

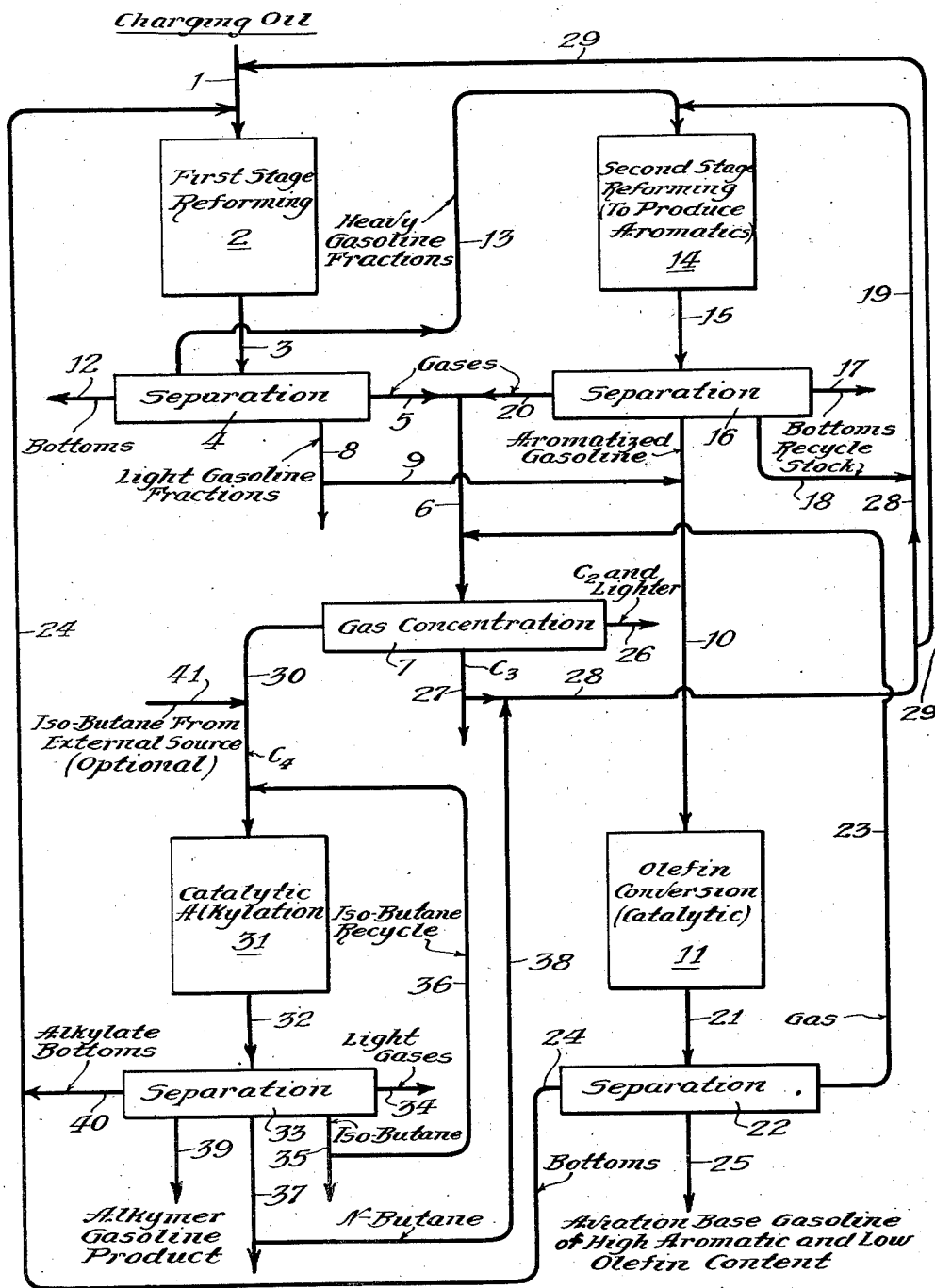
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PRODUCTION OF AROMATICS

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PRODUCTION OF AROMATICS

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The invention is directed to an improved process for the conversion of non-aromatic hydrocarbons to produce aviation base gasoline of high aromatic content and low bromine number. It is also directed to the production of selected aromatic fractions substantially devoid of olefins. The process involves a sequence of conversion and separating steps which are interdependent and mutually cooperate to produce the desired final product.

