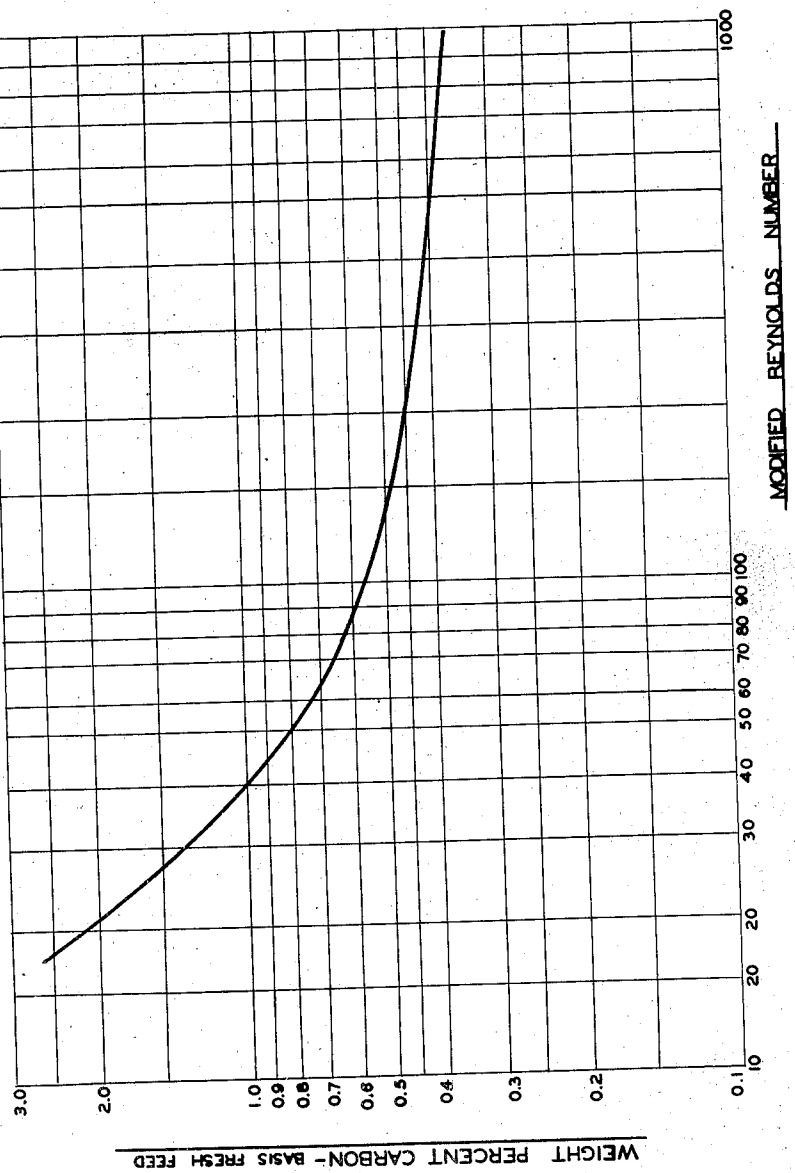
July 23, 1946. C. RICHKER ET AL 2,404,595

