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LIQUID PHASE CRACKING OF HYDROCARBONS WITH WATER-SATURATED CATALYSTS

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This invention relates to conversion of hydrocarbons and is more particularly concerned with the low temperature catalytic conversion of hydrocarbons to more desirable forms.

The value of hydrocarbons, particularly those obtained from natural sources such as crude petroleum or from oil shale or indirectly as from the destructive hydrogenation of coals, is greatly enhanced by various methods of refining these hydrocarbons. In their raw state or even in a more or less refined condition these hydrocarbons are often unsuited for many purposes because of lack of conformity to certain requirements. Failure to meet these requirements arises from causes which may include unsuitable boiling range, excessive amounts of deleterious materials which are not hydrocarbons, but which are present all too frequently in natural or partly refined hydrocarbons, or from the very nature of the hydrocarbons which, however, may be altered to more desirable form with appropriate treatment or treatments such as pyrolytic or catalytic procedures.

This invention is directed more specifically to the treatment of heavy petroleum oils and the invention will be described with particular reference to such oils. In heavy petroleum oils such as crude oils. tar and asphalt-like materials are often present in considerable and serious amounts. It is the usual practise to separate and remove these materials from the heavy oils when the oils are employed in the normal manner, for example, as the starting materials for cracking operations for the production of gasoline and fuel oils. Present refinery practise is to dispose of these removed tarry or asphaltic materials either as low grade fuels or as road surfacing agents or in other ways. In any case, such materials are at present considered of little value as starting or charge materials for economic production of more valuable hydrocarbons by customary cracking operations.

Another problem confronting refiners in using heavy hydrocarbon oils is that of contaminants, such as sulfur and nitrogen compounds, inorganic salts and the like. These contaminating materials may either corrode or plug up the pipes and other pieces of the refining equipment; they may pass through the refining operation either in quantity or quality such that the value of the finished product is considerably impaired; they may be deposited on the surface of the catalyst and swiftly inactivate the catalyst or they may inhibit, to a marked degree, the desired reaction leading to the refined product. Usually, there

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exists a combination of two or more of these objectionable features. For instance, in the case of refining by catalytic methods the so-called high sulfur petroleum stocks which have been found also to contain nitrogen compounds, the presence of the nitrogen compounds frequently inhibits the catalytic reaction; the catalytic activity life is seriously impaired by sulfur or sulfur compounds and other salts or the like and the products may contain non-hydrocarbon but related materials which more or less reduce the value of these products.

The present invention particularly has to do with the treatment of hydrocarbons heavier than gasoline such as gas oils, topped or whole crudes, residual fractions, and the like, which may contain contaminants such as referred to above, whereby such hydrocarbons are converted into more desirable forms.

In accordance with this invention hydrocarbons heavier than gasoline, particularly petroleum fractions heavier than gasoline, including distillation residues, gas oil, reduced or topped petroleum crudes and the like, are subjected under conditions of contact described hereinafter to the action of an adsorptive, active cracking catalyst maintained at temperatures below about 700° F., preferably within the range of 200 to 600° F. I have discovered it is essential, if the desired results are to be achieved, that the surface area of the catalyst be previously saturated with water, as by treatment with steam. Thus, it has been found, contrary to expectation. that contacting hydrocarbon fractions heavier than gasoline with relatively large amounts of adsorptive active cracking catalyst saturated with water and maintained at temperatures substantially below those heretofore considered effective for substantial cracking of the stock charged results in a strong endothermic reaction which is highly selective and productive of important effects, as will appear hereinafter. In this reaction high boiling components of the charge, including tarry or asphaltic materials present are converted into lower boiling distillate or distillate-type products. Depending upon the specific operating conditions selected for practice of the invention the nature of these products may be controlled to be largely or substantially entirely clear gas oils or the like or to contain substantial proportions of high anti-knock gasoline.