The process comprises two initial conversion steps in sequence for the production of the desired aromatics, accompanied by the incidental production of corresponding olefins, as well as lower boiling and higher boiling fractions. Selected fractions of the resulting products, consisting essentially of said desired aromatics and other hydrocarbons, including olefins, of corresponding carbon-atom content, are separated from the lighter and heavier products and subjected in a third conversion step of the system to catalytic treatment under conditions regulated to effect substantial conversion of said olefins without any substantial conversion of said aromatics, whereby a product is formed which is rich in the desired aromatics and low in or substantially devoid of olefins having a corresponding carbon atom composition and boiling range. This product is readily separated from lighter and heavier products of the olefin conversion step and recovered for use as aviation base gasoline or any of the numerous uses to which low-boiling aromatics may be put.

When the process is operated to produce aviation base gasoline it will be rich in benzene, toluene and xylenes. On the other hand, by proper selection of the charging stock and segregation of intermediate products, any specific lower boiling aromatic may be produced in predominance to the others.

Normally gaseous fractions produced in each of the initial conversion steps of the system and in the third or olefin conversion step are, in the preferred embodiment of the invention, supplied to a gas concentrating system wherein substantially all of the C_4 hydrocarbons are segregated from lighter gases and from which they are supplied to a catalytic alkylating step. In the alkylating step, iso-butane in said C_4 gases and, when desired, additional iso-butane from an external source, is alkylated with butylenes to produce an alkylmer gasoline of high octane rating and blending value, which may be added in regulated quantities to the aviation base gasoline produced within the system for the purpose of

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increasing or assisting to increase its octane rating to the requirements for aviation gasoline. Thus, in one embodiment of the invention the process will deliver a product which, upon the addition of 4 cc. or less of lead tetraethyl and sufficient quantities of iso-pentane or the like, to bring its vapor pressure to the desired value, meets the rigid requirements for aviation gasoline.

The cooperative and interdependent nature of the various steps of the process has been previously mentioned and will now be explained.

The first conversion step of the process and its succeeding separating step serve to prepare from the initial charging stock, and from intermediate products of the process which are recycled thereto, as will be later described, and deliver selected intermediate liquid fractions highly suitable for aromatization in the second stage of the process. It also produces C_4 fractions for the catalytic alkylation step and light gasoline fractions for the olefin conversion step of the system.

The aforementioned selected intermediate fractions from the first conversion step comprise heavy gasoline rich in olefins and of the desired carbon atom composition which are readily converted to the desired aromatics in the succeeding second step of the process. These fractions also include some desirable aromatics which would be extremely difficult to separate from the paraffins, olefins and naphthenes also present and, in the preferred embodiment of the invention, the second conversion step, whereto these fractions are supplied, is of the type in which no substantial detrimental conversion of the desirable aromatics supplied thereto will occur. However, it converts substantial quantities of the other components of its charge, and particularly the olefins, into aromatics of the desired carbon atom composition, thereby increasing the yield of these fractions from the first step and decreasing the load on the succeeding third or olefin conversion step. This second step of the system also produces C_4 gases for the alkylating step and recycle stock for further advantageous conversion in said second step.

The principal or predominant product of the second step and its adjunctive separating step is a selected fraction comprising essentially the desired aromatics and fractions of corresponding boiling range rich in olefins. The third conversion step catalytically treats this selected fraction to convert all or a major portion of the olefins without appreciable detrimental conversion of the aromatics. At least a substantial portion of the

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products formed from the olefins in this step will boil above the range of aviation base gasoline and, therefore, can be readily separated from the latter by simple fractionation. Furthermore, these higher boiling fractions are of a nature well adapted for recycling to one or both of the initial conversion steps for further conversion therein into additional yields of the desired intermediate and final products, and the invention specifically contemplates their retreatment in this manner.

Thus, the third or olefin conversion step of the system and its adjunctive separating step not only eliminate or substantially eliminate objectionable olefins from the final highly aromatic product, but also produce from the latter higher boiling fractions which may be advantageously retreated within the system to produce additional yields of the desired products. It also produces some normally gaseous fractions which are supplied to the gas concentrating step of the system and augment the C_4 fractions available for catalytic alkylation.

The alkylating step of the system derives all or a major portion of its alkylation stock from the other steps, as above described. It produces useful alkylmer gasoline of high antiknock and high blending value. An additional product of the alkylating step comprises alkylmer bottoms which, in the preferred embodiment of the invention, are segregated from the lighter products and returned to the initial conversion step of the system for retreatment in the latter and in the subsequent steps to produce additional yields of the desired intermediate and final products.

