle operations are usually effected with process periods in the order of 20 to 60 minutes. The most economical process period for any given operation, however, depends largely upon economic factors and may range from about 10 minutes to about three hours.

The treating step is endothermic whereas the regeneration step is exothermic. On the other hand, the temperatures required in the treating step are considerably below those prevailing during the catalyst regeneration step. This condition therefore presents a difficult problem of heat control. In general, in the conventional method of operating such processes in any given cycle the temperature of the catalyst is at the maximum at the end of the regeneration step. During the conversion the temperature of the catalyst gradually declines due to the endothermic heat of reaction and reaches a minimum at the end of the process period. This condition usually prevails even when heat exchange means such as embedded coils are provided in the catalyst cases. This has, moreover, been considered a desirable condition since a considerable proportion of the heat of regeneration is thereby stored up in the catalyst during the regeneration and is utilized in the subsequent process period. In some cases, however, if elaborate heat exchange means are provided, the heating and regeneration steps may be effected at substantially constant but different temperatures.

I have now found that superior quality products may be produced in short cycle catalytic cracking processes of the described type by providing an increasing temperature gradient in the reaction zone during the process period. I have found that, although the same qualitative changes take place in the treatment at both lower and higher temperatures, these changes may be suppressed by continuously increasing the temperature during the process period. Thus, by gradually increasing the temperature conditions in the catalyst bed during the process period, the decline in octane number and lead susceptibility with time is much slower, and equal or superior yields of gasoline having higher octane number may be produced. The process of the present invention in its broader aspects therefore comprises passing the hydrocarbon to be treated in contact with a fixed bed of regenerated cracking catalyst of the clay type under the desired treating conditions, gradually increasing the temperature of the catalyst mass during the treating period to a temperature approaching that prevailing in the regeneration of the catalyst, and periodically regenerating the catalyst by burning carbonaceous materials therefrom by means of a combustion supporting gas.

The improvement in the quality of the gasolines produced according to the process of the invention is dependent upon and is more or less proportional to the magnitude of the time-temperature gradient employed. This is illustrated, for example, in the attached drawings, Figure VI, wherein the octane number of the gasoline obtained with a fixed process period and at the same average temperature of 1050° F. under typical conditions is plotted against the temperature gradient in degrees per hours. It is seen that substantial octane number increase of the gasoline may be obtained with a temperature gradient as low as 20° per hour. The applicable temperature gradients are, however, limited by the

thermal stability of the catalysts and, from an economic standpoint, by the temperature employed in the regeneration. It is quite advantageous to employ temperature gradients which tend to bring the temperature of the catalyst mass up to or approaching that used in the subsequent regeneration step. It is, however, inadvisable to exceed this temperature. The regeneration temperatures which may be employed depend upon the particular catalyst used. In some cases the regeneration temperatures may approach 1500° F.–1600° F. but in most cases they are usually between about 900° F. and 1400° F. In general, temperature increases in the process period from about 50° up to 200° are most suitable.

It is to be particularly pointed out that the actual advantage of the present method of operation is materially greater than indicated in the above. The improvement in the octane numbers shown is over that obtained by constant temperature operation. As previously noted, however, the catalytic cracking of hydrocarbons with clay-type catalysts, particularly as presently employed with short cycle operation, is effected with a decreasing time-temperature gradient during the process period. In fact, it is common to employ adiabatic-type catalyst cases wherein the required heat is stored in the catalyst mass during the regeneration period. In such cases, there is a quite large temperature drop in the catalyst mass during the conversion period.

It is known that, in certain catalytic processes wherein the catalytic activity of the catalyst gradually declines during use, a certain extension of the useful life of the catalyst may be realized by increasing the temperature when the conversion tends to drop. This expedient is utilized in these processes, however, as a means of increasing the effective life of the catalyst and is entirely different from the process of the invention, both in purpose and effect. The present process is directed primarily to the improvement in the quality of the products obtained in short cycle catalytic cracking.

