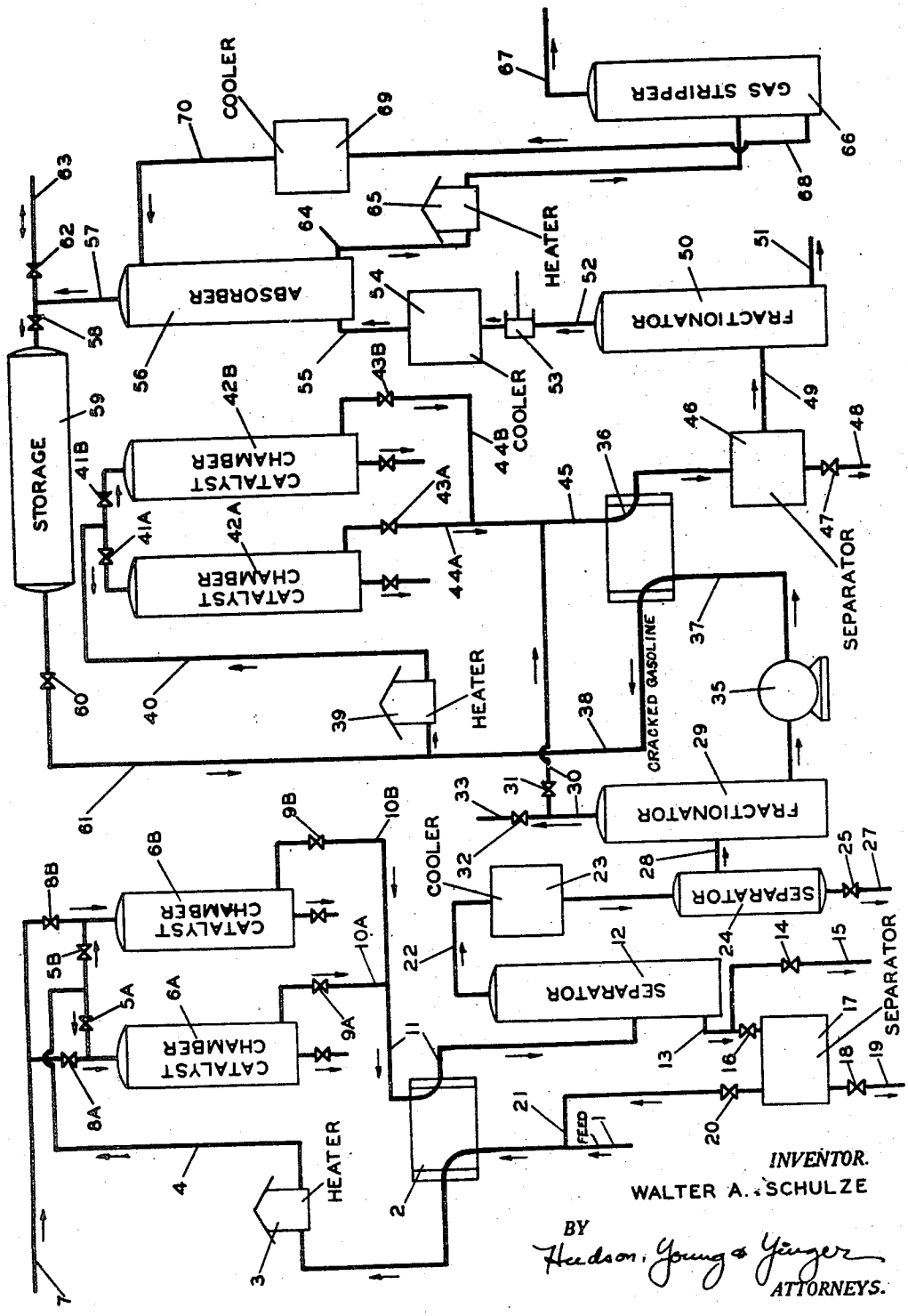
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PROCESS FOR HYDROCARBON CONVERSION