Normal butane fractions, supplied to the alkylation step with the iso-butane and butylenes, pass through this step without substantial conversion. This unconverted normal butane is preferably segregated from the other products in the separating step to which they are supplied and, in the preferred embodiment of the invention, is returned, all or in part, to one or both of the initial conversion steps wherein it is usefully employed. I do not attempt to offer a conclusive explanation of the advantage of this feature but have found that its incorporation in the process gives improved yields of the desired products in the initial conversion steps wherein olefins and aromatics are produced. It may be that the normal butane is cracked or dehydrogenated and resulting products condensed by polymerization, alkylation or the like to desirable liquid fractions or they may simply serve, by their dilution effect, to improve the selectivity of the initial conversion steps. It is also beneficial to recycle some or all of the C_3 fractions from the gas concentrating step of the system, and, although neither of these features are essential, they are included within the scope of the invention.

No patentable novelty is claimed herein for any of the several conversion steps of the process per se. The inventive concept is believed to reside in the novel and advantageous manner in which the various steps have been combined in cooperative and interdependent relation.

One of the advantageous characteristics of the invention resides in the relatively wide choice which it offers with respect to type of equipment, operating conditions, catalysts and the like for conducting the process. This will enable many refiners to make judicious use of existing equipment, now employed for less profitable purposes, as satisfactory equipment in which to conduct one or more of the various steps of this highly attractive and profitable process.

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First conversion step

The first stage of the process, indicated at 2 in the drawing, may comprise an operation similar to that widely known as "thermal reforming." In thermal reforming operations, light distillates, such as gasoline, naphtha and the like, of low antiknock value, are subjected to high cracking temperature at substantial superatmospheric pressure to effect their conversion into substantial yields of gasoline boiling range fractions of materially improved antiknock value. The improvement in antiknock value results to a large extent from the formation of olefins and some aromatics. At somewhat more severe conditions (higher temperature, higher pressure or longer conversion time or any combination thereof) than ordinarily employed for the same charging stock in such operations, the yield of aromatic fractions may be improved and it is this more severe type of reforming treatment which I propose to employ for the first stage of the system in one embodiment of the invention. The most suitable charging stock for this type of operation is selected naphtha or heavy gasoline fractions having a boiling range of the order of 200 to 400° F., or an even narrower boiling range within these approximate limits. The temperature employed is preferably of the order of 950 to 1250° F. with a high superatmospheric pressure of the order of 500 to 1000 pounds, or more, per square inch at the outlet of the heating coil. The oil preferably is quickly heated in the coil to a temperature approaching the maximum employed and is maintained at or near this maximum temperature for a sufficient time to effect its desired conversion, whereupon the resulting products are quickly cooled to prevent detrimental further conversion. This cooling may be accomplished by pressure reduction, the injection of cooling oil or other convenient method, and the products are preferably cooled to a temperature of the order of 700° F., or less.

When the charging stock comprises a heavier oil than that above mentioned or an oil of substantially wider boiling range, thermal cracking conditions of less severity than those above specified are preferably employed in the first step of the system in order to avoid coking difficulties. Such an operation will not produce as high a yield as the treatment above specified of the selected fractions for treatment in the second stage of the system, in a once-through operation, but the yield of the desired fractions may be materially increased by recycling higher boiling products from the succeeding separating step to the first conversion step for further treatment. Thermal cracking in the initial step of the system, as applied to such charging stocks as kerosene, kerosene distillate, gas oil, topped crude and the like, will employ a coil outlet temperature of the order of 875 to 950° F., or thereabouts, and a superatmospheric pressure at this point in the system ranging from 150 to 800 pounds, or more, per square inch. In general, operating conditions of greater severity (higher temperature and higher pressure, or both) are employed for the lighter and more refractory oils as compared with those employed for the heavier and less refractory oils.

The invention also contemplates catalytic cracking of the charging oil in the first step of the system, particularly when charging stocks of the nature of gas oil are employed. The preferred catalyst for this type of operation is of the silica-alumina type comprising either a synthetic catalyst, substantially free of alkali metal ions

and prepared by any of the several well known methods, or a treated natural clay from which all or a major portion of the alkali metals have been removed, or a thus treated natural clay fortified by the subsequent addition of alumina, to at least partially compensate for that removed in the acid treatment. This type of operation is preferably conducted at a temperature of the order of 900 to 950° F. and at substantially atmospheric or low superatmospheric pressure with a weight hourly space velocity (defined as the weight of oil supplied to the reaction zone per hour, per unit weight of catalyst present in the reaction zone) of the order of 1:1 to 10:1.

The catalytic cracking operation, when employed, may be of the fixed bed type in which the catalyst is periodically regenerated, by burning combustible contaminants therefrom, in the same zone in which the cracking operation has been previously conducted. However, I prefer to employ a moving bed type of operation having a reaction chamber and a separate regenerating chamber, wherein catalyst is continuously transferred from the reaction zone to the regenerating zone and hot regenerated catalyst continuously returned from the regenerating zone to the reaction zone.

