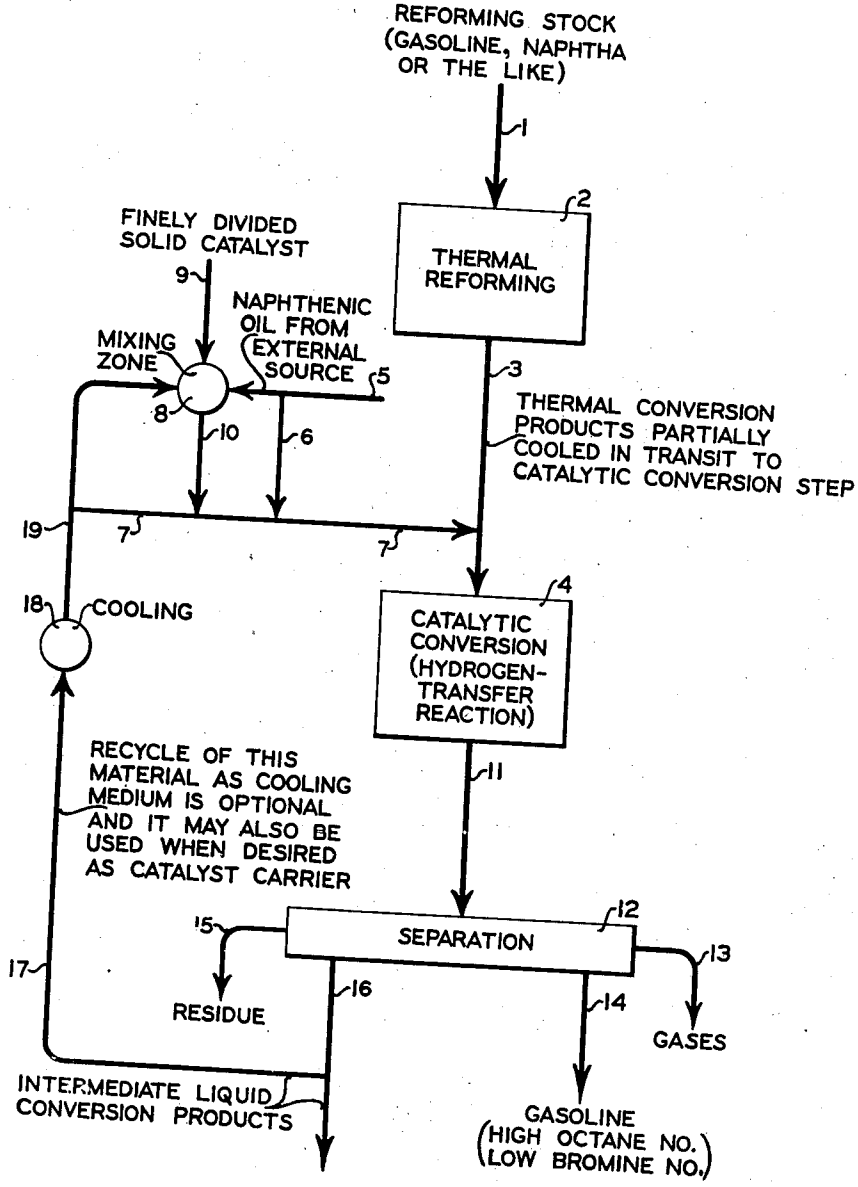
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CONVERSION OF HYDROCARBON OILS

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CONVERSION OF HYDROCARBON OILS

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The invention relates to an improved process for the production of high yields of substantially saturated hydrocarbons boiling within the range of gasoline and of high antiknock value from gasoline or gasoline fractions of inferior antiknock value, naphtha and the like.

The process of the invention comprises an interdependent combination of thermal and catalytic conversion steps which cooperate to produce a gasoline of high antiknock value and of substantially saturated nature, suitable, for example, as aviation gasoline, from light hydrocarbon oil distillates, such as gasoline or gasoline fractions of inferior antiknock value, naphtha and the like.

The thermal conversion step of the process is predominantly a thermal cracking operation of the type now well known in the art as "reforming," whereby gasoline or gasoline fractions of relatively poor antiknock value or light distillates, such as naphtha, are converted into high yields of gasoline of materially improved antiknock value.