CATALYTIC CONVERSION OF HYDROCARBON OILS

Filed Dec. 16. 1942 2 Sheets-Sheet 1

FIG. 1



CHARLES RICHKER
DUBOIS EASTMAN
INVENTORS

BY R. J. Dearborn
attorney

July 23, 1946. C. RICHKER ET AL 2,404,595

CATALYTIC CONVERSION OF HYDROCARBON OILS

Filed Dec. 16, 1942 2 Sheets-Sheet 2

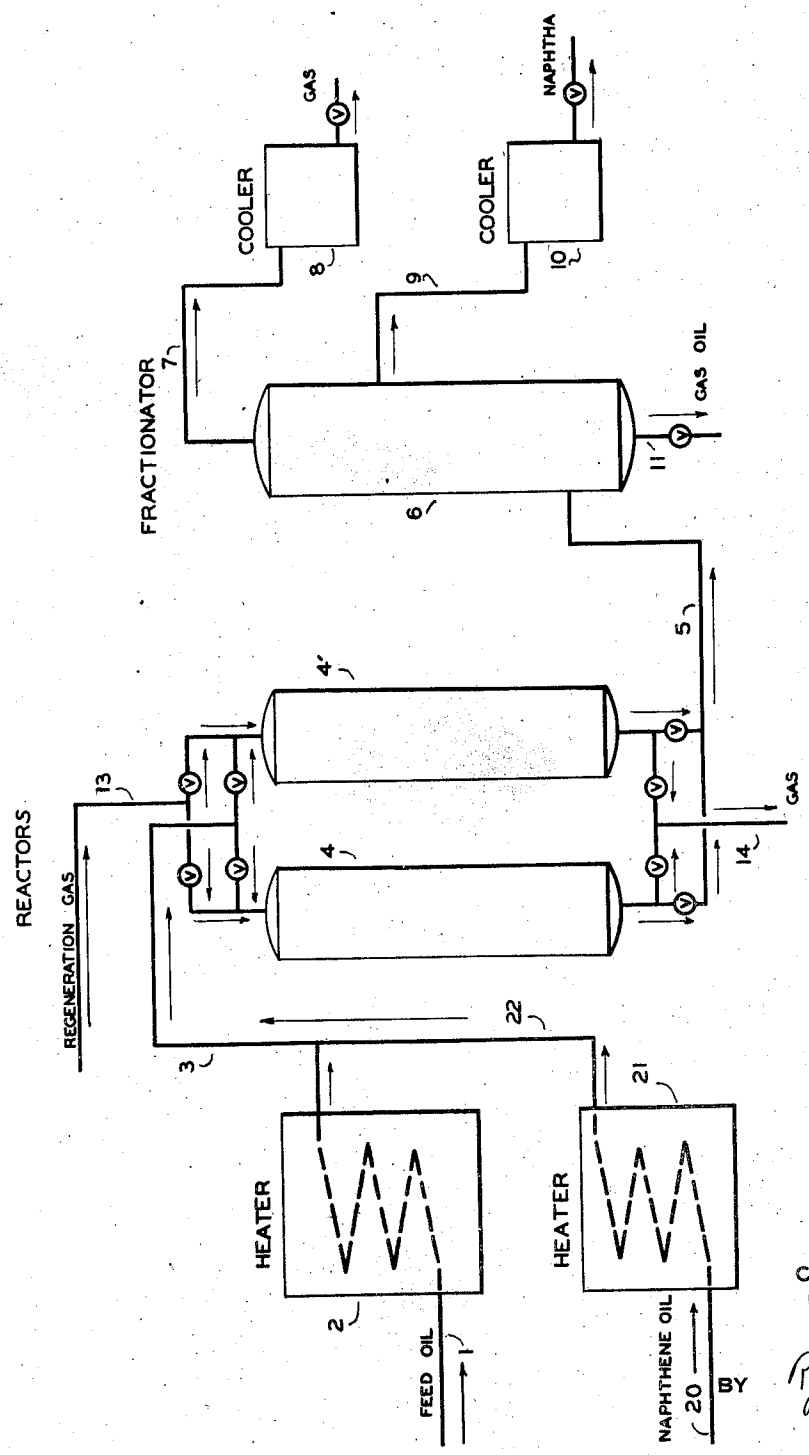


FIG. 2

CHARLES RICHKER
DUBOIS EASTMAN
INVENTORS

R. J. Dearborn
attorney

Patented July 23, 1946 2,404,595

UNITED STATES PATENT OFFICE

2,404,595

CATALYTIC CONVERSION OF HYDROCARBON OILS

Charles Richker and du Bois Eastman, Port Arthur, Tex., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

Application December 16, 1942, Serial No. 469,156

6 Claims. (Cl. 196—49)

1

This invention relates to the catalytic conversion of hydrocarbon oils to convert them to gasoline hydrocarbons suitable for motor fuel.