This moving bed type of operation has numerous well recognized advantages over the fixed bed type and in its preferred form the bed of catalyst in the reaction zone is maintained in a turbulent fluid-like state by passing the hydrocarbon reactants and resulting fluid conversion products upwardly through the bed in the reactor at a sufficient velocity to impart a fluid-like condition to the catalyst particles. A similar fluid-like condition is also preferably maintained in the catalyst bed in the regenerator, by passing the air or other oxidizing gas employed for regeneration and the resulting combustion gases upwardly through the catalyst bed at a sufficient velocity to fluidize the catalyst particles. The gas velocities are maintained at a higher value than the net upward velocity of the catalyst particles so that a two-phase condition is obtained in each of the catalyst beds, the lower portion of each bed being relatively dense due to pronounced hindered settling of the catalyst particles therein, and the upper portion of each bed being materially less dense, due to the absence or reduction of hindered settling in this zone.

With the fluid bed type of operation, transportation of the stream of catalyst particles from the dense phase of the fluid bed in the reaction zone to the dense phase of the fluid bed in the regenerating zone and back from the dense phase of the fluid bed in the regenerating zone to the dense phase of the fluid bed in the reaction zone is readily accomplished, without mechanical conveyers and the like, by maintaining a higher hydrostatic pressure in the transfer lines, as compared with that in the regions of the fluid beds into which they discharge. The details of this type of operation, as well as the fixed bed type of operation, are now well known to those conversant with the catalytic cracking art and their specific illustration is not considered necessary to an understanding of the fundamental features of the invention. With a fluid bed type of cracking operation employed in the first step of the process, the catalyst-oil weight ratio (defined as the weight of freshly regenerated catalyst entering the reaction zone per unit weight of hydrocarbons entering the same) is preferably of the order of 0.5:1 to 10:1.

Second conversion step

The second conversion stage of the process, indicated at 14 in the drawing, may comprise an additional thermal reforming step, similar to that employed in the initial step and operated under substantially the same conditions or at higher temperature, pressure and/or conversion time, to produce additional yields of the desired low-boiling aromatics from the selected fractions of the initial step which are supplied thereto.

The second stage of the process may alternatively be a catalytic aromatizing operation of either the fixed bed or the fluid bed type described above, but employing an aromatizing rather than a cracking catalyst. Such an operation is more selective and will produce higher yields of the desired lower boiling aromatics than will thermal treatment in the second step.

In addition to the advantages of fluid bed operation over fixed bed operation as applied to catalytic cracking, it has additional advantages as applied to catalytic aromatization, due to the relatively large amounts of catalyst deposits formed in the aromatizing operation. In the fluid bed type of operation, these contaminating deposits can be readily handled due to continuous regeneration of the catalyst, and the necessity for periodic and extremely frequent periods of regeneration with short intermediate processing periods, as encountered in fixed bed operation, is avoided without the danger of excessively fouling the catalyst bed. In fluid bed operation, the catalyst may be kept at the desired high degree of activity and the aromatizing operation is also conducted at a substantially uniform temperature without necessitating the use of a heat exchange type reactor and a circulating heat transfer fluid to supply heat to the reaction zone and abstract heat from the regenerating zone. I, therefore, prefer to conduct the catalytic aromatizing step in a fluid bed type system.

Any of the numerous catalysts capable of promoting the aromatizing reaction may be employed within the scope of the invention. In general, any good dehydrogenating catalyst will produce suitable results, although their order of activity for promoting aromatization is not necessarily the same as for dehydrogenation. Such catalysts include those containing oxides of the metals appearing in the left-hand column of groups V and VI of the periodic table, deposited on or incorporated with a relatively inert carrier, such as alumina, silica, kieselguhr, diatomaceous earth, clays and the like. Alumina or clays of relatively high alumina content are the preferred carriers and chromia, molybdena and vanadia, alone or in various admixtures, are the preferred promoters.

One specific catalyst which has been found particularly suitable for aromatization is a synthetic composite of alumina, chromia and magnesia, containing approximately 12% chromia determined as the sesquioxide (Cr_2O_3) and approximately 2% magnesia, which acts as a stabilizer for the alumina to prevent conversion of the active gamma alumina to the relatively inactive alpha alumina at the high temperatures encountered in regenerating the catalyst. The magnesia is also believed to perform the additional and possibly more important function of preventing or reducing the formation of deleterious alumina-chromia complexes.

