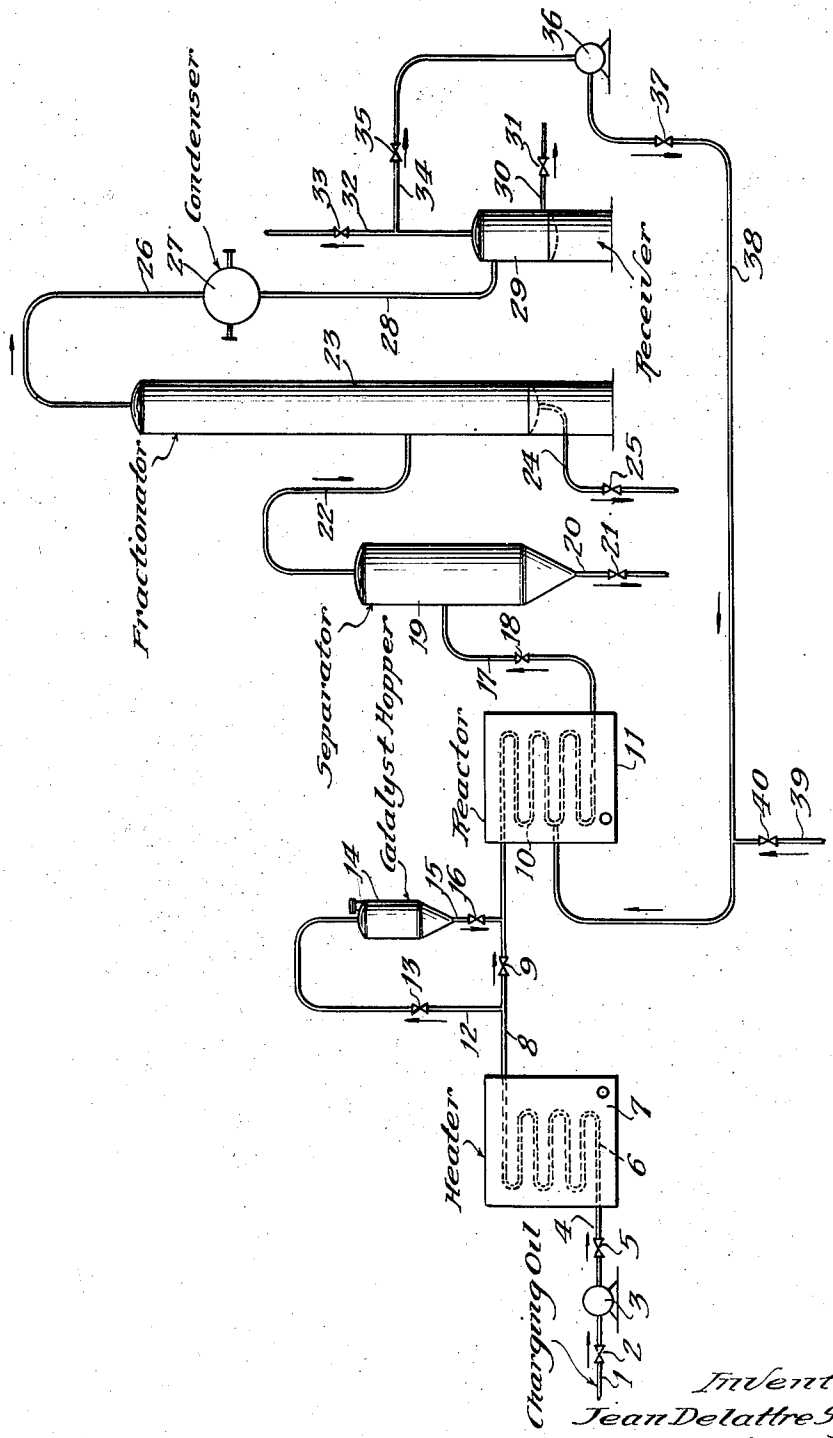
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CONVERSION OF HYDROCARBONS

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CONVERSION OF HYDROCARBONS

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This invention relates to a process for producing substantial yields of high quality gasoline from hydrocarbon oils containing substantially no gasoline. More specifically the invention is concerned with a catalytic method for converting relatively high boiling hydrocarbon fractions such as gas oil, crude oil, topped crude oil, and other hydrocarbon fractions from any source into high yields of gasoline of high antiknock value.