More specifically the invention contemplates a process wherein a feed hydrocarbon such as gas oil is rapidly heated to a cracking temperature in the range about 900° F. and above and then passed through a mass of active cracking catalyst maintained at the desired cracking temperature. The heating of the feed oil prior to contact with the catalyst is carried out under conditions such that there is substantial formation of gasoline hydrocarbons by pyrolytic action. The entire body of heated oil containing cracked gasoline hydrocarbons is then subjected to contact with an active cracking catalyst. Advantageously the heated hydrocarbon vapors are passed through a mass of the cracking catalyst at relatively high space velocity and under conditions of flow through the mass such that carbon deposition upon the catalyst is materially reduced. The flow of hydrocarbons through the contact mass is continued for a substantial period of time, for example, several hours and more, without interruption for catalyst reactivation. Thereafter, contact between feed hydrocarbons and used catalyst is discontinued so that the used catalyst may be reactivated.

In our pending application, Serial No. 383,900, filed March 18, 1941, for Catalytic conversion of hydrocarbon oils, which has matured as Patent 2,378,292, we have described heating the feed oil to a catalytic conversion temperature in a heating zone under conditions such that the soaking volume factor for this heating zone does not exceed about 1, the purpose being to avoid substantial cracking prior to contact with the catalyst.

One reason for avoiding thermal cracking prior to contact with the catalyst in Serial No. 383,900, now Patent 2,378,292, is to minimize the formation of unsaturated hydrocarbons and also to inhibit the formation of bodies which are readily converted to carbon upon contact with the catalyst. The absence of unsaturated hydrocarbons from the gasoline product is essential from the standpoint of producing a gasoline of high lead susceptibility which is desired in the case of gasoline to be used in aviation engines.

The process of the present invention has to do with the production of gasoline suitable for use in automobile engines so that a greater degree of unsaturated constituents may be tolerated in the cracked product. Accordingly, the present invention involves carrying out the preliminary heat treatment of the feed hydrocarbon

2

so that a substantial amount of cracking occurs prior to contact with the catalyst. The invention contemplates effecting the heating in a heating zone under conditions such that the soaking volume factor for the heating zone is in the range 0.5 to about 10. Under such conditions as much as 8 to 10% by volume of the feed hydrocarbons may be converted into gasoline hydrocarbons through pyrolytic action and without substantial carbon formation occurring in the heating zone.

An important advantage of this procedure is that the naphtha production capacity of a given contact mass of cracking catalyst is substantially increased. It appears that with as much as 8 to 10% of pyrolytic cracking occurring prior to contact with the catalyst the resulting catalytic naphtha is satisfactory as motor fuel. It will have a CFRM octane number of about 79 to 80, a lead susceptibility of 0.6 to 0.7 as measured on the Hebl, Rendal and Garton scale, and an acid heat value of about 160 to 170. The Hebl, Rendal and Garton scale is referred to in an article entitled "Effect of tetraethyl lead on octane number" by these authors, pages 187 to 191 inclusive, in the February, 1933, issue of Industrial and Engineering Chemistry.

The occurrence of substantial pyrolytic cracking prior to contact with the catalyst is usually regarded as undesirable from the standpoint of giving rise to excessive carbon deposition upon the catalyst as already intimated but in accordance with the present invention this difficulty is overcome by maintaining high rates of flow through the contact mass as will be described later in more detail.

Specifically the invention involves treating a gas oil type of feed stock which is relatively clean and of good color, namely, having a carbon residue of less than 0.2% and a color of less than 200 as measured on the Lovibond scale using a ½ inch cell. A stream of this feed oil is continuously passed through a tubular heating coil wherein the oil is vaporized and heated to a temperature in the range 900 to 1050° F. employing a soaking volume factor in the range 0.5 to as high as 10 as will be described below. The resulting vapors containing gasoline hydrocarbons formed as a result of pyrolytic action are passed through a stationary bed of active cracking catalyst at a space velocity in the range about 3 to 10 and higher (space velocity is volume of liquid oil at 60° F. per hour per volume of catalyst). The rate of flow of hydrocarbons through the contact mass is maintained such that it may be expressed

by reference to a modified Reynolds number in the range 100 to 1000.

The flow of hydrocarbon vapors through the contact mass is continued without interruption for at least 3 or 4 hours and may be continued for a substantially greater period of time as, for example, 10 hours or more, the weight ratio of gasoline to carbon being produced in the period beyond 3 to 4 hours being substantially greater than that obtaining during a period of 1 hour and less.

In other words the flow of hydrocarbons through the contact mass is continued until the carbon deposition upon the catalyst is in excess of 3% and advantageously amounts to about 5 to 20% by weight of the catalyst.