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PROCESS FOR HYDROCARBON CONVERSION

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The present invention relates to an improvement in the art of manufacturing motor fuels, and more particularly, to a process involving the combination of certain elements of hydrocarbon conversion which results in the production of motor fuels and/or components suitable therefor, which are of superior antiknock value. More specifically, this invention is concerned with an arrangement wherein a series of operations provide a process which is highly flexible and adaptable to a variety of starting materials and treating requirements. The process of this invention is further arranged and controlled in a manner to minimize reactions unfavorable to the quality and volume of the products. These operating improvements result from the direct co-action of catalytic treatments associated in this process.

The art of manufacturing motor fuel is extensive and varied, ranging from simple distillation of crude petroleum to highly specific reactions employing special catalysts and closely controlled operation conditions. As a result of the evolution of automative engines, and later the development of the aircraft power plants, the supply of fuels from natural sources has become increasingly inadequate; accordingly, progressively greater amounts of automotive and aviation fuels have had to be manufactured by methods adapted to convert naturally available materials into fuels meeting particular specifications. Typical of conversion processes, and perhaps the earliest developed, is thermal cracking, which yields a major proportion of present-day fuel. A more recent development in this field is cracking in the presence of catalysts; this ordinarily employs charge stocks similar to those which have been used for thermal conversion methods. Another refining treatment which has been used in some cases has been a direct treatment of gasoline itself in order to convert the hydrocarbons naturally present into more desirable substances from the standpoint of utilization as motor fluel. These so-called reforming methods, like cracking, have been performed both with and without reaction promoters. The various methods of hydrocarbon conversion of the types of cracking and reforming have enjoyed varying degrees of acceptance in the refining industry in accordance with their applicability to individual situations. However, in all cases, the nature of the processes demanded a careful balance of operating conditions with resultant effects upon quality and/or yield of the desired products. For example, in catalytic cracking, conversion to maximum gasoline yield may be obtained only by operation which generally results in a product of less than maximum quality. On the other hand, uneconomic losses of product are often sustained when operating for the highest possible antiknock value.

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An object of this invention is the manufacture of motor fuel components as well as finished motor fuel blends of improved antiknock and stability characteristics.

Another object of this invention is to provide an improved method for the manufacture of such superior fuels, whereby the compromise between quality and yield is substantially eliminated, and increased amounts of products of high quality are uniformly obtained.

Since the process of this invention comprises important features of two ordinarily distinct operations, a further object is to achieve an economy of equipment by suitable mutual use of certain types of apparatus by the two processes, which is not ordinarily possible in processes which do not cooperate as in the present case.

Still another object of this invention is to unify the separation of various low-boiling components in such a manner that they are more readily available for any desired use in other synthetic or conversion processes.

Additional advantages and benefits will be apparent from the disclosure which follows.

The present process comprises two co-acting steps, the first, a catalytic cracking operation which employs suitable cracking stock of elevated boiling range as its starting material, and supplies a selected product to the second step, which is an operation designed to reform a portion of the effluent from the cracking step. Arrangements are made within the process to perform certain advantageous separations of products which are, as shown hereinafter, simply accomplished within the process, and which might be of increased complexity if performed externally to the apparatus employed in this invention.

In the accompanying figure is given a diagrammatic representation of a preferred arrangement of refining elements adapted to the operation of the process of this invention. While the objectives of the invention may be attained by the employment of various types of equipment, the detailed description of the process will be made in connection with the arrangement portrayed in the diagram in order to simplify the discussion.

