

Dec. 11, 1945.

R. F. RUTHRUFF

2,390,556

CATALYTIC CRACKING OF PARTIALLY OXIDIZED HYDROCARBONS

Filed July 7, 1941

4 Sheets-Sheet 1

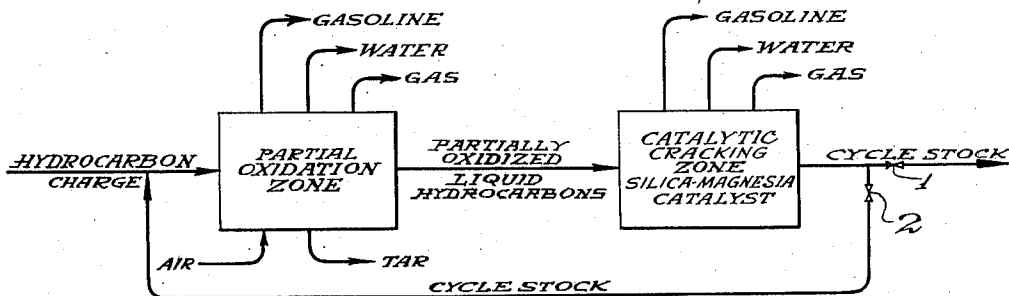


Fig. 1.

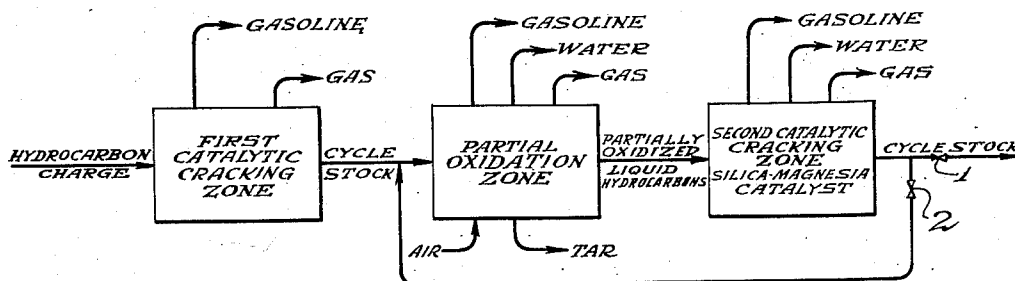


Fig. 2.

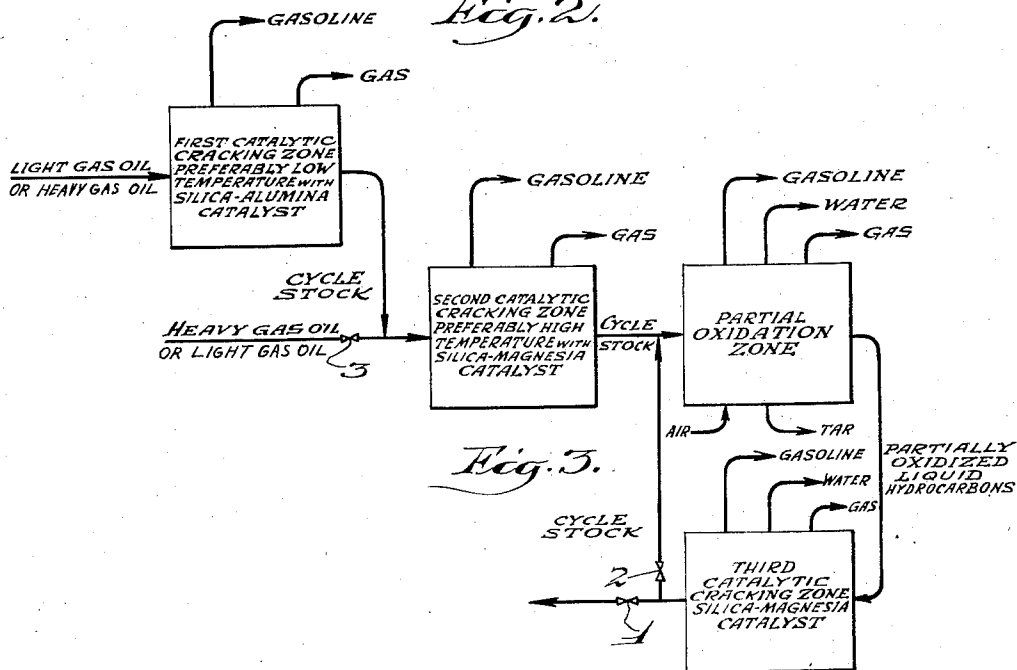


Fig. 3.

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4 Sheets-Sheet 2

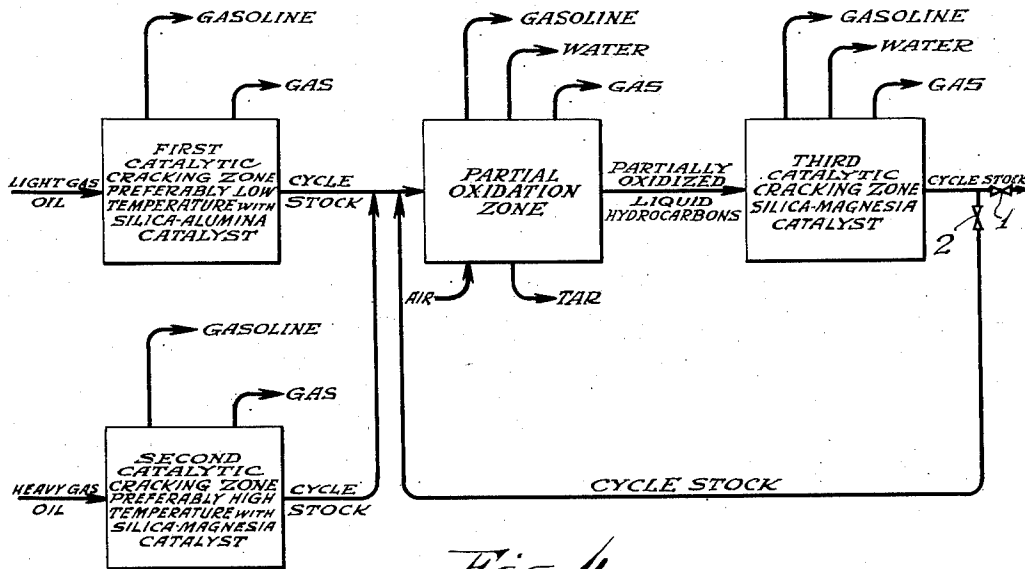


Fig. 4.

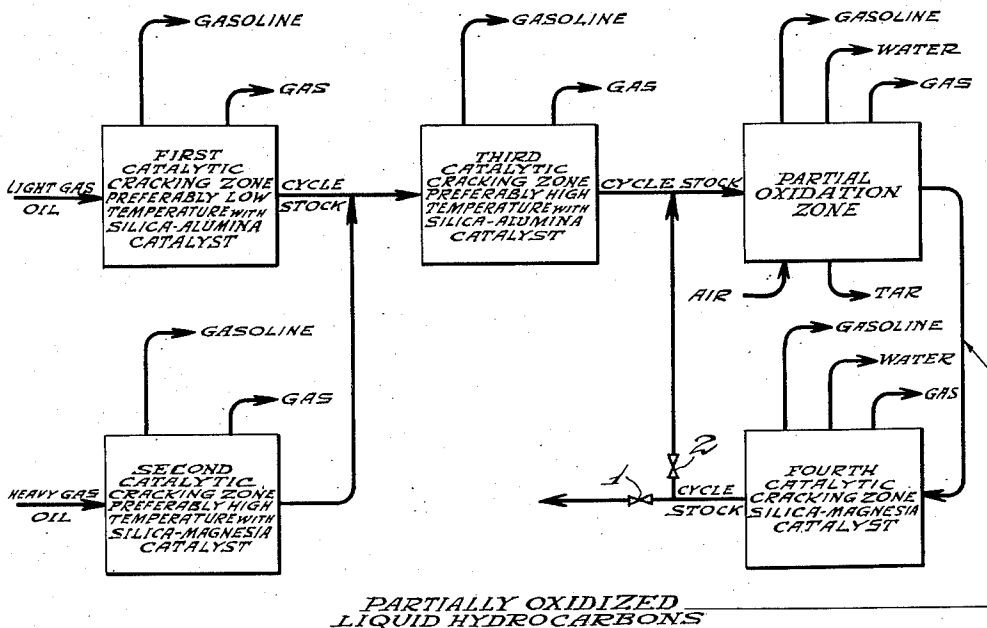


Fig. 5.