It has been found that with this amount of carbonaceous deposit upon the catalyst the catalyst can be reactivated in a relatively short period of time by passing therethrough reactivating gas containing 1 to 2% oxygen and effecting removal of substantially all of the heat of combustion as sensible heat in the effluent regenerating gas without exposing the contact mass to temperatures substantially in excess of 1200° F. The combustion under these conditions is confined to a relatively thin section which propagates from inlet to outlet of the reactor in the direction of gas flow through the reactor.

When the foregoing amount of carbon has been deposited upon the catalyst the stream of hydrocarbons is diverted to an adjoining reactor containing fresh or freshly reactivated catalyst. The offstream contact mass contaminated with carbonaceous deposit then undergoes reactivation which can be effected, if desired, in about ½ the length of time that the contact mass is maintained onstream.

The catalytic cracking reaction may be carried out under a pressure ranging from atmospheric to substantially above and preferably at a pressure of about 75 to 150 pounds so as to favor the hydrogen transfer effect.

The soaking volume factor may be determined by the method described in the aforesaid Serial No. 383,900, now Patent 2,378,292.

The following tabulation indicates the relationship between soaking volume factor and the yields of 400° F. end point naphtha having a 9.5 pound Reid vapor pressure expressed as volume per cent of feed oil. In each case a gas oil of about 30 A. P. I. gravity, boiling in the range 500 to 750° F., is vaporized and the vapors at a temperature of about 950° F., passed through a mass of active catalyst at a space velocity of 4 for an onstream period of about 3 hours without interruption for catalyst regeneration. The conditions of flow through the catalyst corresponded to a modified Reynolds flow number of approximately 260.

Table 1

Soaking volume factor	Thermal naptha	Catalytic naptha	Total naptha	Carbon, per cent by wt. of feed oil
0.2	0	27.2	27.2	0.75
0.4	0	27.2	27.2	0.82
0.5	0.8	27.2	28.0	0.85
0.7	1.8	27.2	29.0	0.9
1.0	2.8	27.2	30.0	0.95
3.0	6.0	27.2	33.2	1.1
6.0	8.0	27.2	35.2	1.2
10.0	9.5	27.2	36.7	1.3

The naphtha yields are expressed as volume per cent of the feed oil while the carbon yields are expressed as per cent by weight of the feed oil. It will be observed that with a soaking volume factor of 0.4 there is no naphtha produced as a result of thermal or pyrolytic action during the heating step prior to contact with the catalyst but with a soaking volume factor of 0.5 a small amount of naphtha does result due to thermal action; also as the soaking volume increases there is also an increase in the carbon production.

The rate of carbon deposition is also influenced by the flow conditions prevailing through the contact mass. The data reported in Table 1 above are representative of those obtained with a modified Reynolds flow number of approximately 260. Table 2 below indicated by how much the foregoing carbon yields are increased by operating with a flow number substantially below 100, namely, approximately 30.

Table 2

Soaking volume factor	Per cent carbon, basis feed with modified Reynolds flow number of 260	Per cent carbon, basis feed with modified Reynolds flow number of 30
0.2	0.75	1.8
0.4	0.82	2.0
0.5	0.85	2.1
0.7	0.9	2.2
1.0	0.95	2.4
3.0	1.1	2.8
6.0	1.2	3.0
10.0	1.3	3.4

As previously mentioned it is desirable to operate the process so that the yield of carbon deposited upon the catalyst amounts to about 5 to 20% by weight of the catalyst. A carbon yield of 1.3%, basis feed, amounts to about 19%, basis catalyst, when operating with a space velocity of 4 for an onstream period of about 3 hours. Consequently, in order to maintain the carbon deposited on the catalyst at not more than 20%, basis the catalyst, it is important to operate with a high Reynolds flow number. It also follows that by operating with a high flow number longer onstream periods are possible while still confining the carbon deposit on the catalyst to not in excess of the foregoing limit of 20%, basis the catalyst.