The catalytic aromatizing step may be conducted at a temperature of the order of 900 to 1200° F. with a weight hourly space velocity (as

defined above) of the order of 0.10 to 1.0 and with a catalyst oil weight ratio (as defined above) of the order of 10:1 to 60:1. The preferred operating conditions in most instances are: a temperature of the order of from 950 to 1150° F., a weight hourly space velocity of 0.25 to 0.50 and a catalyst-oil weight ratio of from 20:1 to 50:1. A pressure ranging from sub-atmospheric up to about 75 pounds gauge may be employed in the reaction zone, substantially atmospheric or sub-atmospheric pressure being preferred. The catalyst is ordinarily regenerated at a temperature of the order of 1000 to 1200° F. and preferably care is exercised to prevent the maximum temperature in the regenerating zone from exceeding 1250 to 1300° F.

Third conversion step

The third conversion step of the process, indicated at 11 in the drawing, is conducted to convert all or substantial quantities of the light liquid olefins supplied thereto into heavier olefins boiling above the range of the desired highly aromatic product and readily separable therefrom. Some conversion of these olefinic fractions into aromatics or other non-olefinic hydrocarbons probably also occurs. In any event, olefinic fractions boiling within the range of and corresponding in carbon atom content to the desired aromatic product are substantially eliminated in the olefin conversion step and higher boiling fractions suitable for further treatment, as above described, are produced. There are several catalysts capable of promoting this type of operation and several modes of operation which may be employed in this step within the scope of the invention. These will now be described.

One type of catalyst particularly suitable for use in the olefin conversion step comprises that now generally known in the industry as "solid phosphoric acid." In its most commonly used form this catalyst comprises granules or pre-formed shapes, consisting essentially of a relatively inert siliceous carrier, such as kieselguhr, for example, impregnated with phosphoric acid. Pyrophosphoric acid has been found the most active for producing the desired results and the catalyst is calcined prior to its use to reduce its moisture content to the optimum value for preventing conversion of the pyro acid to the less desirable metaphosphoric acid. After use and regeneration of the catalyst, it is preferably steamed before being reused, to maintain the optimum degree of hydration. With this type of catalyst a temperature of the order of 450 to 600° F. and preferably from 500 to 550° F. is employed with sufficient pressure in the reaction zone to maintain the reactants in liquid state or in a state of high density resembling that of liquid. The liquid hourly space velocity (defined as the volume of reactants supplied to the reaction zone, per hour, per unit volume of catalyst present in the reaction zone) may be of the order of 0.5 to 5 and is preferably within the range of 1 to 2. The fixed bed type of operation is preferably employed with the solid phosphoric acid catalyst, since relatively infrequent regeneration is ordinarily required.

Silica-alumina type cracking catalysts, such as previously mentioned, are also suitable for the olefin conversion step of the system and a wide range of temperatures may be successfully employed with this catalyst. The wide temperature range permissible is of the order of 600 to 1100° F. At temperatures of the lower order within the range mentioned (600 to 900° F.) a relatively low

catalyst:oil ratio (as above defined) is preferably employed, for example, of the order of 2:1, or less, to 5:1, or thereabouts. At higher temperatures within this range (900 to 1000° F.), a catalyst:oil ratio of the order of 5:1 to 30:1 may be employed. In general, the catalyst oil ratio should be varied in direct relation to the temperature. Substantially atmospheric or low superatmospheric pressure is employed in the reaction zone. Fixed bed or fluid bed type of operation may be employed, the latter being preferred. This olefin conversion step is characterized and distinguished from catalytic cracking as applied to heavier oils by relatively high yields of liquid products low in olefins and boiling within the range of the stock subjected to conversion therein, and by relatively low yields of gas and other light fractions.

Fourth conversion step

The fourth or catalytic alkylation step of the system, indicated at 31, may be conducted employing either sulfuric acid or hydrogen fluoride as the alkylating agent or catalyst. With hydrogen fluoride, a temperature of the order of 30 to 200° F. may be employed, the preferred range being from 50 to 150° F., or thereabouts. A sufficient superatmospheric pressure is maintained in the reaction zone to keep the reactants in essentially liquid state or in a dense phase condition resembling that of a liquid. This operating pressure will, of course, depend upon the temperature employed and is usually of the order of 100 to 250 pounds, gauge. It is essential to obtain good mixing between the reactants and the acid in the reaction zone and various forms of mixers or contactors are available for this purpose, any of which may be employed within the scope of the invention. To prevent or retard polymerization of the olefins, the stream entering the reaction zone should contain a high excess of iso-butane to butylenes. Preferably, an iso-butane:butylene ratio of the order of 3:1 to 10:1 on a mol basis, is maintained in the feed stock, including the iso-butane recycled from the separating step. Preferably, the fresh acid charged to the system is a commercial grade of "anhydrous" acid, containing not substantially more than 1 to 2% water. A water content up to 10% is permissible in the fresh acid, but does not give as good results. A space-time in the reaction zone (defined as the volume of catalyst present in the reaction zone, per unit volume of hydrocarbon reactants entering the reaction zone per minute) may be of the order of 5 to 80 minutes and for best results is preferably of the order of 10 to 30 minutes. The ratio of acid phase to hydrocarbon phase in the reaction zone is preferably of the order of 1:1 and may range, for example, from 0.5:1 to 1.5:1.