The feed stock to the process enters by the line 1. Suitable starting materials may be obtained from a variety of sources. For example, charge stocks well adapted to conversion may be fractions provided by distillation of crude petroleum oils, such as gas oils, distillates of selected boiling ranges, heavy fractions from vacuum distillation, and the like. Synthetic processes which may produce suitable high-boiling residues in addition to the desired low-boiling fractions, shale oil products, and liquids of proper boiling range resulting from any of the numerous treatments of coal may serve as other sources of raw mate-

rials for this process, where convenient. Gas oils and the like are most commonly employed because of ready availability and applicability to this type of treatment. The feed, in line 1, passes through heat exchanger 2 and the warmed oil continues to the primary heating zone 3, wherein the oil is heated to the desired transfer temperature. This is ordinarily in the range of from about 850 to about 1100° F., with from about 900 to about 1025° F. being preferred in order to obtain high yields of gasoline, and to minimize the formation of light gases and carbon. In this first step of the process, the pressure may be maintained as convenient in the range of about atmospheric to about 200 pounds per square inch, although the pressure is preferably in the range of about 15 to about 100 pounds per square inch. Higher pressures may be employed if desired, with proper consideration of the effect thereof upon the contact time of the charge with the catalyst, but no particular advantage results from additional compression in the present process.

Heated to the desired temperature, the oil passes by line 4 through valve 5A to the catalytic zone 6A, wherein the main reaction of the first step is performed. The catalytic zone contains a bed of the contact material which is employed in this process. Bauxite and materials of the bauxite type which display catalytic activity as a result of their bauxite content form a preferred series of catalysts under this invention. However, if desired, there is a large variety of catalysts available, such as various types of silica-alumina catalysts resulting from special methods of preparation, hydrosilicates of alumina and various oxides of the heavy metals and like cracking catalysts, any of which may be used if suitable to particular circumstances, within the scope of this invention. The natural catalysts are ordinarily employed with no more preparation than a crushing and sizing procedure. Artificial catalysts may be produced by a more or less extensive chemical treatment of minerals or by precipitation and/or calcination of materials resulting from directed reactions. Such catalysts may often be formed into special shapes, such as cylinders, spheres and the like, in order to avoid having to use the catalyst in a too finely-divided state, or to take advantage of special benefits deriving from the presence of certain forms.

If desired, a hot diluent and/or catalyst promoter fluid may be supplied by means of line 7 and valve 8A. It is preferred to inject steam as the diluent, in the cracking step, because of its beneficial effect in the catalytic treatment, whereby the catalytic activity is maintained for a longer period, and the tendency of the charge to decompose, especially into carbon deposits on the catalyst, is substantially reduced. Beneficial results may also be obtained by the use of other added fluids, such as hydrogen, light hydrocarbons and the like, whereby the yield may be improved when using special catalysts and/or conditions of operation. The diluents are useful in controlling the contact time of the feed with the catalyst, and also may be used to maintain the temperature in the catalytic zone by carrying sensible heat into and through the reaction chamber, thus aiding in maintaining uniformity of conversion. The effluents from the catalyst zone pass through valve 9A and line 10A to the product line 11. At intervals selected in accordance with the objectives of the operation, the activity of the catalyst may decline below the desired level, whereupon valves 5A, 8A and 9A are closed, valves 5B, 8B and 9B are opened, and the feed stock and fluid addition material are passed into zone 6B containing active catalyst, and of identical construction with zone 6A. The zone 6B carries on the operation, thus maintaining a continuous flow of feed stock into and products from the treating equipment. During this period, while the catalyst in zone 6B is promoting the main reaction, the catalyst in zone 6A may be reactived, for example, by passage of oxygen-containing gas therethrough to aid in removal of deposits formed in the course of the reaction. The means for supplying the reactivating gas are not shown, in order to simplify the diagram, since no departure from common practice is involved in this operation. In like fashion, the catalyst zone 6B may be removed from the circuit and zone 6A reinserted, when the catalyst of zone 6B is no longer able to maintain the minimum desired conversion, or whenever the end of the operating portion of the cycle for that catalyst is otherwise indicated.