This process is advantageous in that it may be carried out so that the liquid products are considerably improved over the condition of the original charge oil while little gas is concurrently

produced and losses including carbonaceous or hydrocarbonaceous deposit on the catalyst are surprisingly low. In fact, recovery of distillate type materials is surprisingly high. When the charge oil contains heavy components usually classified as tars or asphalts the process preferentially effects the greatest amount of conversion of these heavy components and from this conversion is recovered large amounts of distillate or distillate-type hydrocarbons with desirable characteristics. It is further possible to produce from these heavier charge stocks high yields of high anti-knock gasoline by combining the yield of gasoline from this process with the gasoline produced from a subsequent cracking operation of the residual liquid products, either in whole or in part, remaining after gasoline removal.

Thus, from one aspect the invention comprises a complete process for the production of gasoline from a crude or other heavy hydrocarbon oil in which the oil, after removal of the straight run gasoline by distillation, is subjected to a first stage carried out as above described, any gasoline formed is removed, and the fraction heavier than gasoline is subjected to a conventional cracking operation. The several gasoline fractions when combined comprise an exceptionally high yield of gasoline from the original charge stock. For instance, it was found that a Mexican crude petroleum when processed by any of the usual methods such as reduction of the crude, tar separation, and cracking, thermal or catalytic, would produce less than 50% gasoline including the straight-run gasoline and gasolines from subsequent cracking even when running to maximum gasoline production, whereas by the use of this process and not running to maximum gasoline production that same crude petroleum yielded about 70% gasoline, about 20% recycle or fuel oil residue and less than 10% loss to all causes.

Further, depending on the boiling range, composition and other characteristics of the charge stock, the practise of this invention may result, in addition to the change in the boiling characteristics of the charge stock, in one or more of the following changes which result in the improvement of the product over the charge stock: reduction of sulfur content; reduction of nitrogen content; reduction of viscosity; and substantial or complete removal of inorganic components such as metals, metallic oxides and metallic salts.

The process may be carried out from a procedural standpoint in various ways. Effective results have been obtained at the conditions herein outlined by simply flowing the charge oil through a vessel containing the catalyst. The time required may be determined by the emission of products from the opposite end of the bed; in general, depending upon the temperature and pressure at which the oil is introduced to the catalyst bed, the time for this type of operation need be no longer than five minutes although longer times, such as one hour or more, do not appear to have an unsatisfactory effect. The invention, of course, includes methods of procedure wherein the oil is contacted with a moving catalyst under conditions adjusted to accomplish similar times of contact.

As above indicated, the process is carried out at temperatures within the range of about 200° to 700° F. The preferred upper limit in a given case, however, will vary depending upon the charge stock, the result desired, the conversion

of the charge to uneconomic hydrocarbonaceous or coky deposit and gas and other factors. In general, the process is preferably carried out at temperatures below a temperature at which a substantial quantity of gaseous and coky products are obtained; e. g., at which more than 25 per cent by weight of the charge, or better below a temperature at which more than 20 per cent, is converted to gas and coky deposit. The temperature is also related to the physical properties of the hydrocarbon oil undergoing treatment. The present process is particularly designed for the treatment of hydrocarbon oils having dew points (temperature of initial condensation from vapor phase at atmospheric pressure) above 650° F. and therefore, under any conditions of operation, these oils will be substantially in liquid phase; i. e., the majority of the oil will be in liquid phase at the reaction conditions. In any case, however, the full advantages of the process are best obtained with at least a substantial part of the charge in liquid phase.

Generally, temperatures substantially below 700° F. are more desirable, and in most cases, temperatures of 600° F. and below are preferred. For example, a charge stock that was converted to gas oils and about 4% by weight of charge of catalyst deposit at a temperature of about 215° F. was converted to lower boiling material with more than 30% gasoline with about 7% by weight of charge as catalyst deposit at a temperature of 425° F. Thus, the higher temperatures generally appear to result in a more severe or violent reaction. With lighter stocks such as distillate gas oils higher temperatures as in the range of 400 to 700° F. may be used to effect the changes such as lowering boiling points, reducing nitrogen or sulfur, etc.

The present process may be carried out very satisfactorily at about atmospheric pressure and, since this pressure is usually the simplest to obtain and retain, atmospheric pressure will ordinarily be used. The invention, however, is not limited to the use of atmospheric pressure since the pressure employed has not been found to be a critical factor. For instance, superatmospheric pressures may shorten contact time or increase to some extent the severity of the reaction.