The desired increase in temperature in the catalyst mass during the on-stream period may be effected according to the present invention by any suitable means such, for instance, as by the use of auxiliary heating coils in the catalyst case, the use of heating media at increasing temperatures by preheating the hydrocarbon feed to a higher temperature, and the like. According to a preferred embodiment of the invention, the desired increase in the catalyst bed temperature is effected most advantageously by methods illustrated in connection with the description of the attached drawings, Figure VII.

Referring to the drawings, Figure VII illustrates semi-diagrammatically a portion of a catalytic cracking plant adapted to the treatment of hydrocarbons according to the process of the invention. The assembly of apparatus illustrated comprises catalytic cases of conventional design 1, 2 and 3, a stripping column 4, pump 5, and heater 6. Although three catalyst converters are shown, it is understood that the apparatus will usually comprise a larger number of similar converters connected as shown. In practice, one of the converters is usually on regeneration or being purged while the remaining converters are on-stream and are in various stages of their respective conversion periods. Each catalyst case is connected with manifold line 7 for the introduction of the gases required for regeneration and purging. Spent regeneration and purging gases are passed by suitable connections to a lower manifold line 8. Hydrocarbon to be converted is preferably preheated and vaporized, such as by a suitable heating coil 9 in heater 6, and passes via line 10 to manifold line 11 from which it is passed to one or more converters on-stream via lines 12, 13, 14, provided with valves 15, 16 and 17.

The material fed to the heating coil 9 may be any higher boiling hydrocarbon stock of any origin, or any olefinic gasoline or naphtha fraction. Preferred materials are, however, hydrocarbon fractions which may be vaporized without substantial decomposition. Particularly suitable stocks are, for instance, chemically cracked gasolines, olefinic naphthas, gas oils, kerosene extracts, higher boiling polymers, heavier fractions produced in the alkylation of olefines with isoparafins, and the like. The hydrocarbon to be treated, preferably in the vapor phase and at a suitable initial conversion temperature, contacts the catalyst in the respective catalyst cases. Any of the clay-type cracking catalysts of synthetic or natural origin may be employed. Such catalysts usually contain either blends of silica and alumina or activated hydrosilicates of alumina. Thus, for example, an acid-treated Death Valley clay is very effective. Still more effective catalysts are those produced synthetically by depositing alumina in the order of 10–40 mol per cent on silica or depositing small quantities of silica upon the surface of adsorptive alumina. Boron silicate, aluminum fluoride, aluminum phosphate, magnesium fluoride, either alone or in combination with other clay-like materials, are also excellent catalysts. The catalysts may also be impregnated with other metallic oxides including those of nickel, copper, cobalt, thorium, zirconium, lanthanum, etc. which may act as promoters in the cracking or regeneration steps, or both. Also certain promoters may be introduced into the catalyst with the hydrocarbon stream entering the reaction zone. Thus, for example, when cracking certain hydrocarbon stocks it is advantageous to pass small quantities of such materials as the hydrogen halides, organic halides, boric acid, etc., through the reaction zone with the hydrocarbon to be cracked. The catalyst may, if desired, be used in any other conventional form, such as pellets produced by compression or extrusion methods, or the like.

The cracked products leave the respective catalyst cases via lines 18, 19 or 20, provided with vales 21, 22 and 23, to a manifold line 24 and pass to a stripping column 4. In the stripping column 4 the lower boiling cracked products are separated from higher boiling uncracked material and are conveyed overhead via line 25 to a conventional stabilizing plant (not shown). The higher boiling uncracked material is continuously withdrawn from the lower portion of the stripping column 4 via line 26 pump 5, and line 27. A portion of the uncracked material may, if desired, be withdrawn via valve line 28. Another portion may, if desired, be recycled to line 24 to serve as a quenching medium. A further and substantial portion is passed through a heating coil 29 in a suitable furnace 6 wherein it is heated to a temperature appreciably above that of the feed in manifold line 11. The heated bottoms from the stripping tower, hereinafter referred to as recycle stock, pass from heating coil 29 to a manifold line 30 which in turn is connect-