The use of certain metal oxides such as those of chromium, molybdenum, tungsten, and uranium as catalysts to promote destructive hydrogenation of hydrocarbon oils to produce saturated hydrocarbon mixtures of lower molecular weight has been practiced. Normally the octane numbers of gasolines produced in this way are somewhat low. By means of the present invention the disadvantages of excessively high pressures and temperatures can be avoided, and at the same time gasolines of high antiknock value and containing substantially no olefinic hydrocarbons can be produced. In fact, the present process permits the use of lower temperatures and pressures without materially affecting the yields of products sought. At the same time the desirable properties of the gasoline obtained are improved.

In one specific embodiment the present invention comprises a process for converting a hydrocarbon oil containing substantially no gasoline into a substantial yield of high quality gasoline which comprises contacting said oil with a catalytic composite comprising essentially a mixture of a hydrogenating catalyst and a cracking catalyst disposed in a catalyst zone under conditions of temperature and pressure adequate to effect substantial conversion of said oil and introducing a hydrogen-containing gas at intermediate points in said catalyst zone to contact with heated vapors of said hydrocarbon oil during passage through the latter portions of said catalyst zone to produce a substantially olefin-free motor fuel of good antiknock value.

By the process of this invention a hydrocarbon oil obtainable from petroleum or from any other source may be converted into relatively high yields of gasoline with good antiknock value by contact with selected catalytic material in the presence of an added gas containing a substantial proportion of hydrogen or of relatively pure hydrogen introduced at an intermediate point or points in a catalytic reactor. In the cracking zone the first reaction may consist of cracking to produce olefinic hydrocarbons which undergo hydrogenation in subsequent portions of the same catalytic reactor. The hydrogen present may modify the course of the simultaneously occurring cracking reaction by which higher boiling oils may be converted into gasoline or by which hydrocarbons of gasoline boiling range resulting from said cracking reaction may be improved in antiknock value as a result of succeeding reactions such as dehydrogenation, isomerization, cyclization, and hydrogenation the courses of which are not understood clearly or completely. This mechanistic concept concerning the reactions which may be involved in the total conversion should not be misconstrued as limiting the broad scope of the invention.

Suitable catalyst composites may comprise a mixture of one or more compounds known to promote hydrogenation selected from the group consisting of oxides or sulfides of molybdenum, chromium, tungsten, uranium, vanadium, tin (stannous), iron, nickel, manganese, and copper; and metallic nickel, copper, and nickel-copper mixtures together with a catalyst known to promote cracking selected from the group consisting of silica-alumina, silica-zirconia, silica-alumina-zirconia with or without minor amounts of added thoria, and an acid-treated clay at a temperature within the approximate range of 500–1000° F. under a pressure within the range of substantially atmospheric to approximately 3000 pounds per square inch to produce a substantially olefin-free gasoline of high antiknock value.

The catalyst mixture is hereinafter referred to as the hydrogenating-cracking catalyst and consists essentially of a mixture or composite of a material known to promote hydrogenation, and another material known to assist the cracking of hydrocarbon oils to motor fuel.

The hydrogenating-cracking catalyst may be prepared by a number of methods which yield suitable composites that are not necessarily exactly equivalent as to the types of conversions on which they have effect, nor are all of the possible combinations of catalytic agents from those mentioned necessarily exactly equivalent in their effectiveness in promoting the reactions involved in the present process.