As indicated above, the catalysts employed in the process are active cracking catalysts, although it has not been established that the mechanism of the process is the same as in the conventional catalytic cracking processes. It is preferred to use catalysts which exhibit substantially new condition or initial cracking activity of at least 20 activity index and especially 25 to 50 or higher activity index as measured by the method presented by J. Alexander and H. G. Shimp on pages R–537 and R–538 of the Technical Section of the National Petroleum News of issue date August 2, 1944. The need of substantial cracking activity was thoroughly demonstrated by work with a wide variety of contact masses which included, with the active catalytic materials which give the highly desirable results illustrated herein, such material as glass beads and diatomaceous earths which exhibited practically no effect toward improvement of the charge oils other than more or less retention of a very small portion of the objectionable components by a filtering action which is no more than would be expected at the conditions of operation. The use of active cracking catalysts produces, in addition to the filtering action nor-

mal to the nature of the contact mass, highly selective chemical and physical changes in the charge oils, resulting in the liquid products with greatly improved characteristics.

The catalyst may be any of the many known types which include naturally active or activated natural clays or earths such as those of the bentonite or kaolin class, synthesized materials which exhibit like or improved qualities over those of natural origin or of mixtures of natural and synthetic origin. Examples of synthesized materials include silica-alumina, silica-zirconia, silica-beryllia, silica-alumina-zirconia, silica-magnesia, and others such as the foregoing which have additional components such as small amounts of urania, thoria, and the like. They may be used in whatsoever physical form or shape most suited to the mode of adopted operation, which form or shape may be as small grains or granules such as obtained by grinding or may be formed by pelleting or casting or other means into larger aggregates in the form or shape of pills, pellets, or beads. It is desirable to use the larger shapes or forms since the pressure drop is apt to be lower and movement of gaseous or liquid material correspondingly more rapid with the use of the physically larger forms or shapes.

As stated previously, it is necessary to prepare the surface of the catalyst, for example, by treating with steam, such that the catalytic mass is saturated with water in the adsorbed form. Presumably this water is adsorbed on the surface of the catalyst and does not fill the larger pores and openings so that the catalyst is not wet in the ordinary sense. The reason why saturation of the catalyst with water is essential is not understood. However, it has been found that proceeding exactly as described herein but with a dry catalyst, as is customary in the conventional types of catalytic reactions, produces but slight changes in the charge stock so that such a method cannot be considered as having any practical significance.

When treating with steam there usually occurs a considerable exothermic phenomenon caused by the heat of wetting, which in the case of an initial temperature of about 300° F. for both catalyst and steam, using a clay catalyst may represent a rise of 25° F. or more and using a synthetic catalyst may represent a rise of 75° F. or more. It is advisable, therefore, to consider this factor in the adjustment of the temperature of the catalyst to the desired reaction temperature.

For instance, it may be expedient to make use of this exothermic phenomenon to bring the temperature of the water vapor covered catalyst to the desired temperature level at which the oil charge is introduced by effecting the initial contact of the steam and catalyst at such reduced temperature that upon completion of the saturation of the catalyst with the water vapor the heat of wetting has been utilized to establish the desired temperature level at which the oil charge is introduced. If saturation of the catalyst with water vapor is effected at or above the desired temperature, and it is necessary, therefore, to dissipate either the heat of wetting or the heat of wetting plus additional heat such as the residual heat from an exothermic revivification of the catalyst, it is possible to dissipate this heat by the continued addition and removal of an excess quantity of steam in the amount necessary to properly adjust the temperature.

An important feature of the invention resides in the use of relatively high catalyst to oil ratios

in each reaction period. The catalyst to oil ratio (i. e., ratio of volume of catalyst to volume of oil), for a given time of treatment will depend in considerable degree on the nature of the charge oil. In the case of oils that contain large quantities of tarry substances it is preferred to employ a catalyst to oil ratio of not less than about one part of catalyst to two parts of oil. If the operation is continued so that more oil is contacted with the catalyst, the latter increments are not fully treated. When using the charge stock mentioned above and which contained over 40% tar, the most satisfactory ratio was found to be about one part of catalyst to one part of charge oil, and of course any larger catalyst to oil ratio would be technically satisfactory although commercially less desirable. Increasing the amount of oil in that particular case overburdened the catalyst and while the first portion of recovered liquid product was substantially improved over the charge stock, the latter portion of the product showed little improvement. Larger ratios of catalyst to oil were tested and substantial improvements were obtained, but the results were insufficiently better to warrant economic processing at rates much below the maximum. For lighter and/or less tarry stocks such as gas oil, smaller ratios of catalyst to oil may be used, for example, one part of catalyst to three or more parts of oil.