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CATALYTIC CRACKING OF PARTIALLY OXIDIZED HYDROCARBONS

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4 Sheets-Sheet 3

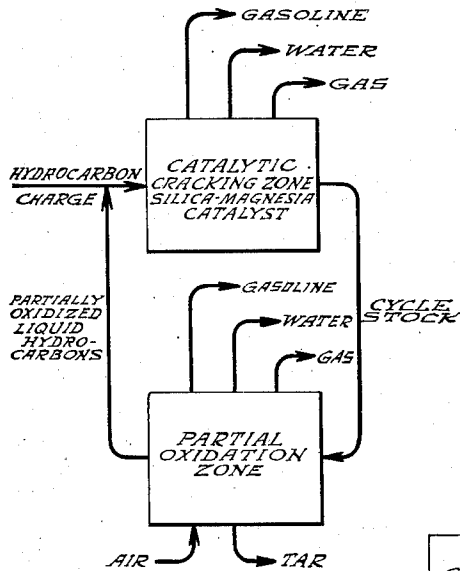


Fig. 6.

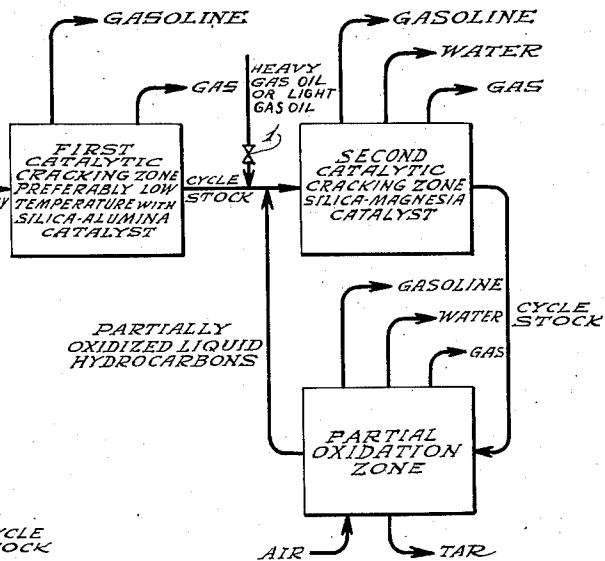


Fig. 7.

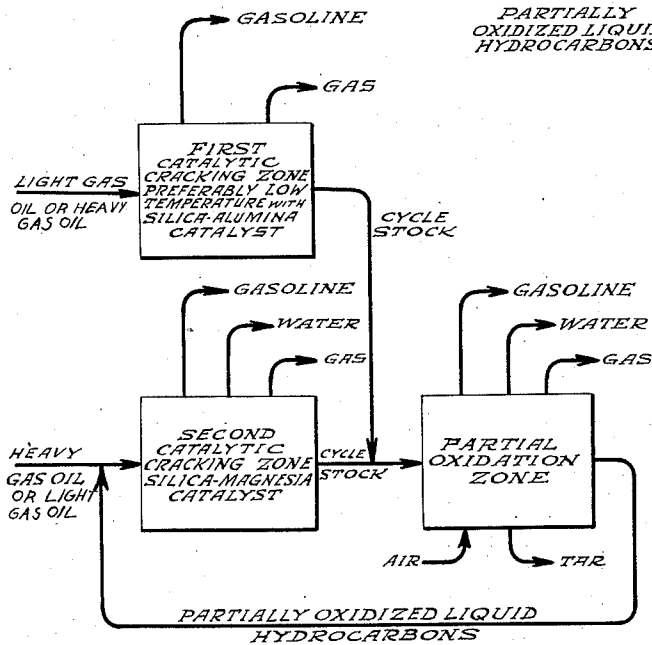


Fig. 8.

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4 Sheets-Sheet 4

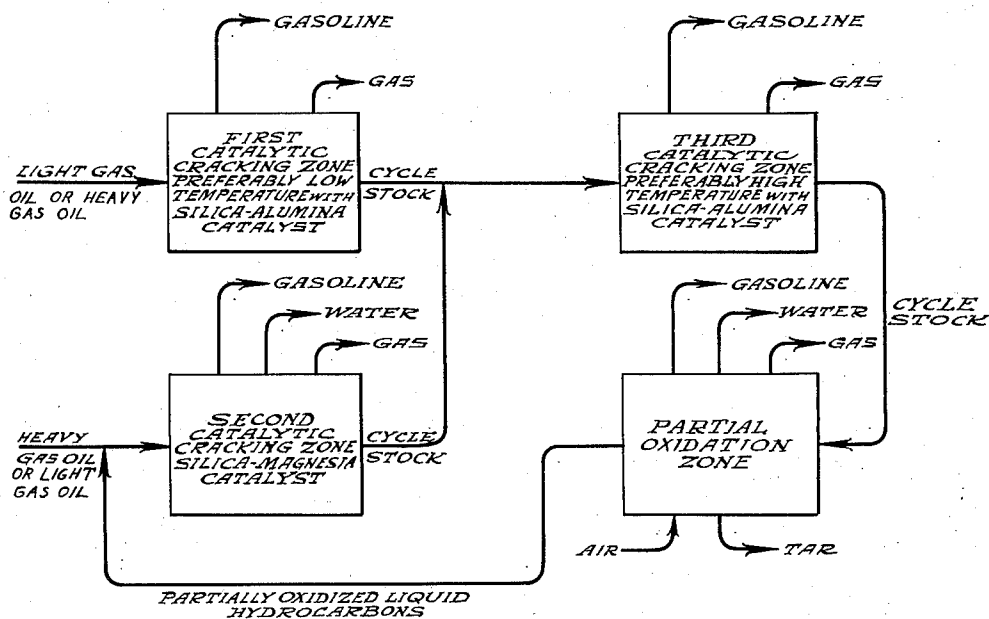


Fig. 9.

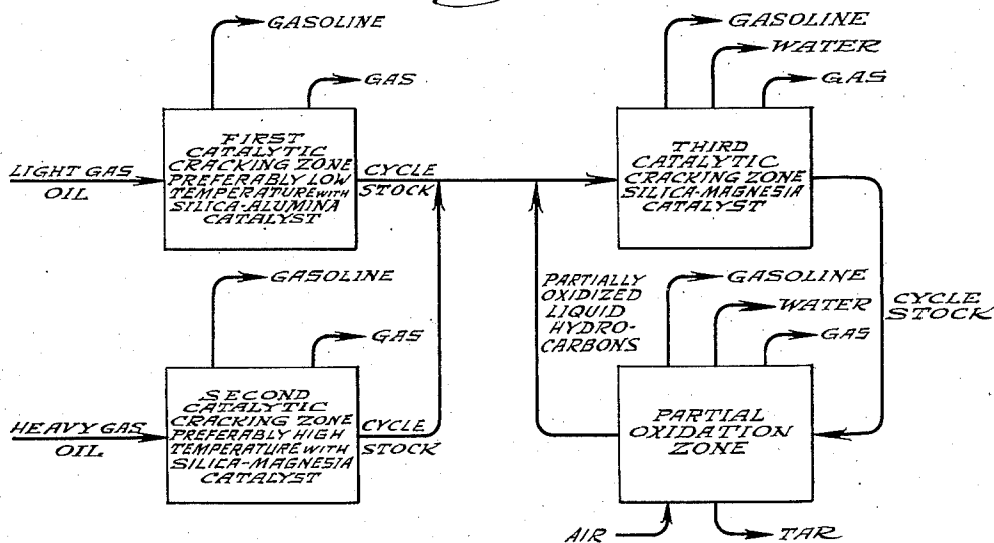


Fig. 10.

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UNITED STATES PATENT OFFICE

2,390,556

CATALYTIC CRACKING OF PARTIALLY
OXIDIZED HYDROCARBONS

Robert F. Ruthruff, Chicago, Ill.

Application July 7, 1941, Serial No. 401,329

34 Claims. (Cl. 196—49)

This invention relates to improved processes for catalytic cracking. More particularly, this invention relates to improved processes for the catalytic cracking of charging stocks comprising or consisting of partially oxidized liquid hydrocarbons.

The thermal conversion of hydrocarbons of higher boiling point into hydrocarbons of lower boiling point and more particularly into hydrocarbons in the motor fuel boiling range is well known in the art. Such thermal conversion processes suffer from many disadvantages; among these may be mentioned the comparatively low octane rating of the motor fuel produced and the high production of undesirable products, such as gas and tar, having little commercial value. These and other disadvantages have led to the development of various catalytic processes for the conversion of hydrocarbons of higher boiling range into hydrocarbons of lower boiling range and more particularly into hydrocarbons in the motor fuel boiling range. In comparison with thermal processes, the motor fuel produced by the catalytic conversion of higher boiling hydrocarbons is of much higher octane rating, the gas production is appreciably lower, and the production of material with a higher carbon to hydrogen ratio than that of the higher boiling hydrocarbon charge is much decreased.