According to one method of preparation the two types of materials forming the hydrogenating-cracking catalyst are separately prepared and intimately mixed prior to use. In another method the catalyst may be composited by precipitation methods wherein the various components are prepared by coprecipitation, or by separate precipitation of one component on the

other in separate consecutive steps. The precipitated mass is then dried and calcined. It is preferably treated with hydrogen at a temperature above 500° F. for a short time prior to use in the process.

The catalyst mass may be used as a powder which is carried in suspension in the oil undergoing treatment, or may be formed into shapes such as pellets, spheres, etc., over which the oil is passed. Alternatively the hydrogenating component and the cracking component of the catalytic composite may be separately formed into shapes such as pellets which are then mixed together and the oil contacted with the mixture. In another variation the individual component pellets may be placed in tubes or towers in alternate layers over or through which the oil is passed.

According to another alternative the catalytic materials may be deposited in the same or in separate steps on relatively inert fillers or carriers such as pumice, alumina, fuller's earth, montmorillonite, porcelain chips, bentonite, crushed firebrick, etc.

The hydrogenating component of the present catalyst comprises an oxide or sulfide and particularly a lower oxide or sulfide of molybdenum, chromium, tungsten, uranium, vanadium, tin (stannous), iron, nickel, manganese, and copper; as well as metallic nickel, copper, or a mixture of nickel and copper. These compounds may be deposited on carriers having relatively little catalytic effect in themselves such as alumina, magnesia, fuller's earth, montmorillonite, silica, kieselguhr, etc., in the form of finely divided powders, or the carrier may be impregnated with a solution of a compound such as the acid, nitrate, oxalate, etc., which is converted to the oxide by heating, or by precipitation of the hydroxide by well known methods. For example, when preparing a chromium oxide-on-alumina component, the alumina is impregnated with a suitable chromium compound such as chromic acid followed by heating at an elevated temperature (900° F. or higher). Alternatively salts of chromium such as the nitrate, oxalate, etc., may be used instead of the acid. The hydroxide may be precipitated on the carrier by the addition of ammonium hydroxide or other suitable volatile alkali, followed by heating to form the sesquioxide. In certain instances the hydrogenating component may be deposited directly on the cracking component by one of the methods described. The amount of hydrogenating component is usually within the limits of 0.5–50% by weight and preferably less than 20% by weight.

The cracking component of the present catalytic composite may comprise any suitable cracking catalyst. Such a catalyst consists of a major proportion of precipitated silica containing thereon a compound selected from the group consisting of precipitated alumina and/or precipitated zirconia to form catalytic composites known as silica-alumina, silica-zirconia, and silica-alumnina-zirconia. To these mixtures may be added small percentages of thoria, for example from 1 to 10% by weight. Acid treated clays may also be used in the present catalytic mixture although these are not necessarily equivalent to the preferred synthetic precipitated composites.

In this specification the terms "silica-alumina, silica-zirconia, and silica-alumina-zirconia" are used in a broad sense in referring to the cracking component of the catalyst composites used. Inasmuch as the chemical knowledge of the solid state has not been developed perfectly, it is not possible to give the structure of all solid substances. All that can be said definitely concerning these cracking components is that they contain silicon, oxygen, aluminum, and/or zirconium in combination. Generally speaking, however, all these components indicate more or less low catalytic activity individually but in the aggregate display high activity. This activity is not an additive function, it being relatively constant for a wide range of proportions of the components, whether in molecular or fractions of molecular proportions. No one component can be determined as the one for which the remaining components may be considered as the promoters according to conventional terminology, nor can any component be determined as the support and the others the catalyst proper.

In the preparation of a preferred cracking catalyst component, precipitated hydrated alumina and/or hydrated zirconia is composited with hydrated silica gel, otherwise known as silica hydrogel, and then the composite is washed, dried, and calcined. When thoria is added it may be incorporated at the same time as the alumina and/or zirconia. Briefly, the methods of preparation involve the precipitation of hydrogels of silica and the added compound, either simultaneously by coprecipitation methods, or by separate precipitation of the hydrogels, followed by mixing in such a manner as to produce a more or less uniform mixture, or by the successive precipitation of silica hydrogel and the added alumina and/or zirconia or thoria hydrogel constituent. The composite is washed with water and/or solutions of salts or mineral acids such as for example ammonium chloride, aluminum chloride, hydrochloric acid, etc., to effect substantially complete removal of alkali metal ions. The preferred synthetic components of the catalyst composites of this invention are all substantially free of alkali metal ions.