When conditions outlined hereinbefore have been met and the charge stock is contacted with the catalytic agent, the reaction starts with considerable rapidity as evidenced by a sharp temperature drop apparently occurring almost simultaneously upon contact. This temperature drop is markedly greater than could be accounted for by a dehydration action on the catalyst. An advantage of this process is that there is little if any tendency to overtreating the oils by extended contact with the catalyst because at the low temperature of operation the reactions that do occur are selective, and few if any other reactions take place even if the contact time is extended considerably beyond the minimum necessary to effect the desired reactions. On the other hand, little, if any improvement appears to result from extended contact times.

The removal of the treated products from the reaction zone after the reaction is complete is effected by any suitable method known to the art and is not considered as part of this invention. In actual practise it has been found that the treated products are readily and efficiently removed by increasing the temperature and purging the system with steam or inert gas. Removal by purging without temperature increase may be affected with a suitable liquid purge medium or a temperature increase alone will tend to vaporize part of the products, which vaporized portion will act as the purge medium. It is preferred to include a temperature rise with a vapor purge medium in that recovery is volumetrically improved, probably through the freeing of small amounts of good oil trapped within the extremely viscous deposit on the catalyst. In any case liquid product recovery is better than 95% complete below 700° F. when the temperature is raised from reaction temperature to 700° F. and higher. If the temperature is raised much beyond this point as to 900° F. there may be some formation of gaseous products and some small amount of cracked liquid product from the thermal breakdown of the coky deposit on the catalyst.

The catalyst, after removal of substantially all

of the recoverable and useful products, may be discarded with its coating of carbonaceous materials; however, in the interests of economy, it is desirable to revivify or reactivate the catalyst for repeated use. Heating the spent catalyst to 900° F. effects a form of reactivation such that the catalyst still containing a relatively large deposit of coke may again be used to treat additional quantities of oil with good results. These results may, however, differ from those obtained from the catalyst which has no coke deposit to start with. For instance, in two operations—one on a coke covered catalyst and the other on catalyst free from coke and other conditions being similar, the chief outstanding difference in the products was that the liquid product of the operation on the coke covered catalyst showed the production of only minor amounts of gasoline whereas the product of the other operation gave better than 20% gasoline. The continuation of cyclic operation of this type, however, soon results in such an accumulation of coke on the catalyst that particularly with heavy, tarry stocks only two or three satisfactory runs may be made. The selectivity and activity of the catalyst fall off with impractical rapidity after reaching the state where the catalyst contains in the order of 100 grams of coke per liter of catalyst.

Where it is desirable to effect each oil treating operation on a catalyst from which most or all of the coke deposit from a previous hydrocarbon conversion operation has been removed, a practical method entails removal of the coke deposit by oxidation with air or other oxygen-containing gas. The temperature of the catalyst in this type of regeneration naturally must be controlled in order that the catalyst is not thermally inactivated through excessively high temperatures induced through the exothermic reaction of the burning of relatively large amounts of carbon. In addition to the removal of carbonaceous and hydrocarbonaceous deposits the regenerated catalyst can periodically be treated with a water wash, dilute acid wash or similar treatment which tends to remove the majority of inorganic materials deposited on the catalyst during the processing of the hydrocarbons, particularly the heavy oils. An accumulation of the inorganic deposit results from continued cyclic operation and will eventually adversely affect the efficiency of this process unless removed periodically.

In order that the invention may be understood more fully reference should be made to the following examples in which are illustrated several methods of practicing the present invention.