The product line 11 carries the effluents from the catalytic zone through the heat exchanger 2 wherein the products are cooled somewhat by indirect contact with the feed stock entering the unit. Line 11 then continues to the zone 12, which is employed for the separation of heavy products and unconverted feed stock. These high-boiling materials are removed from the separating zone 12 by the line 13, and this operation is generally performed continuously, although intermittent removal may be practiced if deemed more suitable. The materials thus removed may be passed through the valve 14 and the line 15 to suitable applications outside the unit if desired. On the other hand, the heavy products may be passed through the valve 16 and into the zone 17 for conditioning prior to being returned to the process for additional conversion. The zone 17 may be employed as a simple tar separator, or more complex treatments may be given the heavy materials in order to separate substances most suitable to be returned to the cracking zone. The materials rejected by the conditioning process are removed through valve 18 and line 19 to any desired further treatment or use. Recirculation stock is conveyed by valve 20 and line 21 to line 1 and then through the treatment as described above and in the succeeding discussion. If desired, a portion of the stream of line 13 may be returned to the process via zone 17 and line 21, and the remainder discarded, using valve 14 and line 15.

Leaving the zone 12, the lighter portions of the products pass by line 22 through the cooling apparatus 23 and into the water separating zone 24. The mixture is sufficiently cool and quiescent in the zone 24 to allow the water condensate therein to settle substantially completely to the bottom of the separating zone, whence it may be drawn off continuously or intermittently, as desired, by valve 25 and line 27. The hydrocarbon components pass from the zone 24 by line 28 to the fractionating equipment 29 for removal of light hydrocarbons from the stock. The fractionating equipment 29 provides efficient stripping of the light components which do not require or do not respond to the succeeding reforming treatment. If it is desired to remove such light substances from the system, use is made of line 30, valve 32 and line 33. The light components may be retained in the process and treated further by passage along line 30 through valve 31

and then as more fully disclosed hereinafter. The products removed by line 30 commonly may include hydrogen, hydrocarbons through normal butane and sometimes may contain hydrocarbons boiling somewhat higher. It may be found desirable in some cases to employ fractionation of extremely high efficiency to segregate isoparaffins containing five and/or six carbon atoms. The corresponding normal paraffin hydrocarbons may be transferred to the second step of the treatment, for improving the selected cracked fraction. The reforming stock, however selected from the cracked products, proceeds from the fractionating equipment 29 to the pumping apparatus 35, and is transferred thence by line 37 through heat exchange zone 36 and line 38 to the heating zone 39, preparatory to entering the second catalytic treatment.

Hydrogen is supplied to the reforming stock in line 38 by line 61, from a source to be discussed in full below. The reforming feed, heated in heating zone 39, passes by line 40 and valve 41A to catalytic reforming zone 42A. The reforming catalyst is usually operated in the temperature range of about 900 to about 1100° F., with preferred conditions lying in the range of about 975–1050° F. Comparatively low pressures are employed, ranging from about atmospheric to about 100 pounds per square inch, in most cases. Excessive pressures are usually avoided because of the possibility of complicating the separations and reducing yields by pressure-induced side reactions. The reforming stock is usually supplied to the catalyst at a rate in the range of about 0.5 to about 10 volumes per volume of catalyst per hour. Thus the operating flexibility of the reforming unit is of great importance in setting up suitable conditions for the improvement of virtually any type of reforming stock which may be selected from the products of the cracking step, by the use of the equipment provided for that purpose within the process. The preferred catalyst for this reforming step is bauxite and minerals of the bauxite type having a suitable alumina content. Various other catalysts, for example, the oxides of various metals, such as aluminum, chromium, molybdenum, tungsten, zinc, zirconium, uranium and the like may be used. Catalytic mixtures of the metallic oxides such as aluminum and chromium oxides, or aluminum and silicon oxides and numerous others are also available if desired. Suitable promoters, for example, oxides of vanadium, nickel and zinc, and the like, may be preferable for special applications. Where necessary for proper operation of particular catalyst modifications, suitable alterations of operating conditions may be made in accordance with the requirements of the catalyst.