ed with each of the converters via lines 31, 32 and 33 provided with valves 34, 35 and 36. By appropriate manipulation of the valves controlling the flow of the feeds from the two manifolds to the various converters which are processing, for instance, valves 15 and 34 for converter 1, it is possible to vary the proportion of the hotter and colder feeds to the catalyst case during the process period. Thus, by continuously or intermittently opening valve 34 and simultaneously throttling valve 15, for instance by an automatic timing mechanism (not shown) connected to both valves, the temperature in the converter may be gradually increased during the process period without substantially changing the throughput or space velocity. Thus, at the beginning of the process period the largest proportion of the cooler feed enters the converter via line 12 and just prior to the end of the process period the largest proportion of the hotter feed enters the reactor via line 31. In such cases where it is not desired to employ recycle, the feed may be simply split into two portions which may be heated to different temperatures.

I claim as my invention:

1. In a process for the catalytic cracking of higher boiling hydrocarbons to produce high anti-knock hydrocarbons of the gasoline boiling range wherein the hydrocarbon to be cracked is contacted under cracking conditions with a fixed bed of a cracking catalyst of the clay type and the catalyst is periodically regenerated by burning carbonaceous deposits therefrom in situ with a stream of combustion supporting gas in an operation employing a process period of not more than three hours, the improvement which comprises effecting the catalytic cracking simultaneously in a plurality of catalytic converters in parallel, continuously separating uncracked hydrocarbon from the product, preheating and recycling said separated uncracked hydrocarbon to the catalytic converters, feeding fresh hydrocarbon to be cracked at a lower temperature than said recycled hydrocarbon to the catalytic converters, and continuously increasing the proportion of said hotter recycled material to each converter during the process periods, thereby causing an increasing temperature gradient in the catalytic converters during each of their respective process periods of at least 20° F. per hour.

2. In a process for the catalytic cracking of higher boiling hydrocarbons to produce high anti-knock hydrocarbons of the gasoline boiling range wherein the hydrocarbon to be cracked is contacted under cracking conditions with a fixed bed of a cracking catalyst of the clay type and the catalyst is periodically regenerated by burning carbonaceous deposits therefrom in situ with a stream of combustion supporting gas in an operation employing a process period of not more than three hours, the improvement which comprises preheating a portion of the hydrocarbon feed to be cracked to a higher temperature than the remainder, and increasing the proportion of hotter hydrocarbon feed to the reaction zone during each process period thereby creating an increasing temperature gradient in each process period of at least 20° F. per hour.

3. In a process for the catalytic treatment of hydrocarbons at a temperature in the cracking range to produce high anti-knock hydrocarbons of the gasoline boiling range wherein the hydrocarbon to be treated is contacted with a fixed bed of a cracking catalyst of the clay type and the catalyst is periodically regenerated by burning carbonaceous deposits therefrom in situ with a stream of combustion-supporting gas in an operation employing a process period of not more than three hours, the improvement which comprises preheating a portion of the hydrocarbon feed to be treated to a higher temperature than the remainder and increasing the proportion of hotter hydrocarbon feed to the reaction zone during each process period, thereby creating an increasing temperature gradient of at least 20° F. per hour.

4. In a process for the catalytic isoforming of an olefinic hydrocarbon fraction wherein the fraction to be isoformed is contacted under isoforming conditions with a fixed bed of a cracking catalyst of the clay type and the catalyst is periodically regenerated by burning carbonaceous deposits therefrom in situ with a stream of combustion-supporting gas in an operation employing a process period of not more than three hours, the improvement which comprises preheating a portion of the hydrocarbon feed to be isoformed to a higher temperature than the remainder and increasing the proportion of hotter hydrocarbon feed to the reaction zone during each process period, thereby creating an increasing temperature gradient of at least 20° F. per hour.

GEORGE E. LIEDHOLM.