Contact agents for the catalytic cracking of hydrocarbons of higher boiling point to form hydrocarbons of lower boiling point, particularly hydrocarbons within the usual motor fuel boiling range, may be divided into three broad classes as follows:

I. Natural or acid treated materials of an argillaceous nature, particularly those of the montmorillonitic or bentonitic type.

II. Synthetic silica-alumina complexes.

III. Natural or synthetic silica-magnesia complexes.

Contact materials falling in class I are relatively cheap but unfortunately they exhibit a more or less rapid decline in activity during continued use which involves alternating periods wherein such contact agents are employed in the conversion reaction and in being regenerated. Such materials are rather sensitive to and are deteriorated by steam, particularly at elevated temperatures. These contact agents are only moderately active which is not necessarily disadvantageous. For example, in catalytic cracking, it is highly desirable to operate in the vapor phase and obviously, to achieve such a condition when charging a hydrocarbon fraction of very high

boiling point such as reduced crude, heavy virgin gas oil, heavy viscosity breaker gas oil, heavy coker gas oil and the like, a very high temperature is required. When highly active contact agents are employed at these elevated temperatures, overcracking of the charge occurs resulting in undesirable secondary decomposition reactions. However, when an only moderately active catalyst is employed, such as a member of class I, high temperatures may be employed without encountering secondary decomposition reactions or overcracking.

Contact materials falling in class II are relatively expensive but exhibit practically constant activity with long continued use. These contact agents are very sensitive to steam and are rapidly deteriorated thereby, particularly at elevated temperatures. These contact agents are highly active.

Contact materials falling in class III range from cheap natural materials to relatively expensive synthetic products. The activity of these materials remains constant with long continued use. They are practically unaffected by steam and are only moderately active which, as has been previously shown, is not necessarily disadvantageous.

As is known to those skilled in the art, the major disadvantage of catalytic cracking processes resides in the highly refractory cycle stocks produced. In the catalytic cracking of a hydrocarbon charge, the less refractory components thereof are preferentially attacked and the resulting cycle stock, even though of the same boiling range or even of slightly lower average boiling point than that of the charge, is scarcely affected if again passed over the catalyst. In once through catalytic cracking it is difficult, as a rule, to obtain much more than 40% gasoline. This leaves a large amount of refractory cycle stock which will give a little additional gasoline on repassage over the catalyst but the yield is so low that recycling to completion, as is commonly done in thermal cracking processes, is impossible or highly undesirable.

Many attempts have been made to obviate the disadvantages arising through the highly refractory nature of the cycle stocks obtained in catalytic cracking operations. For example, it has been suggested that cycle stocks obtained during once through catalytic cracking be cracked thermally, recycling to completion. Obviously, this method of operation means a return in part to thermal cracking with all the disadvantages thereof. Certain operating schemes have been employed in catalytic cracking to accomplish the

same result. For example, the cycle stock obtained in once through catalytic cracking, either at low temperature with a highly active catalyst or at higher temperature with a moderately active catalyst (depending primarily on the boiling range of the charge) is again catalytically cracked once through in a second zone using a highly active catalyst at high temperature. Another such scheme involves the once through catalytic cracking of a comparatively low boiling charging stock at low temperature with a highly active catalyst, admixing the resulting cycle stock with a comparatively high boiling charging stock and processing the mixture at high temperature with a moderately active catalyst. A more complicated but better arrangement involves catalytically cracking a comparatively low boiling charging stock at low temperature with a highly active catalyst, separately catalytically cracking a comparatively high boiling charging stock at high temperature with a moderately active catalyst, admixing the cycle stocks from the two catalytic cracking zones and catalytically cracking the resulting blend in a third zone at high temperature with a highly active catalyst. These, and other similar schemes, while more or less useful, are obviously not perfect since in all of them recycling to completion is impossible or highly undesirable.

It has also been suggested to solvent extract refractory cycle stocks from catalytic cracking, discarding the extract and recycling the raffinate to the catalytic cracking zone. Obviously, this scheme does not provide for the complete utilization of cycle stock. In my copending application, S. N. 334,741, filed May 13, 1940, now U. S. Patent 2,312,445, issued March 2, 1943, a process is disclosed wherein cycle stock from catalytic cracking is catalytically hydrogenated, the resulting liquid product being recycled to the catalytic cracking zone. While by this process complete utilization of cycle stock is achieved, the apparatus required is rather complicated and quite expensive. Also a source of hydrogen must be provided.

I have found that by partially oxidizing refractory cycle stock from catalytic cracking operations or from other sources, the resulting partially oxidized liquid hydrocarbons become quite amenable to catalytic cracking. Such partially oxidized liquid hydrocarbons may be catalytically cracked in the presence of contact agents selected from any of the three classes previously mentioned. However, with catalysts from class I, the usual more or less rapid permanent decline in activity with continued use is observed, sometimes in an enhanced degree in comparison with the same catalysts when employed in processing non-oxidized stocks. With respect to catalysts from class II, a fairly rapid and permanent decline in activity is observed when these are employed in the catalytic cracking of partially oxidized liquid hydrocarbons. On the other hand, the catalysts of class III have been found to be eminently suitable for use as contact agents in the catalytic cracking of partially oxidized liquid hydrocarbons, exhibiting a satisfactory activity, especially at high temperatures, which remains constant or practically so with long continued operations.

I attribute the excellence of class III contact agents, when used as catalysts in the catalytic cracking of partially oxidized liquid hydrocarbons, to the fact that these materials are insensitive to steam. During the catalytic cracking

of partially oxidized liquid hydrocarbons, it is evident that steam is formed which presumably permanently destroys the activity of class I and II contact agents with more or less rapidity but which has no effect on the contact agents of class III. While this explanation is believed to be correct, it is to be understood that it represents theory only and the scope of the instant invention is in no way to be limited thereby.

Many silica-magnesia complexes are suitable for the purposes of this invention and many methods are available for the preparation thereof. Selected illustrative examples of such catalysts and their preparation are presented below in Examples 1 to 23.

One method for the preparation of silica-magnesia complexes suitable for the purposes of the instant invention involves double decomposition as exemplified by a process wherein a suitable soluble silicate, e. g. sodium silicate, is allowed to react with a soluble magnesium compound, e. g. magnesium sulfate or magnesium chloride. Preferably a solution of the soluble silicate is added slowly, with agitation, to a solution of the soluble magnesium compound. If the addition is too rapid or if the reaction mixture is not agitated, local spots of high alkalinity develop which result in the production of zeolitic type precipitates from which it is difficult or impossible to remove alkali metal compounds by washing. These zeolitic type materials are not as suitable for the purposes of the instant invention as are silica-magnesia complexes free from alkali metal compounds. For the same reason, it is inadvisable to add the solution of the magnesium salt to the soluble silicate solution since by this procedure it is almost impossible to avoid formation of zeolitic type compounds.

If desired, the silica-magnesia ratios of the complexes formed may be varied over wide limits by use of alkali metal silicates of varying alkali metal oxide-silica ratios. This is illustrated in Examples 1 to 3 below. A similar result may be accomplished by keeping the alkali metal oxide-silica ratio constant and using a solution of a magnesium salt containing more or less acid so that the anion of the magnesium salt plus the anion of the acid is stoichiometrically equivalent to or in slight excess over the alkali metal oxide of the soluble silicate.

Example 1

To 25 liters of a solution containing a total of 800 g. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ there were added over a period of four hours, with stirring, 1.93 liters of a solution containing 376 g. Na_2SiO_3 . The resulting precipitate was separated by filtration and was washed by making into a slurry with water and filtering, this washing operation being repeated several times. The final product contained 38.5% magnesia and 61.5% silica on the water free basis.

Example 2

To 25 liters of a solution containing a total of 800 g. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ there were added over a period of four hours, with stirring, 2.81 liters of a solution containing 466 g. $\text{Na}_2\text{O} \cdot 1.5\text{SiO}_2$. The resulting precipitate was separated by filtration and was washed by making into a slurry with water and filtering, this washing operation being repeated several times. The final product contained 29.5% magnesia and 70.5% silica on the water free basis.

Example 3

To 25 liters of a solution containing a total of 800 g. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ there were added over a period of four hours, with stirring, 6.18 liters of a solution containing 797 g. $\text{Na}_2\text{O} \cdot 3.25\text{SiO}_2$. The resulting precipitate was separated by filtration and was washed by making into a slurry with water and filtering, this washing operation being repeated several times. The final product contained 15.5% magnesia and 84.5% silica on the water free basis.