One of the characteristics of the gasoline normally produced in thermal reforming operations is its highly olefinic or unsaturated nature which at least partially accounts for its good antiknock value but prevents it from meeting the acid-heat test requirements for aviation gasoline. The hydrogenation of thermally reformed gasoline by conventional methods to saturate its olefinic components and bring it within the acid-heat test requirements for aviation gasoline results in considerable depreciation of its antiknock value and is a rather expensive procedure due to the cost of producing hydrogen and the cost of reduced nickel and similar catalysts which are usually employed to promote hydrogenation.

I have found that the highly olefinic or unsaturated nature of gasoline produced by thermal reforming can be materially decreased without excessively decreasing its antiknock value by subjecting it to a type of reaction which is known as the "low temperature catalytic cracking" or "hydrogen transfer reaction" and in the process herein provided I employ this type of reaction as the second conversion step of the process to which the products of the thermal reforming step are supplied.

No novelty is claimed herein for either of the conversion steps per se, but invention is believed to reside in the cooperative and interdependent manner in which these two steps are herein combined to achieve the desired results above mentioned.

In the thermal reforming step of the process any of the well known forms of apparatus commonly employed for this type of operation may be utilized within the scope of the invention and the same applies to the low temperature catalytic cracking or hydrogen transfer reaction. It is the usual practice in thermal reforming operations to quickly heat the charging oil to a high cracking temperature in a tubular heating coil and then maintain it at or near the maximum temperature attained for a predetermined time in a "soaking" zone which may comprise a relatively mildly heated continuation of the coil in the same or separate furnace structure or an enlarged well insulated or mildly heated reaction chamber, or both, wherein the desired time factor is obtained, the heating and soaking zones normally being operated at a relatively high superatmospheric pressure. The coil or coil and chamber are designed to give the required time of reaction under the temperature and pressure conditions employed and upon discharge of the resulting hot conversion products from the soaking section they are normally cooled in one or a combination of several well known manners to a temperature at which deleterious further conversion is prevented. This temperature normally is of the order of 675 to 750° F. or thereabouts.

In the preferred embodiment of the invention the aforementioned conventional practice may be followed in the thermal reforming step, except that cooling of the reformed products is regulated to reduce them only to a temperature at which the subsequent low temperature catalytic cracking or hydrogen transfer reaction can be advantageously conducted. This temperature may be within the range above specified, but preferably is of a somewhat higher order, for example, up to 850° F., or thereabouts.

The partially cooled products of the thermal reforming operation are, in the present invention, intimately contacted in a reaction zone succeeding the thermal reforming step with a catalytic material capable of promoting the hydrogen transfer reaction, in the presence of a hydrogen donor, such as naphthenic oil derived from within the system or from an external source.

The catalytic material employed may be any of the well known cracking catalysts capable of promoting the desired low temperature cracking or hydrogen transfer reaction. I specifically contemplate the use of catalysts comprising silica and one or more of the metal oxides selected from the group which consists of alumina, zirconia

and thoria. Such catalysts may be prepared from the natural ores which contain silica and one or more of the metal oxides mentioned or may be prepared synthetically, for example, by precipitation of silica from a sodium silicate solution and deposition thereon or co-precipitation of the metal oxide from a solution of the salt of the metal. Since several suitable catalysts for this reaction and several methods of preparing the same are now known by those familiar with the art, the invention is not concerned with and claims no novelty for the particular catalyst composition or its specific method of preparation.

The catalyst may be employed as one or a plurality of fixed beds of solid, granular particles through which the hydrocarbons to be converted are passed at a temperature suitable for conducting the desired reaction or they may be dispersed in finely divided solid form in the stream of the fluid hydrocarbons undergoing treatment, in which latter case they are preferably in the form of a fine powder capable of remaining dispersed in said stream. When employed as a powder, the required quantity of catalytic material is preferably injected, as a slurry or dispersion in oil, into the flowing stream of hydrocarbons to be treated.