Example I

The charge oil stock used in this example was a reduced or topped crude petroleum from a Mexican oil field. Substantially all of the gasoline and other light hydrocarbons having been removed by distillation the remainder was comprised of light and heavy gas oil; considerable amounts of very heavy bottoms classed as tar; and objectionable amounts of fixed carbon, sulfur and nitrogen compounds and inorganic contaminants. In this condition it is generally considered as unsatisfactory for cracking or other direct refining processing other than the removal of the objectionable components by distillation, tar removal or the like.

The catalyst was a siliceous contact mass artificially produced by precipitating a silica-alumina hydrogel in a basic medium; drying the hydrogel; removing from this dried hydrogel the zeolitically held alkali metals by base exchange and water washing; drying, grinding and molding the purified gel into cylinders approximately 4 mm. in length and 4 mm. in diameter; and then calcining these cylinders. The cracking activity of this catalyst when tested by the method for determining catalyst activity referred to above was 46.2.

One volume of the catalyst contained in a reaction vessel was heated to about 300° F. and then was treated with steam at about the same temperature until the catalyst was completely saturated with water and the temperature of the mass returned to about 300° F. from about 370° F.—to which temperature the mass rose due to the heat of wetting. One volume of oil, intermixed with steam in an amount of about 5 to 7% by weight of the oil, was heated to about 300° F. and contacted at about atmospheric pressure with the prepared catalyst. The strong endothermic reaction which started almost immediately caused the temperature of the whole to drop to about 210° F. to 215° F. at which temperature contact was continued for twenty minutes. The treated oil was then removed from contact with the catalyst by purging the system with a small amount of steam and raising the temperature. Most of the recovered liquid product was collected shortly after starting the purge and over 98% of the products were collected before the temperature reached 690° F.

The temperature of the catalyst and its hydrocarbonaceous deposit was raised to 900° F. with the production of several weight per cent of gas from decomposition of the hydrocarbonaceous deposit and some small amount of oil remaining on the catalyst. At this point the flow of steam was stopped and a stream of air passed through the system to effect removal of the coke deposit by burning at temperatures controlled within the range of 900° F. to 1200° F. After removal of the coke the temperature of the catalyst was dropped to 300° F. and the procedure described above repeated for thirty complete cycles. An examination of the products of the last complete cycle was found to be in substantial agreement with the products of the original complete cycle, and the products of both runs so compared were found to be in substantial agreement with the blended liquid products from all cycles with the properties described immediately hereafter. The liquid hydrocarbon products of all cycles were combined and tested to demonstrate the changes effected by this process.

The comparative tests made on the charge stock and the recovered hydrocarbons by standard ASTM procedures showed that the original charge had been converted to a much more desirable form as shown in the following table:

	Charge oil	Recovered oil
Sulfur, Percent Wt.	2.12	1.23
Gravity, °A. P. I.	22.7	34.0
Fixed Carbon	7.0	0.6
Boiling Range:		
Vol. Percent, to 700° F.	42.7	74.5
Vol. Percent, 700° F.–900° F.		18.7
Vol. Percent, 700° F.–1,000° F.+	16.0	
Tar, 1,000° F.+	41.3	None
Coke, Gas and Loss, Vol. Percent		6.8

At best the original oil had less than 60% of its volume available in distillate form for use as is or for further processing such as cracking, whereas the recovered oil after processing in accord-

ance with the invention had better than 90% by volume so available.

Moreover, in the liquid product there was 25.6 volume per cent of 10 R. V. P. motor gasoline (410° F. cut point) which by test proved to have a C. F. R.-motor method clear octane rating of 74.2. The residual liquid fraction remaining after separation of the gasoline was subjected to catalytic cracking. At atmospheric pressure and 800° F. in the absence of steam, the oil in a ratio of 1.5 liquid volumes per 1.0 volume of catalyst per hour was contacted with a 39.2 activity index clay catalyst for 10 minutes. The volume per cent of recovered gasoline was 26.7 and 3.2% of gas by weight of charge was concomitantly produced.

That this process also reduces the amount of nitrogeneous matter is shown by the fact that in the original oil charge there was 0.174% by weight of the oil of nitrogeneous material measured as N_2 and in the liquid product after removal of the gasoline there remained only 0.054% by weight of the oil of nitrogeneous material measured as N_2.