As disclosed in our pending application, Serial No. 409,488, filed September 4, 1941, for Catalytic conversion of hydrocarbon oils, the modified Reynolds number may be determined by the following equation reference to which appears in an article entitled "Pressure drop in packed tubes" by Chilton and Coburn, Industrial and Engineering Chemistry, August, 1931, volume 23, No. 8, pages 913 to 919:

$$N=\frac{DUp}{Z}$$

where

N is the modified Reynolds number;

D is the diameter of the catalyst particles in feet;

U is the average velocity in feet per second of fluid mixture flowing through the catalyst chamber, the chamber being regarded as empty;

p is the average density in pounds per cubic foot of fluid mixture flowing through the empty chamber at the temperature and pressure prevailing during the conversion period;

Z is the viscosity of the fluid mixture flowing through the empty chamber in pounds per foot

per second under the catalytic operating conditions of temperature and pressure.

The value of Z in the foregoing equation is determined by multiplying the absolute viscosity of the reaction mixture in centipoises by the factor 0.000672.

The viscosity of hydrocarbons at the temperature of conversion may be determined by reference to the nomograph on page 608, Industrial and Engineering Chemistry, vol. 28, No. 5 (article entitled "High temperature viscosities of liquid petroleum fractions," by Watson, Wien and Murphy).

Using this method of viscosity determination, the viscosity of the reaction mixture in the usual catalytic cracking operation will range from about 0.08 to 0.15 where a gas oil of about 30 API gravity and boiling in the range of 500 to 750° F. is being catalytically cracked at a temperature of about 950° F. to obtain about 30 to 40 per cent by volume of naphtha comprising gasoline hydrocarbons boiling up to 400° F. end point, basis gas oil.

For example, the characteristics of the gas oil feed and the naphtha produced therefrom are approximately as follows:

	Gas oil	Naptha
API gravity	30.0	60.0.
Specific gravity	0.874	0.739.
Viscosity in centistokes	2.3 at 210° F.	0.65 at 100° F.

Upon reference to the nomographic chart it will be found that a gas oil of the foregoing character will have a viscosity of about 0.19 centistoke at 950° F. while the naphtha will have a viscosity of about 0.09 centistoke at 950° F.

Viscosity in centistokes is converted to viscosity in centipoises by multiplying the former by the specific gravity of the hydrocarbon so that the high temperature viscosities of the gas oil and naphtha in terms of centipoises at the conversion temperature of 950° F. will be:

$0.19 \times 0.874 = 0.166$ centipoise (for gas oil)
$0.09 \times 0.739 = 0.066$ centipoise (for naphtha)

On the basis that the reaction mixture comprises 25% naphtha and 75% gas oil by weight, the weighted viscosity for such mixture would be about 0.141 centipoise. This ignores the presence of normally gaseous hydrocarbons in the reaction mixture so that if the reaction mixture be regarded as containing about 10% normally gaseous hydrocarbons by weight of the gas oil and also if the gaseous constituents be regarded as having zero viscosity at the reaction temperature, then the weighted viscosity for a mixture comprising 65% gas oil, 25% naphtha, and 10% gas would be about 0.124. Increasing the proportion of naphtha in the mixture, of course, effects a further reduction in the weighted viscosity.

It has been found that for practical purposes the effect of pressure in the range atmospheric to about 150 pounds per square inch gauge upon the viscosity may be ignored.

Variations of the fluid flow through the catalyst mass while maintaining the same space velocity may be accomplished by altering the depth and cross-sectional area of the catalyst chamber. Also the catalyst size may vary from about one-sixteenth to four-sixteenths of an inch in diameter.

The graphical relationship between the modified Reynolds number as determined above and

the yield of carbon expressed as per cent by weight of the feed hydrocarbon is shown in Fig. 1 of the drawings. The curve of Fig. 1 is plotted on log log paper and the points on the curve were determined in a series of runs employing a gas oil feed of the foregoing character with an active catalyst under substantially similar conditions of temperature, pressure, and space velocity but with different lineal velocities of hydrocarbon flow through the catalyst bed, the operations being carried out so that substantially no pyrolytic cracking occurred during the heating step.

In each of the runs from which the data were developed for Fig. 1, the gas oil was converted to 30% gasoline by volume or about 25% by weight of the feed oil, the gasoline being characterized by having a Reid vapor pressure of 9½ pounds and an end boiling point of 400° F. The space velocity was maintained at about 4 and the flow of hydrocarbons was continued through the catalyst without interruption for a period of 4 hours, following which the catalyst was reactivated in the usual manner and again placed onstream, the operation being repeated for a minimum of 5 cycles under each lineal velocity condition.