The amounts of alumina and/or zirconia vary over a considerable range, for example, from 1–30 weight per cent and are preferably of the order of approximately 5–30 weight per cent of the compound calculated as Al_2O_3 or ZrO_2. Approximately 1–10% of thoria may be used.

Charging stocks suitable for conversion according to the process may comprise hydrocarbon distillates or fractions such as naphtha, kerosene, gas oil, topped crude oil, crude oil, etc.; fractions of petroleum or similar oils produced by other methods than distillation such as, for example, solvent extraction, or recycle oil from thermal or catalytic cracking operation.

The optimum conditions of operating the present process vary over a wide range depending to a large extent upon the type and boiling range of the oil being processed. Normally the temperatures are within the range of approximately 500–1000° F. and preferably are about 600–850° F. Operating pressures range from substantially atmospheric to approximately 3000 pounds per square inch and are normally approximately 1500 pounds per square inch or less for continuous operation.

At intervals hydrocarbonaceous or carbonaceous deposits develop on the catalytic surfaces and render them less active. With the particular type of catalyst described where the length of operating time between reactivations is considerably greater than for the cracking component alone, reactivation may be carried out by contacting the catalytic mixture with an oxygen-

containing gas at a temperature in excess of approximately 900° F. to remove the deposits from the catalytic surfaces. Care should be taken that temperature of reactivation is not permitted to exceed about 1600° F. and should be maintained preferably within the range of 1000–1400° F. although in some instances it may be preferable to follow the treatment with an oxygen-containing gas by a short interval of contact with hydrogen or a hydrogen-containing gas before introducing the hydrocarbons to be cracked.

The process of this invention may thus be carried out so that cracking occurs in the part of the catalyst zone preceding the point of injection of the hydrogen-containing gas, while in the remainder of the catalyst zone the hydrogenating component of the catalyst functions in the presence of the added hydrogen-containing gas to bring about a reaction which is predominantly hydrogenation. Thus catalytic cracking will occur in the first part of the catalyst reactor promoting the formation of low boiling olefinic hydrocarbons which will thereafter be hydrogenated to substantial saturation by the hydrogenating reaction brought about by the injection of a hydrogen-containing gas at an intermediate point of the catalytic reaction zone.

In order to more clearly illustrate the features and advantages of the present invention, reference is made to the accompanying diagrammatic drawing showing one form of apparatus suitable for conducting the process of the invention.

Charging oil introduced through line 1 controlled by valve 2 enters pump 3 wherefrom it is discharged through line 4 and valve 5 into heating coil 6. Heating coil 6 is disposed within heater 7 maintained at conditions whereby the oil stream is heated to the desired temperature. From heating coil 6 the heated oil is directed by means of line 8 and valve 9 into reaction coil 10. Coil 10 is disposed within housing 11 to which heat may be supplied to maintain the oil stream at the desired conversion temperature. A portion of the stream of oil passing through line 8 is diverted through line 12 and valve 13 into catalyst hopper 14 wherein the oil will become mixed with powdered catalyst and the resultant slurry is then passed through line 15 and valve 16 into line 8. The resultant mixture of catalyst and oil will then flow through reaction coil 10. From reaction coil 10, the conversion products and suspended powdered catalyst are conducted by means of line 17 controlled by valve 18 into separator 19. In separator 19 the catalyst particles will settle along with heavy residuum and be withdrawn therefrom through line 20 controlled by valve 21. The vaporous conversion products will pass from separator 19 through line 22 into fractionator 23 wherein the heavier insufficiently converted products will be separated from gasoline and uncondensable gases, the heavy products being withdrawn from the bottom through line 24 and valve 25 and the gasoline and gases being withdrawn through line 26. The gasoline and gases are cooled in condenser 27 and passed through line 28 into receiver 29 wherein the uncondensed gases will be separated from the distillate and the latter withdrawn from the process through line 30 controlled by valve 31. The uncondensed gases may be removed from the system through line 32 and valve 33 or all or a portion of them may be directed through line 34, valve 35, pump 36, valve 37 and line 38 into an intermediate point in reaction coil 10. When desired, extraneous hydrogen gases may be introduced to the system through line 39 controlled by valve 40 in place of recycling process gases from the receiver.