In preparations made in accord with the above examples one can wash initially with slightly acidulated water followed by several washings with pure water. If this procedure is used, then it is not so necessary to fix the anion of the magnesium salt (or the anion of the magnesium salt plus the anion of an acid added thereto) stoichiometrically equal to or greater than that of the alkali metal oxide of the soluble silicate. Any alkaline complex formed under such conditions will be converted over to the acid form by washing with acidulated water. Even so, silica-magnesia complexes formed in this way are rarely equal in activity to those originally precipitated in the acid form. Also, this method of washing is very apt to give trouble because of the precipitate peptizing. Occasionally, even in the ordinary washing method, peptizing occurs. Whenever the precipitate shows a tendency to peptize it may be coagulated by washing with a dilute solution of a non-reactive electrolyte, preferably one easily removable in subsequent operations such as, for example, ammonium chloride or ammonium nitrate. As will be obvious to those skilled in the catalytic art, when washing the precipitate suitable tests are applied to the filtrate from time to time so as to follow the removal of undesired components.

Precipitates formed in accordance with Examples 1 to 3 may be dried to form a powder which may then be formed into pellets as usual, employing a binder such as Volclay bentonite, if desired. Or, the dry powder may be mixed with wet precipitate and the moist mixture extruded (with a binder if desired) to form spaghetti which is cut to length and dried. Alternatively, the washed but undried precipitate may be suspended in water to give about 7.5% solids and treated with a small amount of a preferably volatile acid, such as carbonic, acetic or hydrochloric, to peptize the precipitate. The resulting thixotropic gel is then cast into pans and slowly dried to form hard particles of appreciable size.

A somewhat different scheme of preparation is used in Example 4. Here the sodium silicate solution is made definitely acid and a magnesium salt solution is added to the resulting rather stable sol. The mixture is then precipitated with an excess of ammonia. Ammonia does not have any deleterious effect on catalyst activity, presumably because it is not a fixed alkali and hence is completely removed during subsequent processing.

Example 4

One liter of a solution containing 34.3% by weight of $\text{Na}_2\text{O} \cdot 3.5\text{SiO}_2$ was diluted with 6 volumes of water. The thus diluted water glass solution was vigorously stirred and 600 cc. concentrated ($d=1.19$) hydrochloric acid were added rapidly. To the resulting silica sol was added 2000 g. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in 1500 cc. water, following which 1000 cc. concentrated ammonia solution ($d=0.88$) were added slowly with stirring. After

standing over night, the resulting precipitate was separated by filtration and was washed by being made into a slurry with water and filtering, this washing operation being repeated several times. The final product contained 31% magnesia and 69% silica on the water free basis.

By a modification of the process of Example 4 no ammonia is required. In this modification the sodium silicate solution is treated with but little more, say 5% excess, acid than is stoichiometrically equivalent to the sodium oxide of the silicate. A magnesium salt solution is added and the desired complex precipitates, a process that may be accelerated to completion by boiling.

By a slight change in the modification described in the previous paragraph, a somewhat more satisfactory catalyst is obtained. The sodium silicate solution is made but slightly acid as before and then is aged prior to treatment with the solution of the magnesium compound. The time of aging depends upon the exact acidity of the slightly acid sodium silicate solution. If the pH is 6, the acidified sodium silicate solution is aged 30 minutes or more, if the pH is 5, the acidified sodium silicate solution is aged 2.5 hours or more.

Example 5

Catalysts made in accordance with the teachings of my copending application, S. N. 313,898, filed January 15, 1940, now U. S. Patent 2,323,728, issued July 6, 1943, especially Examples 1B, 2B and 3B.

Example 6

Seven hundred and fifty cc. of ethyl orthosilicate are diluted with 437.5 cc. 95% ethanol following which 14 cc. water are added. After standing 24 hours, a solution of 81 g. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in 127.5 cc. water is added slowly with agitation. The resulting precipitate is washed and dried as usual.

Example 7

One mole of silicon tetrachloride was diluted with an equal volume of absolute ethanol. This solution was added to a solution prepared by dissolving one half mole of anhydrous magnesium chloride in 200 cc. absolute ethanol. The resulting mixture was treated with an excess of ammonium hydroxide, added slowly with agitation. The resulting precipitate was separated and washed as usual.

Satisfactory catalysts can also be prepared by first forming active silica and then uniting this with magnesia. Active silica suitable for the purpose may be made by a wide selection of methods, some of which will be briefly described.

Silica sol, silica hydrogel or silica gel can conveniently be made from alkali metal silicates. Five hundred cc. of sodium silicate solution containing 8.85% sodium oxide and 28.5% silica are diluted with an equal volume of water. The thus diluted solution and 625 cc. 6N sulfuric acid are simultaneously added, at rates proportional to their respective volumes, to a well agitated reaction vessel. A clear silica sol results. This sets to a hydrogel in 2 to 4 hours, depending upon the temperature. The resulting hydrogel is passed through a 4 mesh, acid proof sieve and the hydrogel particles resulting are thoroughly washed. This may be accomplished by covering them with water, allowing to stand for say 30 minutes and then removing the water, this washing operation being repeated several times, for

example, 6 to 8 times. The washed hydrogel may be dried to give silica gel.

A somewhat more satisfactory active silica from some points of view can be made by allowing the hydrogel to form at elevated temperatures, for example, 70° to 100° C. Since the time of set of acidified sodium silicate solutions decreases with extreme rapidity with increasing temperature, a reaction mixture prepared in accordance with the above directions usually has an inconveniently short time of set at high temperatures. This time of set can be lengthened by using less acid than specified above, for example, 60 to 75% as much. Catalysts made from high temperature active silica are somewhat more easily regenerated than those prepared from active silica made at room temperature.

It is advisable to prepare active silica from acidified sodium silicate solutions but this is not absolutely essential. If desired, a sodium silicate solution may be brought almost but not quite to neutrality. The alkaline hydrogel forms with extreme rapidity. This may be washed as previously described, using however slightly acidulated water in the first few washings. By this procedure a rapid time of set is obtained with the expenditure of a minimum amount of total acid.

Active silica prepared as above may be dried by a variety of methods. For example, the silica sol may be pumped through an atomizer into a heated room or heated gas stream to form silica gel in an extremely fine state of subdivision, the particles then being washed salt free. The same type of product may be made by injecting the sol into boiling liquid immiscible with water, for example, boiling kerosene. When these drying methods are employed it is advantageous to use a volatile acid, for example, hydrochloric or acetic, in making the sol. Hydrogels, preferably after washing, may be dried by adding to a boiling liquid immiscible with water, for example boiling kerosene. Extremely fine active silica particles result.

If desired, washed hydrogel may be spread out on trays and dried in an oven as usual. This produces very fine active silica although the particle size is larger than obtained when the processes described immediately above are used. Frequently, silica gel particles of appreciable size are desired. Such a product may be obtained in several ways. For example, the washed hydrogel, when mechanically worked, knits itself together again into a thixotropic gel. This may be poured onto trays and dried in an oven to give large particles, especially if the drying proceeds slowly at rather low temperature. Or, the silica sol may be poured onto trays to form layers about one inch thick. When the sol has set, the hydrogel is partially dried at a rather low temperature (say 150° F.) in a rapid stream of air. By the time the water content has reached 50 to 60% salts begin to effloresce from the partially dried hydrogel particles which are now about ¼ inch thick and one inch across. Drying is stopped and the particles are covered with water and allowed to stand for say 30 minutes following which the water is removed and replaced with fresh. This operation is repeated several times, for example, 6 or 8 times. The washed, partially dried hydrogel particles are now completely dried to give a silica gel, practically all of which is retained on an 8 mesh screen.

Active silica can also be made from ethyl orthosilicate. Seven hundred and fifty cc. of ethyl

orthosilicate are diluted with 437.5 cc. 95% ethanol following which 14 cc. of water are added. After standing 24 hours, 127.5 cc. additional water are added and the resulting reaction mixture is evaporated slowly to give pure silica gel.

A satisfactory active silica can also be made by slowly adding, with agitation, ammonium hydroxide to silicon tetrachloride, preferably diluted with some solvent such as ethanol. The precipitate is washed and dried as usual.

Active silica, prepared as above or otherwise, may be united with magnesia by any one of a variety of methods, some of which will now be briefly described.

Example 8

Two hundred and seventy five g. of particulate silica gel (from sodium silicate) are added to 2500 cc. water containing 20.4 g. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The reaction mixture is brought to incipient boiling and is held for two hours with occasional shaking following which the activating solution is decanted and the solid washed 6 times, using a total of 3000 cc. of water. The washed catalyst is then dried. It carries a small amount of adsorbed magnesia.

Example 9

Washed silica hydrogel (from sodium silicate) is covered with a 10M solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the mixture is allowed to stand several hours, preferably over night. Excess solution is removed by draining and the impregnated hydrogel is dried at a relatively low temperature (180° F.). After drying, the temperature is raised to decompose the nitrate.

Example 10

Six hundred and fifty grams (dry basis) of washed silica hydrogel and 500 g. (dry basis) of freshly precipitated, undried washed magnesium hydroxide are mixed and worked mechanically to form a homogeneous, somewhat thixotropic gel. This is poured onto trays and slowly dried at low temperature.