In conducting the alkylation step with sulfuric acid, the conditions are approximately the same as given above for hydrogen fluoride, except that a lower temperature should be used and this will permit the use of a somewhat lower operating pressure. A temperature ranging from the freezing point of the acid to as high as 80° F. may be employed and is preferably of the order of 30 to 50° F. The operating pressure may range, for example, from 50 to 150 pounds, gauge, depending upon the temperature employed. Preferably, a concentrated acid of 90% or more should be employed and the concentration is preferably of the order of 94 to 98%. The ratio of iso-butane to butylenes may be approximately the same as specified above for conducting the process with hydrogen fluoride as the catalyst or alkylating

agent, except, for sulfuric acid alkylation, a higher ratio is required than for hydrogen fluoride alkylation when the charge contains a high proportion of iso-butylene.

The drawing

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

Referring to the drawing, the initial charging oil is supplied through line 1 to the first conversion stage 2 wherefrom the resulting products are directed through line 3 to the separating step 4. Normally gaseous fractions are directed from this separating step through lines 5 and 6 to the gas concentrating system 7. Light gasoline fractions, including, for example, the C₅ and heavier hydrocarbons up to an end boiling point of the order of 200 to 250° F., or thereabouts, are separately removed from separating zone 4 through line 8 and all or a portion of this light gasoline may be directed through lines 9 and 10 to the olefin conversion step 11. Heavy liquid products or bottoms, boiling above the range of the desired aromatic fractions to be recovered from the process, are removed from the separating zone 4 through line 12 and may be directed to storage, further conversion treatment in the same or a separate system, or elsewhere, as desired.

In case the initial charge supplied through line 1 is a relatively heavy oil or oil of relatively wide boiling range, regulated quantities of all or selected fractions of the bottoms may be recycled by well known means, not illustrated, to the first conversion stage for further treatment therein.

Fractions of the desired carbon atom content and boiling range, comprising the desired aromatics and corresponding olefins produced in the initial step of the process, are directed from separating zone 4 through line 13 to the second conversion or aromatizing step 14. When the process is operated for the production of aviation base gasoline, the fractions supplied through line 13 to conversion zone 14 will normally be heavy gasoline having an end boiling point of the order of 400° F. or less and an initial boiling point of the order of 200° F. or more. The selection of narrower boiling range fractions for the production of specific aromatics is, of course, also within the scope of the invention.

Fluid products of the second conversion step 14 are directed through line 15 to the subsequent separating step 16 from which relatively heavy bottoms are withdrawn through line 17 to storage or elsewhere, as desired. Intermediate liquid fractions having an end boiling point corresponding to or somewhat greater than that of the fractions supplied from zone 4 to the second conversion step are recycled to the latter for further treatment therein through lines 18 and 19. Normally gaseous fractions produced in the second conversion step 14 are directed from separating zone 16 through lines 20 and 6 to the gas concentrating system 7.

Selected light liquid fractions, containing the desired aromatics produced in and supplied to the second conversion step, as well as olefins boiling within the same range, are directed from separating zone 16 through line 10 to the third or olefin conversion step 11. Resulting fluid products are directed through line 21 to separating zone 22, wherefrom normally gaseous fractions are directed through line 23 to the gas concentrating system 7 and wherefrom liquid fractions boiling above the range of the desired highly aromatic product are returned through line 24 to the

initial conversion step 2. Aviation base gasoline of the desired boiling range, or other desired product rich in low boiling aromatics and of low olefin content or substantially devoid of olefins, is withdrawn from separating zone 22 through line 25 and recovered.

In the gas concentrating system 7, substantially all of the C₂ and lighter gases are segregated from substantially all of the C₃ and C₄ fractions and removed through line 26 to storage or elsewhere, as desired. The C₃ fractions are separately removed through line 27 and may, when desired, be directed, all or in part, through lines 28 and 19 to the second conversion step 14 and/or through lines 28 and 29 to the first conversion step.