As indicated in Fig. 1, the curve is relatively flat in the range 100 and above while below this range it rises rather steeply toward the vertical. In the region below a modified Reynolds number of 100 the yield of carbon deposited on the catalyst increases quite rapidly, whereas in the region above 100 the rate of change in carbon deposition is relatively small with variation in the fluid flow through the bed. It will be observed that with a Reynolds number of about 20 the carbon amounts to approximately 2% by weight of the gas oil. 2% carbon, basis feed oil, amounts to about 38% carbon deposited based on the catalyst during the 4-hour onstream period. Since the gasoline obtained during this period amounted to 25% by weight of feed oil, the weight ratio of gasoline to carbon being produced with a modified Reynolds number of 20 is about 11 pounds of gasoline per pound of carbon.

On the other hand, when operating with a Reynolds number of 500, the carbon, basis feed, is 0.4% which corresponds to about 7.6% basis catalyst, the ratio of gasoline to carbon under these conditions being about 57 pounds of gasoline per pound of carbon produced.

As previously shown in Table 2, when operating with a soaking volume factor of 10 the carbon yield may amount to about 3.4% by weight of the feed oil with flow conditions corresponding to a Reynolds flow number of 30 and with an onstream period of only 3 hours. This would cause an excessively large amount of carbon deposit upon the catalyst; however, by operating the reactor so that a much higher Reynolds flow number prevails, the carbon deposit upon the catalyst may be reduced by nearly 60% and thus will not exceed 20% by weight of the catalyst.

In the foregoing experiments a synthetic silica-alumina-zirconia type of catalyst was employed; however, it is contemplated that other active cracking catalysts may be employed. Various acid treated and metal substituted clays, such as Super-Filtrols are satisfactory. Likewise, the acid treated and metal substituted natural or artificial zeolites such as Doucil can be used. In general a catalyst is employed which is stable at high temperatures of the order of 1400 to 1600° F. as determined by calcining in a muffled furnace at that temperature, and which is a measure or indication of the ability of the

catalyst to maintain its activity under the customary temperatures of reactivation of the order of 1100 to 1400° F. as measured by thermocouples within the catalyst bed during the reactivation period. It is preferred to employ a catalyst which is substantially free from alkali and alkaline earth metals.

An advantageous form of the catalyst comprises rings or small cylinders as, for example, Raschig rings of about one-quarter inch diameter, having a wall thickness of about one-eighth inch. With this type of catalyst it is possible to employ catalyst beds of 10 to 30 feet without encountering excessive pressure drop.

An active cracking catalyst suitable for the purpose of this invention is one of such activity that, upon passing gas oil of about 500 to 700° F. boiling range in vapor form through a stationary mass of the catalyst in particle form at a temperature of about 950° F. and with a space velocity of about 2, for a period of about 2 hours without interruption, the yield of debutanized 400° F. end point gasoline obtained amounts to at least 10% by volume of the gas oil, the gasoline having a clear octane number of at least about 77 to 78 CFRM. This is to be contrasted with a comparatively inactive material such as pumice which under the same conditions gives a gasoline yield of only about 4.9%, and which is not more than is obtained by passing the same gas oil vapor through an empty catalyst case under the same conditions of temperature and space velocity.

The foregoing catalyst are also useful in effecting an isoforming action upon the thermally cracked constituents of the feed vapors passing to the catalyst chamber.

By way of illustrating the method of flow which may be employed with a fixed bed catalytic cracking process, reference will now be made to Fig. 2 of the drawings.

As indicated in Fig. 2, a feed oil, such as gas oil, is obtained from a source not shown and conducted through a pipe 1 to a heater 2 having a tubular heating coil through which the feed oil passes during vaporization and heating to the conversion temperature. Thus, the oil is vaporized and raised to a temperature of about 975 to 1000° F., the heating operation being controlled so that the soaking volume factor for that portion of the heater wherein the oil is at 800° F. and above, is within the range 0.5 to 10. The heated vapors are immediately passed from the heater through a pipe 3 to the upper portion of catalyst cases 4 or 4'.