As a special feature of the invention, which is advantageous and ordinarily employed, powdered catalytic material, when this form is utilized, is mixed with all or a portion of the cooling oil or with all or a portion of the hydrogen donor employed, the latter also serving as cooling oil, and the resulting slurry or dispersion of catalyst particles in the oil is injected in the required quantities into the flowing stream of conversion products passing from the thermal cracking step to the low temperature catalytic cracking or hydrogen transfer step, whereby the injected oil is caused to serve a plurality of functions.

The accompanying drawing is essentially a flow diagram illustrating the process provided by the invention.

Referring to the drawing, the hydrocarbon oil charging stock to be converted, which may comprise such material as gasoline or gasoline fractions of inferior antiknock value, naphtha or the like, is supplied from storage or elsewhere, as desired, through line 1 to thermal reforming treatment in zone 2 wherein it is subjected to well known conditions of high cracking temperature, substantial superatmospheric pressure and time regulated to produce therefrom high yields of gasoline of materially improved antiknock value. This type of operation, now generally known as reforming, is distinguished from the thermal cracking of heavier oils to produce good antiknock gasoline in that it employs generally higher temperatures and pressures and longer conversion time and effects a material improvement in the antiknock value of the gasoline fractions of the charging oil without excessively altering their boiling range (without the excessive production of fixed gases and fractions boiling above the range of gasoline).

The thermal reforming steps will ordinarily be accomplished in an elongated heating coil disposed within a furnace with provision for milder heating of that portion of the coil through which the oil is last passed as compared with the preceding portion of the coil, with the object of quickly heating the charging oil to a relatively high cracking temperature and then maintaining it for a predetermined time at a substantially uniform temperature relatively close to the maximum previously attained. In this type of apparatus the portion of the coil through which the oil last passes and wherein it is maintained at a substantially constant temperature is known as a soaking section. Alternatively, the length of the soaking section of the coil may be decreased and augmented or entirely replaced by a well insulated or mildly heated enlarged vessel or reaction chamber to which the higher heated products from the coil are supplied and wherein their thermal conversion is continued for a sufficient time to accomplish the desired results.

The products of the thermal reforming step are directed therefrom through line 3 to the catalytic conversion step 4 wherein the hydrogen transfer action is conducted. Instead of cooling these products, as is done in conventional practice, to a temperature at which no substantial further cracking thereof will occur and thereafter separating the same into selected light and heavy fractions, they are, in the improved process provided by the invention, cooled only to a temperature at which the desired subsequent catalytic conversion reaction can be advantageously conducted and supplied, without separation thereof and in commingled state with the cooling oil employed to reduce their temperature, to the desired degree, to the catalytic conversion step.

As implied in the foregoing statement, cooling of the thermally reformed products in transit from the thermal reforming to the catalytic conversion zone is accomplished, at least in part, by commingling a suitable cooling oil therewith. Ordinarily, since the hydrogen transfer reaction is usually conducted at a substantially lower pressure than that employed in the thermal reforming step, part of the cooling is preferably accomplished by reducing the pressure imposed upon the stream of reformed products as they flow from the thermal reforming zone to the catalytic conversion zone. This may be accomplished in a conventional manner by providing a pressure reducing valve of suitable well known form, not illustrated, in line 3 and, to reduce pumping costs, the cooling oil is preferably added to the stream of reformed products after passage of the latter through the pressure reducing valve, although it may, when desired, be supplied, all or in part, to line 3 on the up-stream side of the pressure reducing valve or directly to the valve.

As previously mentioned, the type of catalytic conversion reaction herein contemplated is believed to involve the liberation of hydrogen from a portion of the reactants present, by dehydrogenation or cracking thereof, and the chemical addition of thus liberated hydrogen to olefinic gasoline fractions formed in the thermal reforming step. Napthenic oil is one of the best sources of hydrogen for this reaction and provision is made for commingling the desired quantity of naphthenic oil from an external source and/or from within the system with the thermally reformed products as they pass from the thermal reforming to the catalytic conversion step. The naphthenic oil is introduced, in the case here illustrated, into line 3 via lines 5, 6 and 7 or, alternatively, through mixing zone 8, as will be later described, and, when so supplied to the system, will serve as all or a portion of the cooling oil for reducing the temperature of the thermally reformed products to the desired degree.