Example 11

To a very slightly acid silica hydrosol (containing 650 g. silica on the dry basis) are added 500 g. (dry basis) of freshly precipitated, undried magnesium hydroxide. The suspension is stirred and brought to a boil, agitation at the boiling point being continued for four hours. The resulting product is removed by filtration, washed and dried.

Example 12

Six hundred and fifty g. of finely divided silica gel are mixed with 300 g. (dry basis) of freshly precipitated, washed but undried magnesium hydroxide. The mixture is mechanically homogenized, is extruded, cut to length and dried.

Example 13

Three hundred and fifty g. of dry, active magnesia are added to 650 g. (dry basis) of washed silica hydrogel. The mixture is mechanically homogenized, is extruded, cut to length and dried.

Example 14

Three hundred and fifty g. of dry, active magnesia and 650 g. of finely divided silica gel are mixed together in a ball mill for several hours. The resulting mixture is pelleted to form the final catalyst.

Example 15

Six hundred and fifty g. (dry basis) of washed silica hydrogel and 210 g. of activated, finely divided magnesium metal are mixed together thoroughly, spread out on trays and dried. The magnesium metal is preferably in activated form; activation may be accomplished by forming a superficial bi-metallic couple on the individual metal particles using an element far from magnesium in the E. M. F. series, for example, mercury.

Certain proprietary silica-magnesia complexes are also suitable contact agents for the purposes of the instant invention. Among these may be named:

Example 16

This silica-magnesia complex has been described in my copending application, S. N. 300,390, filed October 20, 1939 now U. S. Patent 2,278,590, issued April 7, 1942.

Example 17

This silica-magnesia complex has been described in my copending application, S. N. 398,242, filed June 16, 1941.

Example 18

This silica-magnesia complex is prepared by the hydrothermal reaction of e. g. magnesium carbonate with silica, either alone or in the presence of an alkali, e. g. sodium carbonate or the hydrothermal reaction of e. g. magnesium carbonate with sodium silicate as described, for example, in U. S. Patents 1,945,534; 1,999,210; 2,203,614 and 2,173,085.

I have also found that numerous natural silica-magnesia complexes, for example, of the nature of sepiolite and the like, may be employed as contact agents in the practice of the instant invention. Among these may be mentioned the following:

Example 19

This silica-magnesia complex is the mineral known as coenite found, for example, at Clay City, Nye County, Nevada some nine miles north of Death Valley Junction, California. This mineral contains (dry basis, ex. CO_2) about 60% SiO_2 , 10% Al_2O_3 and 20% MgO and is quite efficient as a catalyst for the purposes of this invention, especially after a light acid treat.

Example 20

This silica-magnesia complex is the mineral known as eyerite found, for example, near Hector, California. This mineral contains (dry basis, ex. CO_2) about 35% SiO_2 , 30% CaO and 15% MgO . It is fairly efficient as a contact agent for the purposes of this invention, especially after a light acid treat. A much more efficient catalyst can be made by the hydrothermal reaction of finely ground eyerite with a solution of a magnesium salt, for example, magnesium chloride. In this treatment most of the lime is isomorphically replaced by magnesia. If desired, the mineral may be lightly acid treated either before or after or both before and after the hydrothermal reaction.

Satisfactory contact agents for the purposes of the instant invention may be made by rather drastically modifying certain natural materials. Illustrative of these methods, the following may be mentioned:

Example 21

This silica-magnesia complex is the material described in Example 3 of my copending appli-

cation, S. N. 317,770, filed February 7, 1940, now U. S. Patent 2,320,799, issued June 1, 1943.

Example 22

An argillaceous material of the montmorillonitic or bentonitic type in finely divided condition is subjected to hydrothermal reaction with a solution of a magnesium compound, for example, magnesium chloride. The resulting product is separated by filtration, washed and dried. The speed of the hydrothermal reaction may be greatly increased by conducting the reaction at superatmospheric pressure in an autoclave.

Example 23

An argillaceous material of the montmorillonitic or bentonitic type is drastically overtreated with acid whereby all or practically all of the activity as a cracking catalyst is lost. Six hundred and fifty g. (dry basis) of the resulting material is thoroughly mixed with 500 g. (dry basis) freshly precipitated, washed but undried magnesium hydroxide. The resulting mixture is then dried.

If desired, the silica-magnesia contact agents of the instant invention may be activated or treated with activators prior to use. The catalysts may be improved to a greater or less degree by giving them a light treatment at elevated temperatures with a dilute acid such as sulfuric acid or hydrochloric acid. Or, a small amount, for example 5% by weight, of hydrofluoric acid may be added to the catalyst and the resulting mixture gently calcined. These treatments seem to loosen the structure by removing a little magnesia and silica respectively. If desired, both treatments may be applied to a single catalyst.

Certain beneficial results follow the addition of selected activators in relatively small amounts to the catalysts of the instant invention. These activators may be added during the preparation of the catalysts or the finished catalysts may be impregnated with thermally decomposable salts of the activators following which the impregnated catalysts are calcined. Among activators found to be more or less beneficial may be mentioned boric oxide, beryllia, thoria, zirconia and alumina. About 5% or less of these activators, based on the weight of the catalyst, may be used.

Having now described by illustrative examples a representative selection of silica-magnesia catalysts suitable for the purposes of the instant invention, attention will be directed to a description of some illustrative process flows, employing the silica-magnesia catalysts of the instant invention, whereby the objects of the present invention are accomplished. For the better understanding of the instant invention, attention is directed to the accompanying sheets of drawings forming a part of this application and wherein

Figures 1 to 10 each comprise a diagrammatic representation of a process flow whereby the objects of the present invention are accomplished.

It will be noted that each one of the figures is in flow sheet form, such essential but conventional pieces of equipment as pumps, pipe still furnaces, reaction vessels, evaporators, flash and fractionating towers, heat exchangers, lines, valves, etcetera are for the most part not indicated. Also, the several possible methods for utilizing catalysts, for example, by means of fixed bed catalytic reactors, moving bed catalytic reactors, suspended catalytic reactors and the like are not shown. Additionally, there is no indica-

tion of the means employed to regenerate the catalysts periodically, for example, by burning carbon and/or carbonaceous residues from the active surfaces thereof. All of these details and many others are by now familiar to those skilled in the art. If further information on these or other similar points is desired, reference may be had to my copending application, S. N. 334,741, filed May 13, 1940 now U. S. Patent 2,312,445, issued March 2, 1943.

Example 24

Turning now to a more detailed consideration of Figure 1, a suitable hydrocarbon charge, for example, virgin gas oil, viscosity breaker gas oil, coker gas oil, reduced crude or the like, is subjected to partial oxidation. The resulting reaction products are separated, eliminating preferably the gas and water formed during the oxidation, together with, if desired, any material within the usual motor fuel range of boiling point. It is also preferable to eliminate as bottoms any small amount of tar like material that may have formed during the oxidation. The resulting partially oxidized liquid hydrocarbons, preferably of approximately the same boiling range as the hydrocarbon charge, are passed to the catalytic cracking zone wherein they are contacted with a silica-magnesia catalyst, similar, for example, to that described in Example 1. The resulting products are separated into gas, water, gasoline and cycle stock. If desired, cycle stock may be sent to storage through valve 1, valve 2 being closed, or it may be recycled to the partial oxidation zone through valve 2, valve 1 being closed.

The exact process of partial oxidation employed forms no part of the instant invention per se. Any one of the many processes described in the prior art may be employed. Briefly, one suitable method for accomplishing this partial oxidation comprises vaporizing a hydrocarbon fraction and passing the vapors at 450° to 750° F., more or less, to a reactor wherein they are contacted with 300 to 600 volumes of air (measured as gas at standard conditions) per liquid volume of oil charged. The air is preferably added portion-wise at a plurality of points along the reaction vessel which may contain an oxidizing catalyst if desired, such as vanadium oxide on pumice. The resulting products are worked up as usual and water (containing certain water soluble oxidation products) is separated from the partially oxidized liquid hydrocarbons, the resulting partially oxidized liquid hydrocarbons containing from 3 to 8% oxygen, more or less. When a relatively high boiling hydrocarbon fraction (such as a heavy gas oil or a reduced crude) is to be oxidized, vaporization may be aided with steam, recycle gas from the unit, or even a portion of the air to be used in the subsequent oxidation step.