The catalyst, after completion of the aforesaid thirty cycles, was subjected to spectrographic analysis and this analysis compared with a similar analysis of a sample of the same, but unused catalyst. This comparison showed that inorganic substances had been removed from the oil and were retained on the used catalyst.

Example II

On another run with the same charge stock and catalyst, all conditions of operation were the same except that the starting temperature was 650° F. which dropped with the start of the reaction to 425° F. at which temperature contact of oil and catalyst was effected. The recovered oil amounting to 91.1% by volume of the charge, had a boiling range of 132° F. to 825° F. with approximately 35% by volume of gasoline, and A. P. I. gravity of 38.9°, sulfur 1.02% by weight, fixed carbon 0.19 and a Saybolt viscosity at 100° F. of 32.0 as compared with 321 for the charge.

Example III

The process in this example is similar to that of Example I except that a different catalyst was used. The catalyst was an acid activated clay which had been formed into cylinders of approximately the same dimensions as those of the synthetic catalyst, and calcined prior to use in this process. The cracking activity of this catalyst was 39.2 as measured by the previously mentioned procedure.

The hydrocarbon products from this operation were tar free and boiled below 1000° F. with about 20% yield of motor gasoline. The A. P. I. gravity was 31.1°, the sulfur was 1.36% by weight, the fixed carbon value was 1.44 and the viscosity was 41.7.

Example IV

After an operation similar to that of Example III, the catalyst and catalyst deposit, amounting to about 40 grams of coke per liter of catalyst, was heated to 900° F. to remove most of the residual gaseous and liquid residue and the temperature of the coke covered catalyst reduced to about 300° F. where it was pretreated with steam and then contacted for twenty minutes with the same type oil charge of Example I. The other conditions of treatment were also similar to those

of Example I. The liquid product was substantially tar free and boiled below 1000° F. with however practically no gasoline production. Sulfur was 1.62% by weight, fixed carbon was 1.9, the viscosity was 56.0 and the A. P. I. gravity was 28.5°.

It will be obvious to those skilled in the art that the processes illustrated in the examples may be employed with advantage in the treatment of heavy hydrocarbon oils in general. Thus, by substituting for the charge stocks used in the examples any of the class of heavy oils previously mentioned, advantageous changes in the characteristics of the oils are obtained. For example, the beneficial results of this process have been obtained on charge stocks from other oil fields having different properties, such as those containing more tars or those containing no tar such as distillate gas oils. The improvements were similar to those outlined above. However, this process is not applicable to the declorizing of heavy stocks where it is desired to maintain the viscosity such as in the processing of lube stocks.

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

Having thus described my invention and demonstrated its operation by example I claim:

1. The process of treating hydrocarbon fractions heavier than gasoline to convert such fractions into lower average boiling distillate type products without concomitant conversion to substantial quantities of normally gaseous hydrocarbons and coky products, said process comprising contacting such a fraction substantially in the liquid phase with a bed of solid, particulate, adsorptive, active cracking catalyst under mild reaction conditions including a catalyst bed temperature of 200° F. to 700° F., said catalyst as a result of previous treatment with steam being saturated with adsorbed water vapor to its adsorptive capacity under the conditions of temperature and pressure employed in initially contacting said fraction therewith; maintaining reactive contact at substantially liquid phase conditions between said fraction and said catalyst for a period at least sufficient to effect substantial conversion of said fraction, and recovering hydrocarbons resulting from the conversion.

2. The process in accordance with claim 1 wherein the contact of said fraction with said water vapor saturated catalyst is carried out in the presence of water vapor in excess of that saturating the catalyst.

3. The process of treating hydrocarbon fractions heavier than gasoline and containing appreciable amounts of contaminants to produce therefrom high yields of distillate type products with considerably improved characteristics, said process comprising contacting such a fraction substantially in the liquid phase with a bed of solid, particulate, adsorptive, active cracking catalyst under mild reaction conditions including a catalyst bed temperature of 200° F. to 700° F., said catalyst as a result of previous treatment with steam being saturated with adsorbed water vapor to its adsorptive capacity under the conditions of temperature and pressure employed in initially contacting said fraction therewith and wherein said reactive contact is maintained at substantially liquid phase conditions for a period at least sufficient to effect substantial reduction of contaminants in the liquid products, and re-

covering normally liquid hydrocarbon products resulting from the conversion.