In case the quantity of naphthenic oil required for conducting the hydrogen transfer re-

action is not sufficient to effect the desired cooling of the reformed products, a sufficient additional quantity thereof to accomplish the desired cooling may be employed or the naphthenic oil may be supplemented by another cooling oil from within or external to the system. When, on the other hand, the quantity of naphthenic oil required for the hydrogen transfer reaction is in excess of that which would be required at normal temperature to cool the reformed products, it may be preheated sufficiently prior to commingling the same with the reformed products to limit cooling of the latter to the desired degree. As a feature of the invention, when the catalyst employed for promoting the hydrogen transfer reaction is in the form of powdered or finely divided solid material which flows with the oil undergoing treatment through the catalytic conversion zone, it is preferably commingled with the reformed products as a dispersion in a portion or all of the cooling oil employed, whereby the latter also acts as a carrier for the catalytic material. Thus, in one embodiment of the invention the naphthenic oil functions as hydrogen donor, cooling oil and carrier for the catalyst. When employed as a catalyst carrier, all or a regulated portion of the naphthenic oil may be supplied through line 5 to mixing zone 8, wherein finely divided solid catalyst particles supplied to this zone through line 9 are dispersed in the oil, and the dispersion directed therefrom through lines 10 and 7 into line 3.

The catalytic conversion zone 4, wherein the hydrogen transfer reaction is conducted, may, within the scope of the invention, comprise an insulated or mildly heated coil or reaction vessel wherethrough the catalyst is passed as a dispersion of finely divided solid particles in the stream of fluid hydrocarbon reactants undergoing treatment in this zone or, alternatively, one or a plurality of reaction vessels containing one or more fixed beds of granular catalyst may be employed. In the latter case, provision is preferably made for periodically reactivating the catalyst in situ. This may be accomplished in a conventional manner by employing a plurality of reactors which are each alternately employed as a zone in which the hydrogen transfer reaction is conducted and a zone in which the previously used catalyst is reactivated. Ordinarily, reactivation will comprise burning deleterious, heavy, hydrocarbonaceous conversion products deposited on the catalyst particles therefrom by passing a stream of hot oxygen-containing gases through the fouled catalyst bed or beds.

Each of the types of catalytic conversion systems mentioned, as well as the provisions mentioned for periodically reactivating catalyst when fixed beds thereof are employed, are now familiar to those conversant with the art. A detailed illustration thereof is therefore unnecessary for an understanding of the invention by those familiar with the art to which the invention is addressed. This also applies to the thermal reforming step and to the conventional methods and means which may be employed for separating the intermediate and final products of the process into the desired fractions.

The products of the catalytic conversion step are supplied from zone 4 through line 11 to separation in zone 12, which may comprise conventional separating and fractionating equipment. Normally gaseous products of the process, exclusive of some of the relatively heavy gases which may be left dissolved in the gasoline product to impart the desired vapor pressure thereto, are removed from the separating step through line 13 to storage or elsewhere, as desired. The gasoline product of the desired vapor pressure and end-boiling point is directed from the separating step through line 14 to storage or to any desired further treatment. This material will be a substantially saturated gasoline of materially improved antiknock value, as compared with the gasoline or gasoline fractions supplied to the reforming step, and will ordinarily meet the requirements for aviation gasoline. The higher boiling components of the products supplied to the separating step are, in the particular case here illustrated, separated into relatively light and relatively heavy fractions, the latter comprising the residual product of the process and the former comprising the intermediate liquid conversion products. It is, of course, also within the scope of the invention to separate the intermediate liquid products into any desired number of selected fractions, although the drawing illustrates separation of only one stream of this material from the lighter and heavier products of the process.

Residual liquid is removed from the separating step, in the case here illustrated, through line 15 and, in case the catalyst employed for promoting the hydrogen transfer reaction is in the form of finely divided solid material dispersed in the oil, it will be removed with the conversion products from the catalytic conversion step and largely concentrated in the residual liquid removed from the separating step through line 15. In such instances, suitable well known means, not ilustrated, such as settling chambers, filters or the like, may be provided for recovering catalyst in substantially dry state from the liquid residue, whereafter the recovered catalyst may be reactivated for further use within the system, discarded or employed for other purposes or returned, in part, to the catalytic conversion step without reactivation by burning. In the latter instance, the recycled catalyst is preferably washed substantially free of readily soluble deleterious deposits before it is returned to the catalytic conversion step.