After a period of operation, the activity of the catalyst in zone 42A is reduced, and a treatment to restore the activity is usually employed before additional conversion is carried out, in order to maintain the reaction at an efficiently high level of activity. In order to operate the equipment continuously, a second catalyst zone, 42B, is provided. The zone 42B is identical with 42A in construction and content and is connected into the operating circuit by closing valves 41A and 43A, and opening valves 41B and 43B. During the interval when zone 42B is employed in the main reaction, the catalyst in zone 42A may be reactivated and placed in readiness for participation in the conversion of hydrocarbons when the catalyst of zone 42B requires regeneration.

In this manner the flow of feed stock and product need not be interrupted, although the operation of each catalyst zone is discontinuous.

Following the catalytic reaction in the zone 42A, the hydrocarbons pass by valve 43A and line 44A to the product line 45, flowing through the heat exchange apparatus 36 for cooling by indirect contact with the reforming feed stock, and then to the heavy component separation device 46. If it is desired to submit the light gases, which were extracted from the cracking products in preparing the reforming charging stock, to the separating procedures incorporated into the final stages of the process, the said light gases are passed through valve 31, as previously shown, and then flow by line 30 into line 45, where they join the reforming reaction products. Thus isoparaffins of five and six carbon atoms and other desirable components may be recombined with the reformed gasoline fraction and recovered in the gasoline fraction from subsequent fractionation as desired. Small amounts of polymers or high-boiling residues may be formed in the reforming reaction. These are separated in the separator 46, which is included for that purpose. The materials which are retained in the separator 46 may be removed as desired by valve 47 and line 48. In some cases it may be desirable to return these residues to the cracking step, and this may be done (means not shown); however, if desired, the high-boiling substances may be removed from the unit and used in other applications suited to their properties. The major portion of the reforming products, comprising gasoline components, normally gaseous hydrocarbons and hydrogen, and the recombined light components pass to the fractionating zone 50 by line 49. The zone 50 delivers the finished gasoline of superior antiknock characteristics by the line 51 to storage. The light hydrocarbons are removed by line 52 to further segregation according to volatility in the remaining units of the process. The light materials pass by line 52 to compressor 53 and then through the cooler 54, and line 55 to the absorbing zone 56. The compressed fluids flow upward in the zone 56 countercurrent to a descending stream of suitable absorption oil, which is selected according to well-known principles. It is ordinarily intended to operate the absorbing zone 56 at fairly high pressures in order to retain in the absorption oil substantially all hydrocarbons boiling higher than methane. However, this procedure may be modified in accordance with specific requirements which are at variance with such operation. The hydrogen and methane, in ordinary operation, pass out of the absorbing zone by line 57 and may be directed either by valve 58 to the gas storage equipment 59, or by valve 62 and line 63 to some application outside of the present process.

The absorption oil enriched with the absorbed hydrocarbons passes from the absorbing zone 56 by line 64 through the heater 65 and then into the stripping apparatus 66, wherein the hydrocarbons are distilled from the oil, and the oil is reconditioned for further absorbing of hydrocarbons in the absorbing zone 56. The distilled hydrocarbons pass overhead by line 67 to subsequent applications. The hydrocarbons contained in the line 67 may comprise a variety of light hydrocarbons applicable to various processes such as alkylation, dehydrogenation, polymerization and simple fractionation to remove components directly applicable to specialized fuels merely by blending in regulated proportions. The absorp-

tion oil leaves the stripping apparatus 66 by line 68, passes through the cooling zone 69 and then is transferred along line 70 to the absorption zone 56 to contact further amounts of hydrocarbons.