4. The process of treating hydrocarbon fractions heavier than gasoline and containing deleterious components to produce therefrom high yields of distillate type liquid products containing reduced amounts of said deleterious components, said process comprising subjecting such a fraction substantially in the liquid phase to contact with a bed of solid, particulate, active, adsorptive cracking catalyst at mild reaction conditions of atmospheric pressure, temperature within the range of 200° F. to 700° F. and time within the range of 5 to 20 minutes; said catalyst having been saturated with water vapor adsorbed thereon prior to contact with said fraction from an atmosphere of steam at substantially the same conditions of temperature and pressure as those of the initial contact of said fraction with said catalyst, said mild reaction conditions resulting in an endothermic reaction characterized by an average reduction in boiling point of the liquid products of said endothermic reaction and the concomitant deposition on the surface of said catalyst of a carbonaceous deposit; and recovering liquid products of said reaction by effecting their removal from said reaction zone by application of heat to said reaction zone.

5. A process in accordance with claim 4 wherein removal of said liquid products from said reaction zone is effected by the application of heat to said reaction zone subsequent to said reaction period, and with the addition to said reaction zone of purging amounts of gas relatively inert to said reaction.

6. A process in accordance with claim 5 wherein said catalyst prior to contact with said fraction has deposited thereon a carbonaceous deposit not in excess of 100 gms./liter of catalyst, which catalyst containing said deposit has been heated, prior to contact with said charge, to at least 900° F.

7. A process in accordance with claim 4 in which the cracking catalyst is a synthesized siliceous catalystically active mass.

8. A process in accordance with claim 4 in which the cracking catalyst is an active clay.

9. The process comprising establishing a bed of particulate, solid, adsorptive, active cracking catalyst in a reaction zone; adsorbing on said catalyst a saturating amount of water vapor and simultaneously adjusting the temperature of said catalyst to an operating temperature within the range of 200° F. to 600° F. by contacting said catalyst with a flowing atmosphere of steam which is in excess of that necessary to effect saturation and which has temperature and quantity to adjust the temperature of said catalyst to said operating temperature; maintaining in said reaction zone an atmosphere of steam to retain adsorbed steam on said catalyst; introducing to said reaction zone and to direct contact with the catalyst bed a charge comprising hydrocarbon fractions heavier than gasoline and containing deleterious materials, under conditions such that said charge is maintained substantially in the liquid phase; controlling the catalyst to oil ratio to one part of catalyst to no more than two parts of oil; maintaining contact of said charge with said catalyst to effect a mild decomposition, characterized by its endothermic nature, of said charge to high yields of distillate-type oils with small concomitant production of gases and coke deposit which remains on the catalyst causing the inactivation thereof; recovering liquid products characterized by reduced content of deleterious materials and lower average boiling point, from said reaction zone by heating said reaction zone to 700° F. and purging said catalyst bed with an inert gas.

10. A process for the production of high yields of gasoline from a crude petroleum oil which comprises separating a straight run gasoline fraction from said crude petroleum oil and recovering a heavy fraction, subjecting said heavy fraction substantially in the liquid phase to contact with a bed of solid, particulate, active, adsorptive cracking catalyst at mild reaction conditions of atmospheric pressure and temperature within the range of 200° F. to 700° F.; said catalyst having been saturated with water vapor adsorbed thereon prior to contact with said fraction from an atmosphere of steam at substantially the same conditions of pressure and temperature as those of the initial contact of said fraction with said catalyst, said heavy fraction being converted to conversion products including a substantial portion of gasoline hydrocarbons; separating said conversion products from said catalyst, fractionating said conversion products into a gasoline fraction and a resulting heavy fraction, subjecting the resulting heavy fraction to catalytic cracking to convert said heavy fraction to a substantial percentage of gasoline, recovering said last named gasoline fraction, and combining all of the gasoline hydrocarbons produced as described to obtain a high yield of gasoline from said petroleum oil.

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