Intermediate liquid products of the process are removed from the separating step through line 16 and may be supplied therefrom to storage or to cracking treatment in another system or elsewhere, as desired. The invention also contemplates the use of regulated quantities of the total or selected fractions of the intermediate liquid conversion products as cooling oil for the thermally reformed products and, when desired, as a catalyst carrier. In some instances, selected fractions of the intermediate liquid conversion products will be sufficiently naphthenic in character that they may also be employed as a hydrogen donor in the catalytic conversion step of the system. When employed for any or all of these purposes, intermediate liquid conversion products may be directed from line 16 through line 17 to cooling zone 18, wherein their temperature is reduced to the desired degree to permit their efficient use as cooling oil for the thermally reformed products, and wherefrom the cooled oil is directed through line 19 and may thence be introduced through line 7 into line 3 to commingle therein with the reformed products from zone 2. When used as a carrier for the catalyst, the cooled intermediate liquid conversion products may be directed through line 19 to mixing zone 8, wherein the catalyst supplied to this zone

through line 9 is dispersed in the oil supplied to the mixing zone and wherefrom the resulting dispersion is directed through lines 10 and 7 into line 8.

The following example of a specific operation will further illustrate the usefulness and practicability of the process, but is not to be construed as limiting the invention to the particular operating conditions and results therein given since they will vary with different stocks and different catalysts. In view of the preceding description, one familiar with the art may select suitable operating conditions for the particular stock and catalyst employed.

A Mid-Continent naphtha having an octane number of approximately 33 as determined by the C. F. R. motor method and a boiling range of approximately 194 to 410° F. comprises the charging oil which is supplied to the thermal reforming coil of the system. A temperature of approximately 950° F. and a superatmospheric pressure of about 800 pounds per square inch is employed at the outlet of the reforming zone and the time in the soaking section corresponds to a cold oil feed rate of approximately 20 gallons per hour per cubic foot of soaking space.

The products of the thermal reforming step are commingled with straight-run gasoline in the proportion of approximately 1 volume of kerosene to 3 volumes of naphtha charging stock and are cooled to a temperature of approximately 775° F. The kerosene functions as cooling oil, hydrogen donor and carrier for the catalyst employed. The catalyst is a fine powder consisting essentially of silica and alumina in the proportion of approximately 10 mols of silica to 1 of alumina.

An average temperature of approximately 725° F. is maintained in the catalytic conversion or hydrogen transfer step wherein the partially cooled thermal conversion products and kerosene are reacted in the presence of the catalyst at a superatmospheric pressure of approximately 100 pounds per square inch. The space velocity in the catalytic conversion zone, expressed as the ratio of reaction space in this zone (in cubic feet) per cubic foot of reactants (on a cool liquid basis) pressed through this zone per hour is approximately 1.

The products of the catalytic reaction or hydrogen transfer step are separated to recover a 400° F. end-point gasoline which amounts to approximately 87 volume per cent of the naphtha charged to the thermal reforming step, and has an octane number of aproximately 71.5 as determined by the C. F. R. motor method and a bromine number of approximately 1.

I claim as my invention:

1. A process for the conversion of a hydrocarbon distillate such as gasoline, naphtha and the like into high yields of substantially paraffinic gasoline of improved antiknock value, which comprises thermally reforming said distillate, cooling the resulting products to a predetermined lower cracking temperature and contacting the same, in the presence of an added substantially naphthenic oil, with a cracking catalyst under conditions such as to effect partial dehydrogenation of the naphthenic oil and the transfer of hydrogen thus produced to the reformed gasoline, and recovering substantially saturated gasoline from the resulting products.

2. The process defined in claim 1 wherein said cooling of the reformed products is accomplished, at least in part, by commingling said naphthenic oil, at a lower temperature, therewith.