In some cases, there may be a small net consumption of hydrogen in the reforming step. In such cases, additional hydrogen may be supplied to the system by passing the new supply along line 63 through valves 62 and 58 to the gas storage zone 59. As a result of the extreme complexity of composition of any hydrocarbon mixture having even the molecular weight range of gasoline, to say nothing of a gas oil, the details of the transformations occurring in either of the steps of the present process are obscure, and the course of the reaction can be measured only in terms of general properties of the mixture. The following example is a description of a typical operation in a plant of the type hereinbefore described:

The feed stock employed was a somewhat refractory Mid-Continent gas oil, 37.3° A. P. I., and boiling between 450° and 634° F. This gas oil was treated over a bauxite catalyst using a temperature of about 950° F. and a pressure of about 75 pounds per square inch gage, with steam diluent. The flow rate was 1 volume per volume of catalyst per hour. The gasoline product from a single pass comprised about 40 per cent of the feed and the unconverted gas oil was returned for further treatment, to the cracking unit. The gasoline had an ASTM octane number of 74 after the treatment in the cracking step. This material after removal of C_5 and lower-boiling compounds was charged to the reforming step at 2.5 volumes per hour, 985° F. and about 50 pounds per square inch. Ten mol per cent of hydrogen was also contained in the feed stock in accordance with the foregoing discussion. The reformed gasoline amounted to about 95 per cent of the gasoline feed, and had an ASTM octane number of 81 without addition of lead.

I claim:

1. In a process producing a motor fuel of improved antiknock characteristics, the steps comprising introducing a stream of gas oil at a temperature between about 850 and 1100° F. and at a relatively slightly superatmospheric pressure into a closed zone containing a bauxite catalyst wherein the gas oil is cracked, removing unconverted gas oil and relatively heavy hydrocarbon material from the effluent of the preceding cracking step and recycling the unconverted gas oil into said cracking step, fractionating the remaining effluent into a gasoline fraction and a lighter fraction containing free hydrogen and isoparaffins of five and six carbon atoms, adding a gas rich in free hydrogen to the gasoline fraction, passing said mixture at a temperature between about 900 and 1100° F. and at a relatively slightly superatmospheric pressure into a second closed zone containing a bauxite catalyst wherein the gasoline is reformed in the presence of said hydrogen-rich gas, introducing the said lighter fraction into the effluent from the second closed zone thereby forming a combined fluid, separating components heavier than gasoline from the combined fluid, and fractionating the remaining combined fluid for separation of said isoparaffins together with a gasoline of improved antiknock properties and of a gaseous fraction containing free hydrogen, separating a gas boiling higher than methane from said gaseous fraction to obtain a gas rich in free hydrogen and recycling at least a portion of said hydrogen-rich gas to said second closed zone.

2. In a process of producing a motor fuel of improved antiknock characteristics, the steps comprising introducing a stream of gas oil at a temperature between the approximate limits of 850 to 1100° F. and at a pressure between substantially atmospheric and about 200 pounds per square inch into a closed zone containing a bauxite catalyst wherein the gas oil is cracked, removing unconverted gas oil and relatively heavy hydrocarbon material from the effluent of the preceding cracking step and recycling the unconverted gas oil into said cracking step, fractionating the remaining effluent into a gasoline fraction and a lighter fraction containing free hydrogen and isoparaffins of five and six carbon atoms, adding gas rich in free hydrogen to the gasoline fraction in an amount sufficient to give a mixture containing about 10 mol per cent hydrogen, passing said mixture at a temperature between about 900 and 1100° F. and at a pressure between about atmospheric and 100 pounds per square inch into a second closed zone containing a bauxite catalyst wherein the gasoline is reformed in the presence of said added hydrogen-rich gas, introducing the said lighter fraction into the effluent from the second closed zone thereby forming a combined fluid, separating components heaver than gasoline from the said combined fluid, and fractionating the remaining combined fluid for separation of said isoparaffins together with a gasoline of improved antiknock properties and of a gaseous fraction containing free hydrogen, separating a gas boiling higher than methane from said gaseous fraction to obtain a gas rich in free hydrogen and recycling at least a portion of said hydrogen-rich gas to said second closed zone.

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