Four carbon atom fractions, including iso and normal butane and butylenes, substantially free of lighter gases, are directed from the gas concentrating system through line 30 to the catalytic alkylating step 31 wherein substantially all of the iso-butane is alkylated with butylenes to form a substantially saturated alkylmer gasoline rich in iso-octane. Hydrocarbon products of the alkylating step are directed therefrom through line 32 to separating zone 33 wherefrom C₃ and lighter gases are removed through line 34 and may, when desired, be directed by well known means, not illustrated, back to the gas concentrating zone 7 or removed from the system to storage or elsewhere, as desired. A separation of iso and normal butane is made in separating zone 33, the iso-butane being withdrawn therefrom through line 35 and regulated quantities thereof being recycled through line 36 to the alkylating step to maintain a relatively high ratio of iso-butane to butylenes in the alkylating zone and thereby repress polymerization. Normal butane is removed from separating zone 33 through line 37 and regulated quantities thereof may be returned via line 38, line 28 and line 19 to the second conversion step and/or directed from line 28 through line 29 to the first conversion step.

Three carbon atom gases and/or normal butane recycled, as above described, are preferably directed to the first conversion step 2 when the second conversion step 14 is a catalytic aromatizing operation. When the second conversion step 14, as well as the first conversion step 2, is a thermal operation, the C₃ gases and/or normal butane may be recycled to the second step in addition to or instead of returning the same to the first conversion step.

The desired alkylmer gasoline product which, as previously indicated, is rich in iso-octane, has a high antiknock value, a high blending value and is substantially free of olefins, is removed from the separating zone 33 through line 39 and recovered. The invention specifically contemplates blending regulated quantities of this alkylmer product with aviation base gasoline recovered from separating zone 22.

Liquid fractions produced in the alkylating step which boil above the range of the desired alkylmer gasoline are directed from separating zone 33 through line 40 and returned through line 24 to the initial conversion step 2.

When desired, iso-butane from any desired source may be supplied to the alkylating step through line 41, to augment the supply from within the system.

Example

As an example of a specific operation of the process conducted in accordance with the provisions of the invention, the initial charging stock

is a straight-run naphtha having a boiling range of approximately 248 to 410° F. and a motor method octane number of approximately 50.

This charging stock, together with the recycle stock subsequently specified, is subjected to thermal treatment in the initial step of the system at a temperature of approximately 1000° F., measured at the coil outlet, with a pressure at this point in the system of approximately 800 pounds, gauge. The resulting products discharged from the heating coil are quickly cooled to a temperature of approximately 660° F. and are fractionated to separate bottoms which are removed from the system, heavy gasoline fractions which are supplied to the second conversion step, light gasoline fractions which are supplied to the third or olefin conversion step and normally gaseous fractions which are supplied to the gas-concentrating system.

The heavy gasoline fractions supplied from the initial conversion operation to the second conversion step have a boiling range of approximately 212 to 392° F., a motor method octane number of approximately 75 and amount to about 55% of the oil charged to the initial step. These fractions are thermally treated in the second conversion step, together with normal butane from the alkylating step and some C₃ fractions from the gas-concentrating system, and with bottoms from the succeeding separating step, at a coil outlet temperature of approximately 1025° F. The operating pressure at the outlet of the heating coil is approximately 100 pounds, gauge.

The products of the second conversion step are quickly cooled, followed their discharge from the heating coil, to a temperature of approximately 635° F. and resulting products are separated into heavy bottoms which are removed from the system, recycle stock which is returned to the second conversion step, normally gaseous fractions which are supplied to the gas concentrating system and a light distillate, rich in aromatics and also containing substantial quantities of olefins, which is supplied to the third or olefin conversion step of the system. The recycle stock has a boiling range of approximately 375 to 450° F. The C₃ fractions and normal butane supplied to the second conversion step amount to approximately 12% by weight of the oil charged to this step.

The olefin conversion step of the system employs a solid phosphoric acid catalyst, such as above mentioned, containing approximately 70% by weight of phosphoric acid. The oil supplied to this step from the second conversion step has an end boiling point of approximately 350° F., amounts to approximately 46% by weight of the initial charging oil to the first conversion step, and has a bromine number of approximately 25. In addition the highly olefinic light gasoline fractions from the first conversion step are supplied to the third conversion step and amount to about 28% of the initial charging oil. The olefinic conversion step is a fixed bed type of operation employing a temperature of approximately 525° F. and a gauge pressure of approximately 800 pounds, with a liquid hourly space velocity of approximately 1.35.

The products of the olefinic conversion step are fractionated to separate bottoms, having an initial boiling point of approximately 350° F., which are returned to the initial conversion step, normally gaseous fractions which are supplied to the gas-concentrating system and an aviation base gasoline. The latter amounts to approximately 62% of the initial charge to the first con-

version step, has a bromine number of approximately 5 and an end boiling point of approximately 350° F. This product has a high octane rating and lead susceptibility which, together with its low bromine number, make it excellent blending stock for aviation gasoline.