3. The process defined in claim 1 wherein said thermal reforming of the distillate is accomplished at a substantial superatmospheric pressure and said cooling of the reformed products is accomplished, in part, by substantially reducing the pressure thereon as they pass from the thermal reforming step to the catalytic conversion step and, in part, by commingling therewith said naphthenic oil at a lower temperature.

4. The process defined in claim 1 wherein said catalyst is in the form of finely divided solid particles dispersed in oil and wherein said cooling of the reformed products is accomplished, at least in part, by commingling regulated quantities of said dispersion therewith.

5. The process defined in claim 1 wherein said catalyst is in the form of finely divided solid particles dispersed in at least a portion of said naphthenic oil, and wherein said cooling of the reformed products is accomplished, at least in part, by commingling regulated quantities of said dispersion therewith.

6. The hydrocarbon oil conversion process which comprises heating a distillate comprising gasoline fractions of inferior antiknock value to a high thermal cracking temperature at a substantial superatmospheric pressure to convert the same into high yields of olefin-containing gasoline of improved antiknock value, cooling the resulting hot reformed products to a predetermined lower temperature within the catalytic cracking range, contacting the cooled products, in the presence of an added hydrogen donor, with a catalyst of the silica-alumina type under conditions such as to convert olefinic components of the reformed gasoline into substantially saturated gasoline fractions, and recovering from the resulting products a substantially saturated gasoline product of materially improved antiknock value as compared with the gasoline fractions of said distillate.

7. The hydrocarbon oil conversion process which comprises heating a distillate comprising gasoline fractions of inferior antiknock value to a high thermal cracking temperature at a substantial superatmospheric pressure to convert the same into high yields of olefin-containing gasoline of improved antiknock value, materially reducing the pressure on the resulting reformed products and commingling therewith regulated quantities of a naphthenic oil of lower temperature, whereby to reduce the temperature of said reformed products to a predetermined value within the catalytic cracking range, contacting the commingled oils in a catalytic conversion zone with a catalyst and under conditions capable of promoting the transfer of hydrogen from said naphthenic oil to olefinic components of the reformed gasoline, effecting said hydrogen transfer at said reduced temperature and pressure and recovering from the resulting products a substantially saturated gasoline product of good antiknock value.

8. The process defined in claim 7 wherein said catalyst is disposed within the catalytic conversion zone to which said commingled oils are supplied.

9. The process defined in claim 7 wherein said catalyst is in the form of porous solid particles disposed in at least one fixed bed in said catalytic conversion zone.

10. The process defined in claim 7 wherein said catalyst is in the form of finely divided solid particles dispersed in oil and wherein said dispersion is added to the stream of reformed

products supplied to said catalytic conversion zone.

11. The process of hydrocarbon oil conversion which comprises heating a distillate comprising gasoline fractions of unsatisfactory antiknock value to a high thermal cracking temperature at a substantial superatmospheric pressure and maintaining it in the thermal cracking zone for a sufficient time to convert the same into substantial yields of olefin-containing gasoline of materially improved antiknock value, thereafter cooling resulting hot reformed products to a predetermined lower temperature within the catalytic cracking range, commingling therewith a naphthenic oil and passing the cooled commingled materials at substantially reduced pressure through another reaction zone in intimate contact therein with a catalyst of the silica-alumina type, under conditions such as to convert olefinic components of said thermally reformed gasoline into substantially saturated gasoline fractions by the transfer thereto of hydrogen from said naphthenic oil, and recovering from the resulting products a substantially saturated gasoline of improved antiknock value.

12. A process for improving hydrocarbon distillate containing gasoline fractions of low antiknock value, which comprises thermally reforming the distillate, thereby forming olefinc gasoline, commingling a relatively cool naphthenic oil with the heated products of the reforming step and cooling said products to a lower temperature suitable for catalytic conversion of olefins to paraffins, subjecting the resultant mixture at said lower temperature to catalytic conversion under conditions such as to effect the transfer of hydrogen from said naphthenic oil to the olefinic gasoline, thereby effecting substantial saturation of the olefinic gasoline, and recovering the substantially saturated gasoline thus produced.

13. The process as defined in claim 12 further characterized in that finely divided catalyst for the catalytic conversion step is dispersed in the naphthenic oil which is commingled with the heated products of the thermal reforming step.

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