By introducing the hydrogen gases to an intermediate point in reaction coil 10, the hydrocarbons passing through the first portion thereof will be cracked to form an olefinic gasoline. This olefinic gasoline will then be hydrogenated in the latter portion of the reaction coil by hydrogen introduced thereto.

The following may be given as a specific example of the process of this invention, but with no intention of unduly limiting its generally broad scope.

A hydrogenating-cracking catalyst composite consisting of 2.5% by weight of molybdenum oxide deposited on a silica-alumina-zirconia cracking component may be contacted with a Mid-Continent gas oil in the presence of hydrogen introduced at approximately the midpoint of the catalyst zone, said zone being maintained at 750° F. under a pressure of 900 pounds per square inch to produce approximately 59% of 400° F. end point gasoline with an octane number of 75 which may be increased to 94 by the addition of approximately 0.2% by volume of lead tetraethyl.

The character of the invention and the type of results obtainable by its use in practice will be evident from the preceding specification and the examples of results obtained, although they are not to be considered as imposing undue limitations upon its generally broad scope.

I claim as my invention:

1. A process for producing high anti-knock gasoline of relatively low olefin content which comprises introducing hydrocarbon oil heavier than gasoline and a powdered cracking and hydrogenating catalyst to a reaction zone, maintaining said zone under catalytic cracking and hydrogenating conditions of temperature and pressure and passing the hydrocarbons and powdered catalyst therethrough from one end thereof to the other, cracking a substantial portion of the oil into olefinic gasoline in the substantial absence of added hydrogen in the portion of said zone adjacent the inlet end thereof, introducing hydrogen at an intermediate point in the reaction zone to commingle with the olefinic reaction products of said cracking, and effecting substantial olefin saturation during the passage of the hydrocarbons and hydrogen through the remaining portion of the reaction zone.

2. A process for producing high anti-knock gasoline of relatively low olefin content which comprises introducing hydrocarbon oil heavier than gasoline and a powdered catalytic composite comprising silica, alumina and a hydrogenating catalyst to a reaction zone, maintaining said zone under catalytic cracking and hydrogenating conditions of temperature and pressure and passing the hydrocarbons and powdered catalytic composite therethrough from one end thereof to the other, cracking a substantial portion of the oil into olefinic gasoline in the substantial absence of added hydrogen in the portion of said zone adjacent the inlet end thereof, introducing hydrogen at an intermediate point in the reaction zone to commingle with the olefinic reaction products of said cracking, and effecting substantial olefin saturation during the

passage of the hydrocarbons and hydrogen through the remaining portion of the reaction zone.

3. A process for producing high anti-knock gasoline of relatively low olefin content which comprises introducing hydrocarbon oil heavier than gasoline and a powdered catalytic composite comprising silica, zirconia and hydrogenating catalyst to a reaction zone, maintaining said zone under catalytic cracking and hydrogenating conditions of temperature and pressure and passing the hydrocarbons and powdered catalytic composite therethrough from one end thereof to the other, cracking a substantial portion of the oil into olefinic gasoline in the substantial absence of added hydrogen in the portion of said zone adjacent the inlet end thereof, introducing hydrogen at an intermediate point in the reaction zone to commingle with the olefinic reaction products of said cracking, and effecting substantial olefin saturation during the passage of the hydrocarbons and hydrogen through the remaining portion of the reaction zone.

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