The catalyst cases comprise vertical vessels containing a mass of solid catalytic material, such as a synthetic silica-alumina-zirconia catalyst comprising about 80% by weight SiO_2, 10% Al_2O_3 and 10% ZrO_2. Such a catalyst is an active cracking catalyst having the characteristics previously described. The catalyst may be in the form of powder, pellets, particles, rings, etc.

The vessels are manifolded together as indicated to permit maintaining one vessel onstream while the other is offstream undergoing regeneration. Thus, vessel 4 may be regarded as onstream in which case the heated hydrocarbon vapors pass downwardly through the catalyst mass within the vessel during which passage the hydrocarbons undergo conversion. The products of reaction are removed from the bottom of the vessel 4 and are drawn off through a pipe 5 leading to a fractionator 6.

In the fractionator 6 converted hydrocarbons

are subjected to fractionation to form a light fraction comprising normally gaseous hydrocarbons which may be removed through a pipe 7 and cooler 8. A side fraction comprising naphtha hydrocarbons may be removed through pipe 9 and cooler 10 while a higher boiling liquid fraction comprising gas oil may be drawn off through a pipe 11 for such further disposition as may be desired.

The flow of hydrocarbons through the vessel 4 is continued for a period of several hours and may be continued for a period of 4 to 8 hours or even more until it becomes necessary to regenerate the catalyst.

When regeneration becomes necessary the flow of hydrocarbon vapors is switched from the vessel 4 to the vessel 4' containing fresh or regenerated catalyst. This is accomplished by adjusting the valves in the pipe manifolds leading into and away from the vessels 4 and 4'. The vessel 4 is then offstream during which time the catalyst contained therein undergoes regeneration. Regeneration is advantageously accomplished by passing through the contact mass a reactivating gas containing about 1 to 2% oxygen in sufficient volume and at such a temperature that substantially all of the heat of combustion is removed as sensible heat in the effluent gas without exposing the contact mass to temperatures substantially in excess of 1200° F.

The regenerating gas is introduced from a source not shown through a pipe 13 and is discharged from the contact mass through a pipe 14 advantageously leading to a waste heat boiler wherein sensible heat is removed from the gas following which a portion of the cooled gas at a temperature which may range from 750 to 950° F. is recycled.

While not shown in the drawings, it is contemplated that a portion of, or any fraction of the reaction products being discharged through the pipe 5 may be recycled through the onstream reactor, with or without reheating, as a means of maintaining a high rate of fluid flow through the reactor. The material so recycled may be a distillate or a gaseous fraction separated from the products of the cracking reaction.

According to a further modification of the process naphthene base hydrocarbons may be charged directly to the reactor, advantageously in a heated condition, to act as hydrogen donors for the olefins in the thermal naphtha formed in the heater 2. This naphthene stock may be naphtha or gas oil derived from Gulf Coastal crudes. It may be separately heated under conditions of low soaking volume factor, i. e., in the range 0.1 to 0.05 and below, and not in excess of 0.5, so that no thermal cracking occurs prior to contact with the catalyst.

Thus referring to Fig. 2, naphthene oil, from a source not shown, may be charged through a pipe 20 to a heater 21 wherein it is heated under conditions of low soaking volume factor to a temperature corresponding substantially to that of the oil passing from the heater 2. The heated naphthene oil, in vapor form, is passed through a pipe 22 which communicates with the pipe 3.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In the catalytic cracking of hydrocarbon oil

to produce gasoline involving alternate periods of conversion and reactivation, the method comprising continuously passing through a heating zone a stream of feed hydrocarbon oil having a carbon residue of less than 0.2% and a color of less than 200 on the Lovibond ½'' cell, heating and vaporizing the oil stream during passage through the heating zone in the absence of a catalyst so as to convert about 8 to 10 volume per cent of the oil into thermally cracked gasoline hydrocarbons, thereafter passing the heated vapors at a temperature in the range 900 to 1050° F. and at a space velocity in the range about 3 to 10 through a catalytic cracking zone and in direct contact with a substantially stationary mass of granular adsorbent catalyst of such activity that upon passing gas oil vapor through the mass at a temperature of about 950° F. and with a space velocity of about 2 for about two hours without interruption the cracked gasoline so obtained amounts to at least 10% by volume of the gas oil and has an octane number of at least about 77 to 78 CFRM, maintaining a rate of hydrocarbon flow through said mass such that the modified Reynolds number is in the range 100 to 1000, continuing without interruption the hydrocarbon flow through the mass for a conversion period of about three to ten hours until carbonaceous deposit formed on the catalyst amounts to about 5 to 20% by weight of the catalyst and such that the weight ratio of gasoline to carbon being produced in the period beyond three to four hours is substantially greater than that obtaining during a period of one hour and less, thereafter discontinuing the flow of hydrocarbons through the mass and reactivating the catalyst mass in situ, by contact with a flowing stream of combustion gases containing about 1 to 2% oxygen, and effecting removal of substantially all heat of combustion as sensible heat in the effluent gas without exposing the mass to temperatures substantially in excess of 1200° F.