More specifically illustrative of such an oxidation process is the following: A light virgin gas oil boiling in the range 375° to 650° F. was vaporized and passed at about 680° F. to the oxidizing reactor at a rate of 1.75 volumes liquid oil per hour per volume of reaction space. The reaction space was filled with pumice carrying vanadium oxide thereon. Just at the entrance of the oxidizer, air was added to the vaporized charge at a rate of 125 volumes of air (measured as a gas at standard conditions) per liquid volume of oil. Three additional injections of air, each in the volume previously stated were made, one at one quarter through the reactor, one at the midpoint of the reactor and one at three quarters through

the reactor. Temperature was so regulated that thermocouples immersed in wells embedded in the pumice mounted catalyst registered an average temperature of approximately 700° F. The reaction products were cooled and separated, the gas passing overhead from the separator being scrubbed in an absorber with a portion of the hydrocarbon liquid bottoms from the separator, the resulting rich absorber oil being mixed with the remainder of these bottoms. Water was separated from the partially oxidized liquid hydrocarbons and the latter were fractionated, taking overhead about 15% material falling in the gasoline boiling range and eliminating a trace of bottoms as tar.

The partially oxidized liquid hydrocarbons, formed as above described (after removal of material in the motor fuel boiling range and after removing the small amount of tar like material that was present), were brought to a temperature of 975° F. and passed over the silica-magnesia catalyst of Example 1 at a rate of 2.25 liquid volumes per hour per volume of reactor space. The gasoline yield was about 30%.

A separate portion of the partially oxidized liquid hydrocarbon charging stock prepared as above described was heated to 1000° F. and passed over the catalyst of Example 17 at a rate of 3.0 liquid volumes per hour per volume of catalyst reactor space. The resulting product contained 25% by volume of gasoline of 80 octane number.

Supplementary experiments were run in which cycle stock from the catalytic cracking of partially oxidized liquid hydrocarbons was recycled to the partial oxidation zone. By this procedure a fairly high ultimate yield of gasoline was obtained.

It will be obvious immediately that the above described process is of rather limited utility. Since virgin stocks as well as non-refractory processed stocks such as viscosity breaker gas oils and coker gas oils give satisfactory yields of gasoline on once through catalytic cracking, there is little if any utility in oxidizing them prior to catalytic cracking. If a refractory processed stock is available, for example, a distillate obtained from pressure tar, then the process of this example is of no little value. A process of more general utility is described in the example to follow which is:

Example 25

Referring to Figure 2, a suitable hydrocarbon charge, for example, virgin gas oil, viscosity breaker gas oil, coker gas oil, reduced crude or the like is catalytically cracked in a first catalytic cracking zone. The resulting products are separated into gas, gasoline and cycle stock, the latter being subjected to partial oxidation essentially as described in Example 24, or otherwise, as desired. The partially oxidized liquid hydrocarbons are vaporized and passed through a second catalytic cracking zone containing a silica-magnesia catalyst, similar, for example, to that described in Example 17. The products are separated into gas, water, gasoline and cycle stock. This last may be sent to storage through valve 1, valve 2 being closed, or it may be recycled to the partial oxidation zone through valve 2, valve 1 being closed.

In a typical operation by this procedure, using a light virgin gas oil (375° to 650° F. boiling range) as charge to the first catalytic cracking zone, the partially oxidized liquid hydrocarbons

resulting from processing the cycle stock from the first catalytic cracking zone, gave a once through gasoline yield of 26% when catalytically cracked in the second catalytic cracking zone at 1000° F. at a flow rate of 2.25 liquid volumes of charge per hour per volume of catalytic reactor space, the previously mentioned silica-magnesia contact agent being employed. By recycling cycle stock from this second catalytic cracking zone to the partial oxidation zone a high ultimate yield of gasoline is attained.

The nature of the contact agent in the first catalytic cracking zone is largely a matter of choice although certain rules in its selection are preferably to be followed. If the hydrocarbon charge is not refractory and is one of comparatively low boiling point, for example, with an A. S. T. M. endpoint of 750° F. or less, as exemplified by light virgin gas oil, light viscosity breaker gas oil or light coker gas oil then, preferably, a catalyst from class II is employed, for example, a synthetic silica-alumina catalyst of the prior art, many of which have been described in certain of my copending applications such as S. N. 277,580, filed June 6, 1939 now U. S. Patent 2,353,624, issued July 11, 1944; S. N. 277,885, filed June 7, 1939; S. N. 305,472, filed November 21, 1939; S. N. 305,473, filed November 21, 1939; S. N. 313,898, filed January 15, 1940 now U. S. Patent 2,323,798, issued July 6, 1943; S. N. 317,770, filed February 7, 1940 now U. S. Patent 2,320,799, issued June 1, 1943; S. N. 321,651, filed March 1, 1940; S. N. 334,741, filed May 13, 1940 now U. S. Patent 2,312,445, issued March 2, 1943; and S. N. 346,809, filed July 22, 1940 now U. S. Patent 2,366,217, issued January 2, 1945. When a highly active synthetic silica-alumina catalyst is employed, satisfactory conversions of non-refractory, easily vaporized charging stocks to gasoline are obtained at relatively low catalytic cracking temperatures and relatively high throughputs. A relatively low temperature is all that is necessary to achieve complete vaporization of such stocks so it is accordingly distinctly advantageous to use a catalyst exhibiting satisfactory activity at such a relatively low temperature. Catalysts of class I, as exemplified by Super Filtrol and Tonsil (both being trade names applied to acid treated argillaceous materials of a montmorillonitic or bentonitic type) may be employed but here the low activity is preferably overcome in part by either increasing the cracking temperature or decreasing throughput or both, preferably by decreasing the flow rate, since at relatively high catalytic cracking temperatures class I catalysts give poor product distributions, that is, a low ratio of desired conversion product to undesired conversion products. Also, class III catalysts, several examples of which have already been given, may be employed, but here again low activity is preferably overcome as mentioned above. Class III catalysts however have an advantage over class I catalysts in that the former usually give a better product distribution at relatively high catalytic cracking temperatures.

If, on the other hand, a non-refractory, comparatively high boiling hydrocarbon charge is employed, such as heavy virgin gas oil, reduced crude, heavy viscosity breaker gas oil or a heavy coker oil, a relatively high temperature is required for vaporization. If the highly heated vapors are passed over a class II catalyst, considerable over-cracking occurs, giving a poor product distribution which may however be overcome to a certain extent by increasing the throughput. Class I

catalysts are more satisfactory but they exhibit previously mentioned disadvantages. Class III catalysts, several of which have been mentioned in previous examples, are about ideal since they give a good product distribution and exhibit satisfactory activity at high temperatures. Furthermore, with class III catalysts, steam may be employed to aid in vaporization of the heavy stock without affecting catalytic activity.

When refractory cycle stocks are charged, for example, cycle stocks from either thermal or catalytic cracking processes, a class II catalyst is preferably employed, regardless of the boiling range of the charge. Due to the refractory nature of the charge, a high temperature and a highly active catalyst must be used to achieve relatively high conversions. Class III catalysts may be used but are less satisfactory due to their lower activity but if the charge is so high boiling that steam as a vaporization aid is almost essential then class III catalysts are preferable to class II catalysts.

To summarize the above the following table is presented:

Charging stock	Preferred catalyst
I. Non-refractory:	
A. Low boiling.....	Class II.
B. High boiling.....	Class III.
II. Refractory:	
A. Low boiling.....	Class II.
B. High boiling.....	Class II or III.

Obviously, the above represents generalities only since catalytic activities in the various classes overlap to a certain extent. In other words, the most active silica-magnesia catalyst is more active than the least active silica-alumina catalyst but in general one may say that class II catalysts are highly active while class III catalysts are only moderately active. In the above discussion, the term relatively low catalytic cracking temperature, contemplates the range of about 800° to about 925° F. while relatively high catalytic cracking temperature contemplates the range of about 925° to 1050° F.

Example 26

A light, non-refractory gas oil, for example, a light virgin gas oil, a light viscosity breaker gas oil or a light coker gas oil is contacted preferably with a synthetic silica-alumina catalyst at a relatively low catalytic cracking temperature as shown in Figure 3. Cycle stock from this operation is mixed, if desired, with a heavy gas oil of a non-refractory nature for example, a heavy virgin gas oil, a heavy viscosity breaker gas oil or a heavy coker gas oil introduced through valve 3, and the blend is contacted preferably with a silica-magnesia catalyst, for example, the contact agent of Example 10, at a relatively high catalytic cracking temperature in a second catalytic cracking zone. Cycle stock from this operation is partially oxidized as before described or otherwise and the resulting partially oxidized liquid hydrocarbons are contacted preferably with a silica-magnesia catalyst, for example, the contact agent of Example 10, at a relatively high catalytic cracking temperature in a third catalytic cracking zone. Cycle stock from this operation may be sent to storage through valve 1, valve 2 being closed, or it may be recycled to the partial oxidation zone through valve 2, valve 1 being closed.