2. The method according to claim 1 in which naphthene hydrocarbons heated to the reaction temperature without substantial cracking are added to the feed hydrocarbon vapors passing from the heating zone to the catalytic cracking zone.

3. The method according to claim 1 in which virgin naphthene oil heated to the reaction temperature without substantial cracking is added to the heated feed hydrocarbons prior to contact with the catalyst.

4. The method according to claim 1 in which the catalytic cracking reaction is effected in the presence of naphthene hydrocarbons which have been separately heated to the reaction temperature without substantial cracking.

5. In the catalytic cracking of hydrocarbon oil to produce gasoline, the method comprising passing through a heating zone a stream of feed hydrocarbon oil having a carbon residue of less than 0.2% and a color of less than 200 on the Lovibond ½'' cell, heating and vaporizing the oil stream during passage through the heating zone

in the absence of a catalyst so as to convert about 8 to 10 volume percent of the oil into thermally cracked gasoline hydrocarbons, thereafter passing resulting heated vapor mixture to a catalytic reaction zone containing a substantially stationary mass of granular adsorbent cracking catalyst at a temperature in the range about 900 to 1050° F., separately heating and vaporizing a stream of virgin naphthene oil to substantially the aforesaid temperature without substantial cracking, commingling the resulting naphthene vapors with the heated feed oil vapors passing to the catalytic reaction zone, passing commingled hot hydrocarbon oil vapor mixture through the catalyst mass maintained at cracking temperature at a space velocity in the range about 3 to 10, maintaining a rate of hydrocarbon flow through the mass such that the modified Reynolds number is in the range 100 to 1000, continuing without interruption the hydrocarbon flow through the mass for a conversion period of about 3 to 10 hours until carbonaceous deposit formed on the catalyst amounts to about 5 to 20% by weight of the catalyst, thereafter discontinuing the flow of hydrocarbons through the mass and reactivating the mass in situ by contact with a flowing stream of combustion gases containing about 1 to 2% oxygen, and effecting removal of substantially all heat of combustion as sensible heat in the effluent gas without exposing the mass to temperatures substantially in excess of about 1200° F.

6. In the catalytic cracking of hydrocarbon oil to produce gasoline wherein the oil in vapor phase is passed through a mass of granular adsorbent cracking catalyst of such activity that upon passing gas oil vapor through the mass at a temperature of about 950° F. and with a space velocity of about 2 for about two hours without interruption, the cracked gasoline so obtained amounts to about 10% by volume of the gas oil and has an octane number of about 77 to 78 CFRM, the method which comprises passing feed hydrocarbon oil having a carbon residue of less than 0.2% and a color of less than 200 on the Lovibond ½'' cell through a heating zone, heating and vaporizing the feed oil therein in the absence of a catalyst to a temperature in the range of about 900 to 1050° F. so as to convert about 8 to 10 volume percent of the oil into thermally cracked gasoline hydrocarbons, separately heating and vaporizing virgin naphthene oil to about the aforesaid temperature without substantial cracking, commingling resulting hot naphthene vapors with said heated feed oil vapors, passing resulting commingled hot vapor mixture to a catalytic reaction zone containing said cracking catalyst maintained at cracking temperature, passing the hydrocarbon vapors through the catalyst mass at a space velocity of about 3 to 10 and maintaining a rate of hydrocarbon flow through the mass such that the modified Reynolds number is in the range 100 to 1000.

CHARLES RICHKER.
DU BOIS EASTMAN.