Example 27

In Figure 4, light, non-refractory gas oil of the nature previously described, is contacted preferably with a synthetic silica-alumina catalyst at a relatively low catalytic cracking temperature while heavy, non-refractory gas oil of the nature previously described is separately contacted, preferably with a silica-magnesia catalyst, for example, that of Example 18, at a relatively high catalytic cracking temperature. Cycle stocks from these two operations are mixed and the resulting blend is partially oxidized as previously described or otherwise and the resulting partially oxidized liquid hydrocarbons are contacted in a third catalytic cracking zone with a silica-magnesia catalyst, for example, that of Example 18, preferably at a relatively high catalytic cracking temperature. Cycle stock from this operation may be sent to storage if desired through valve 1, valve 2 being closed, or may be recycled to the partial oxidation zone through valve 2, valve 1 being closed.

Example 28

In Figure 5, light, non-refractory gas oil of the nature previously described is contacted preferably with a synthetic silica-alumina catalyst at a relatively low catalytic cracking temperature. Heavy, non-refractory gas oil of the nature previously described is separately contacted, preferably with a silica-magnesia catalyst, for example, that of Example 1, at a relatively high catalytic cracking temperature. Cycle stocks from these two operations are mixed and the resulting blend is contacted preferably with a synthetic silica-alumina catalyst at a relatively high catalytic cracking temperature in a third catalytic cracking zone, whereby a substantial conversion of this refractory charge is achieved. Cycle stock from this third catalytic cracking zone is partially oxidized as previously described or otherwise and the resulting partially oxidized liquid hydrocarbons are contacted, in a fourth catalytic cracking zone, with a silica-magnesia catalyst, for example, that of Example 3, preferably at a relatively high catalytic cracking temperature. Cycle stock from this operation may be sent to storage through valve 1, valve 2 being closed, or may be recycled to the partial oxidation zone through valve 2, valve 1 being closed.

In several examples to follow, process flows that require less equipment but on the other hand are less flexible than those shown in Figures 1 to 5 are described.

Example 29

A non-refractory hydrocarbon charge of the nature previously described, in admixture with a material subsequently to be specified, is catalytically cracked over a silica-magnesia catalyst, for example, that of Example 16, preferably at a relatively high catalytic cracking temperature. Cycle stock from this operation is partially oxidized as previously described or otherwise and the resulting partially oxidized liquid hydrocarbons are mixed with the previously mentioned hydrocarbon charge to the catalytic cracking zone and the resulting blend is passed thereto. See Figure 6.

Example 30

In Figure 7, a light non-refractory gas oil of the nature previously described is catalytically cracked, preferably at a relatively low catalytic

cracking temperature and with a silica-alumina catalyst. Cycle stock from this operation, in admixture with a material subsequently to be specified and also, if desired, with a heavy, non-refractory gas oil of the nature previously described, introduced through valve 1, is catalytically cracked in a second catalytic cracking zone over a silica-magnesia catalyst, for example, that of Example 4, preferably at a relatively high catalytic cracking temperature. Cycle stock from this second catalytic cracking zone is partially oxidized as previously described or otherwise and the resulting partially oxidized liquid hydrocarbons are mixed with cycle stock from the first mentioned catalytic cracking zone, the blend being passed to the second catalytic cracking zone.

Example 31

In Figure 8, a light, non-refractory gas oil of the nature previously described is catalytically cracked, preferably at a relatively low catalytic cracking temperature with a silica-alumina catalyst. A heavy, non-refractory gas oil of the nature previously described in admixture with a material subsequently to be specified is charged to a second catalytic cracking zone employing a silica-magnesia catalyst, for example, that of Example 9, and preferably operating at a relatively high catalytic cracking temperature. Cycle stock from both catalytic cracking zones is blended and the mixture is partially oxidized as previously described or otherwise, the resulting partially oxidized liquid hydrocarbons being admixed with the aforementioned heavy gas oil following which the blend is passed to the second catalytic cracking zone.

Example 32

In Figure 9, a light, non-refractory gas oil of the nature previously described is catalytically cracked, preferably at a relatively low catalytic cracking temperature in the presence of a silica-alumina catalyst. Heavy non-refractory gas oil of the nature previously described, in admixture with a material subsequently to be specified, is processed in a second catalytic cracking zone in contact with a silica-magnesia catalyst, for example, that of Example 2, and preferably at a relatively high catalytic cracking temperature. Cycle stocks from both catalytic cracking zones are blended and the resulting mixture is passed to a third catalytic cracking zone operating at a high catalytic cracking temperature relatively and employing a silica-alumina catalyst. Cycle stock from this third catalytic cracking zone is partially oxidized as previously described or otherwise and the resulting partially oxidized liquid hydrocarbons are admixed with the heavy gas oil prior to passage to the second catalytic cracking zone previously mentioned.

Example 33

In Figure 10, a light, non-refractory gas oil of the nature previously described is catalytically cracked, preferably at a relatively low catalytic cracking temperature in the presence of a silica-alumina catalyst. Heavy, non-refractory gas oil of the nature previously described, is processed in a second catalytic cracking zone preferably at a relatively high catalytic cracking temperature in contact with a silica-magnesia cracking catalyst, for example, that of Example 1. Cycle stock from both catalytic cracking zones is blended and in admixture with a material subse-

quently to be specified is processed in a third catalytic cracking zone in contact with a silica-magnesia catalyst, for example, that of Example 1, preferably at a relatively high catalytic cracking temperature. Cycle stock from this third catalytic cracking zone is partially oxidized as previously described or otherwise and the resulting partially oxidized liquid hydrocarbons are admixed with the charge to the third catalytic cracking zone and the resulting blend is passed therethrough.

This application is in part a continuation of my copending application, S. N. 398,242, filed June 16, 1941.

While the instant invention has been described largely through the medium of certain specific examples thereof, it is to be understood that these examples are illustrative only and are in no way to be construed as limitations upon the spirit and scope of the invention.

I claim:

1. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point comprising admixing said hydrocarbons of higher boiling point with air, maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said hydrocarbons of higher boiling point, separating the resulting partially oxidized liquid hydrocarbons from materials boiling within and below the usual motor fuel range and contacting said partially oxidized liquid hydrocarbons with a silica-magnesia cracking catalyst at a cracking temperature for a time sufficient to effect substantial conversion of said partially oxidized liquid hydrocarbons to hydrocarbons of lower boiling point.

2. The method of claim 1, further characterized by the fact that cycle stock is separated from the products resulting from the catalytic cracking of said partially oxidized liquid hydrocarbons and is recycled to the partial oxidation zone.

3. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point comprising contacting said hydrocarbons of higher boiling point with a cracking catalyst at a cracking temperature for a time sufficient to effect substantial conversion of said hydrocarbons of higher boiling point into hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock, admixing said cycle stock with air, maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said cycle stock, separating the resulting partially oxidized cycle stock from materials boiling within and below the usual motor fuel range and contacting said partially oxidized cycle stock with a silica-magnesia cracking catalyst at a cracking temperature for a time sufficient to effect substantial conversion of said partially oxidized cycle stock to hydrocarbons of lower boiling point.

4. The method of claim 3, further characterized by the fact that cycle stock is separated from the products resulting from the catalytic cracking of said partially oxidized cycle stock and is recycled to the partial oxidation zone.

5. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point, comprising contacting said hydrocarbons of higher boiling point with a cracking catalyst in a first catalytic cracking zone at a cracking temperature for a time sufficient to ef-

fect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock, contacting said cycle stock with a cracking catalyst in a second catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock, admixing the cycle stock from said second catalytic cracking zone with air, maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said last-named cycle stock, separating the resulting partially oxidized cycle stock from materials boiling within and below the usual motor fuel range and contacting said partially oxidized cycle stock with a silica-magnesia cracking catalyst in a third catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said partially oxidized cycle stock to hydrocarbons of lower boiling point.

6. The method of claim 5, further characterized by the fact that cycle stock is separated from the products resulting from the catalytic cracking of said partially oxidized cycle stock and is recycled to the partial oxidation zone.

7. The method of claim 5, further characterized by the fact that said hydrocarbons of higher boiling point are of the nature of light gas oil.

8. The method of claim 5, further characterized by the fact that said hydrocarbons of higher boiling point are of the nature of light gas oil and that cycle stock is separated from the products resulting from the catalytic cracking of said partially oxidized cycle stock and is recycled to the partial oxidation zone.

9. The method of claim 5, further characterized by the fact that said hydrocarbons of higher boiling point are of the nature of heavy gas oil.

10. The method of claim 5, further characterized by the fact that said hydrocarbons of higher boiling point are of the nature of heavy gas oil and that cycle stock is separated from the products resulting from the catalytic cracking of said partially oxidized cycle stock and is recycled to the partial oxidation zone.

11. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point comprising contacting a first hydrocarbon fraction of higher boiling point with a cracking catalyst in a first catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock, admixing a second hydrocarbon fraction of higher boiling point which is of substantially different boiling range from that of said first hydrocarbon fraction with said cycle stock, contacting the resulting blend with a cracking catalyst in a second catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock, admixing the cycle stock from said second catalytic cracking zone with air, maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said last-named cycle stock, separating the resulting partially oxidized cycle stock from materials boiling within and below the usual motor fuel range and con-

tacting said partially oxidized stock with a silica-magnesia cracking catalyst in a third catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said partially oxidized cycle stock to hydrocarbons of lower boiling point.

12. The method of claim 11, further characterized by the fact that a third cycle stock is separated from the products resulting from the catalytic cracking of said partially oxidized cycle stock and is recycled to the partial oxidation zone.

13. The method of claim 11, further characterized by the fact that said first hydrocarbon fraction is of the nature of light gas oil and said second hydrocarbon fraction is of the nature of heavy gas oil.

14. The method of claim 11, further characterized by the fact that said first hydrocarbon fraction is of the nature of light gas oil and said second hydrocarbon fraction is of the nature of heavy gas oil and that a third cycle stock is separated from the products resulting from the catalytic cracking of said partially oxidized cycle stock and is recycled to the partial oxidation zone.

15. The method of claim 11, further characterized by the fact that said first hydrocarbon fraction is of the nature of heavy gas oil and said second hydrocarbon fraction is of the nature of light gas oil.

16. The method of claim 11, further characterized by the fact that said first hydrocarbon fraction is of the nature of heavy gas oil and said second hydrocarbon fraction is of the nature of light gas oil and that a third cycle stock is separated from the products resulting from the catalytic cracking of said partially oxidized cycle stock and is recycled to the partial oxidation zone.

17. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point, comprising contacting a hydrocarbon fraction of the nature of light gas oil with a cracking catalyst in a first catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock; contacting a hydrocarbon fraction of the nature of heavy gas oil with a cracking catalyst in a second catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock; combining the cycle stocks from said first and second catalytic cracking zones, admixing the resulting blend with air and maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said cycle stock blend, separating the resulting partially oxidized cycle stock blend from materials boiling within and below the usual motor fuel range and contacting said partially oxidized cycle stock blend with a silica-magnesia cracking catalyst in a third catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said partially oxidized cycle stock blend to hydrocarbons of lower boiling point.

18. The method of claim 17, further characterized by the fact that a third cycle stock is separated from the products resulting from the catalytic cracking of said partially oxidized cycle

stock blend and is recycled to the partial oxidation zone.

19. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point, comprising contacting a hydrocarbon fraction of the nature of light gas oil with a cracking catalyst in a first catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock; contacting a hydrocarbon fraction of the nature of heavy gas oil with a cracking catalyst in a second catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock; combining the cycle stocks from said first and second catalytic cracking zones, contacting the resulting blend with a cracking catalyst in a third catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said blend to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and a third cycle stock, admixing said third cycle stock with air and maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said cycle stock, separating the resulting partially oxidized cycle stock from materials boiling within and below the usual motor fuel range and contacting said partially oxidized cycle stock with a silica-magnesia cracking catalyst in a fourth catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said partially oxidized cycle stock to hydrocarbons of lower boiling point.

20. The method of claim 19, further characterized by the fact that a fourth cycle stock is separated from the products resulting from the catalytic cracking of said partially oxidized cycle stock and is recycled to the partial oxidation zone.

21. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point comprising contacting said hydrocarbons of higher boiling point, in admixture with a partially oxidized cycle stock subsequently to be described, with a silica-magnesia cracking catalyst at a cracking temperature for a time sufficient to effect substantial conversion of the charge into hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline, water and cycle stock, admixing said cycle stock with air, maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said cycle stock, separating the resulting partially oxidized cycle stock from materials boiling within and below the usual motor fuel range and adding said partially oxidized cycle stock to said hydrocarbons of higher boiling point.

22. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point comprising contacting a hydrocarbon fraction of higher boiling point with a cracking catalyst in a first catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock, contacting said cycle stock, in admixture with a partially oxidized cycle stock subsequently to be described, with a silica-magnesia cracking

catalyst in a second catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of the charge into hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline, water and a second cycle stock; admixing said second cycle stock with air, maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said second cycle stock, separating the resulting partially oxidized cycle stock from materials boiling within and below the usual motor fuel range and adding said partially oxidized cycle stock to the charge to said second catalytic cracking zone.

23. The method of claim 22, further characterized by the fact that said hydrocarbon fraction of higher boiling point is of the nature of light gas oil.

24. The method of claim 22 further characterized by the fact that said hydrocarbon fraction of higher boiling point is of the nature of heavy gas oil.

25. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point comprising contacting a first hydrocarbon fraction of higher boiling point with a cracking catalyst in a first catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock, admixing a second hydrocarbon fraction of higher boiling point and which is of substantially different boiling range than that of said first hydrocarbon fraction with said cycle stock, contacting the resulting blend in admixture with a partially oxidized cycle stock subsequently to be described, with a silica-magnesia cracking catalyst in a second catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of the charge into hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline, water and a second cycle stock, admixing said second cycle stock with air, maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said second cycle stock, separating the resulting partially oxidized cycle stock from materials boiling within and below the usual motor fuel range and adding said partially oxidized cycle stock to the charge to said second catalytic cracking zone.

26. The method of claim 25, further characterized by the fact that said first hydrocarbon fraction is of the nature of light gas oil and said second hydrocarbon fraction is of the nature of heavy gas oil.

27. The method of claim 25, further characterized by the fact that said first hydrocarbon fraction is of the nature of heavy gas oil and said second hydrocarbon fraction is of the nature of light gas oil.

28. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point comprising contacting a first hydrocarbon fraction of higher boiling point with a cracking catalyst in a first catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock; contacting a second hydrocarbon fraction of higher boiling point and which

is of substantially different boiling range than that of said first hydrocarbon fraction, in admixture with a partially oxidized cycle stock subsequently to be described, with a silica-magnesia cracking catalyst in the second catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, water, gasoline and cycle stock; combining the cycle stocks from said first and second catalytic cracking zones, admixing the resulting blend with air and maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said cycle stock blend, separating the resulting partially oxidized cycle stock blend from materials boiling within and below the usual motor fuel range and adding said partially oxidized cycle stock blend to the charge to the second catalytic cracking zone.

29. The method of claim 28, further characterized by the fact that said first hydrocarbon fraction is of the nature of light gas oil and said second hydrocarbon fraction is of the nature of heavy gas oil.

30. The method of claim 28, further characterized by the fact that said first hydrocarbon fraction is of the nature of heavy gas oil and said second hydrocarbon fraction is of the nature of light gas oil.

31. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point comprising contacting a first hydrocarbon fraction of higher boiling point with a cracking catalyst in a first catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock; contacting a second hydrocarbon fraction of higher boiling point and which is of substantially different boiling range than that of said first hydrocarbon fraction in admixture with a partially oxidized cycle stock subsequently to be described, with a silica-magnesia cracking catalyst in a second catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, water, gasoline and cycle stock; combining cycle stocks from said first and second catalytic cracking zones, contacting the resulting blend with a cracking catalyst in a third catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and a third cycle stock, admixing said third cycle stock with air and maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said third cycle stock, separating the resulting partially oxidized cycle stock from materials boiling within and below the usual motor fuel range and adding said partially oxidized cycle stock to the charge to said second catalytic cracking zone.

32. The method of claim 31, further characterized by the fact that said first hydrocarbon fraction is of the nature of light gas oil and said second hydrocarbon fraction is of the nature of heavy gas oil.

33. The method of claim 31, further characterized by the fact that said first hydrocarbon

fraction is of the nature of heavy gas oil and said second hydrocarbon fraction is of the nature of light gas oil.

34. A method of converting hydrocarbons of higher boiling point into hydrocarbons of lower boiling point comprising contacting a hydrocarbon fraction of the nature of light gas oil with a cracking catalyst in a first catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock; contacting a hydrocarbon fraction of the nature of heavy gas oil with a cracking catalyst in a second catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge into hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline and cycle stock; combining cycle stocks from

said first and second catalytic cracking zones, contacting the resulting blend, in admixture with partially oxidized cycle stock subsequently to be described, with a silica-magnesia cracking catalyst in a third catalytic cracking zone at a cracking temperature for a time sufficient to effect substantial conversion of said charge to hydrocarbons of lower boiling point, separating the resulting products into gas, gasoline, water and a third cycle stock, admixing said third cycle stock with air and maintaining the resulting mixture at an oxidizing temperature for a time sufficient to effect substantial partial oxidation of said third cycle stock, separating the resulting partially oxidized cycle stock from materials boiling within and below the usual motor fuel range and adding said partially oxidized cycle stock to the charge to said third catalytic cracking zone.

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