Four-carbon-atom gases from the gas-concentrating system are contacted in the alkylating step with hydrogen fluoride at a temperature of approximately 100° F., at an operating pressure of about 125 pounds, gauge, and with a space time in the reactor of approximately 30 minutes. The ratio of iso-butane to olefins in the feed to the alkylating step, including recycled iso-butane, is approximately 6:1. The fresh hydrogen fluoride charged to the system is substantially anhydrous (containing 1 to 2% water) and the acid to oil ratio in the reaction zone is approximately 1:1. A large portion of the acid is separated by settling from the resulting hydrocarbon products and recycled to the alkylating zone. Iso-butane is also recycled, as previously mentioned.

The alkylating step will yield a highly paraffinic alkymer gasoline rich in iso-octane, amounting to approximately 95 weight per cent of the olefins charged to the alkylating step. This product has an end boiling point of approximately 350° F., an octane number of approximately 92 and a high blending value. Its bromine number is approximately zero. Higher boiling liquid products of the alkylating step are returned to the initial conversion step of the system.

By blending the aviation base gasoline with isopentane, to bring its vapor pressure to the desired value, and with approximately 5% of alkymer gasoline produced in the alkylating step, and adding 4 cc. of tetraethyl lead, a product meeting present requirements for aviation gasoline is produced.

The use of the term "non-aromatic hydrocarbon oil" in the appended claims, as applied to the charging stock for the process, is not intended to preclude the use of charging oil containing some aromatic fractions as well as other components, such as paraffins, olefins and naphthenes. With such stocks non-aromatic fractions are converted in the process to aromatics while some, if not all, of the aromatic fractions in the stock remain unconverted.

The term "cracking" is used in a broad sense in the claims. "Cracking," where a heavy stock is not specified is intended to include the particular type of cracking treatment generally known as reforming, as explained above, as well as including the cracking of relatively heavy oils to form lower-boiling products.

The terms "aromatization treatment" and "reforming under aromatizing conditions," as used in the claims are intended to include either thermal or catalytic treatment to form aromatics by any of the methods above specified.

I claim as my invention:

1. A process for converting non-aromatic hydrocarbon oil to form a product rich in low-boiling aromatics and low in olefins which comprises, cracking said oil in an initial conversion step to form light gasoline fractions and heavy gasoline fractions containing some of the desired aromatics and containing other hydrocarbons, including olefins, of corresponding carbon-atom content, subjecting said heavy gasoline fractions in a second conversion step to aromatization treatment to convert substantial quantities of said other hydrocarbons into additional yields of the desired aromatics, separating from the re-

sulting products a selected fraction consisting predominantly of said desired aromatics and non-aromatic hydrocarbons of corresponding carbon-atom content, including olefins, subjecting said selected fraction together with said light gasoline fractions formed in said initial conversion step to catalytic olefin-conversion treatment in a third conversion step under conditions regulated to leave said aromatics substantially unconverted and to convert substantially all of said olefins and form therefrom fractions boiling above the range of the desired highly aromatic product, recovering the latter and returning said higher boiling fractions to the initial conversion step.

2. A process such as defined in claim 1, wherein liquid products, formed in the second conversion step, which boil above the range of the selected fraction supplied to the third conversion step and are amenable to further aromatization treatment, are returned to the second conversion step.

3. A process such as defined in claim 1, wherein normally gaseous products of the first and second conversion steps are fractionated to separate substantially all of the 4 carbon atom fractions from lighter gases, said 4 carbon atom fractions supplied to a fourth conversion step and therein subjected to catalytic alkylation to chemically combine iso-butane with olefinic C₄ fractions and form a substantially saturated alkylmer gasoline rich in iso-octane, and wherein higher boiling liquid products of said fourth conversion step are returned to the first conversion step.

4. A process for converting non-aromatic hydrocarbon oil to form a product rich in low-boiling aromatics and low in olefins which comprises, thermally reforming a hydrocarbon distillate boiling within the approximate range of 200 to 400° F. in an initial conversion step to form aromatics and olefins boiling within the range of gasoline, separating light and heavy gasoline fractions from the resulting products, supplying said heavy gasoline fractions to a second conversion step, therein subjecting the same to further thermal reforming treatment to form low-boiling aromatics and reduce the olefin content of said heavy gasoline fractions, separating from the resulting products a selected fraction consisting predominantly of the desired aromatics and other hydrocarbons, including olefins, of corresponding carbon-atom content, commingling said selected fraction with said light gasoline fractions formed in the initial conversion step and supplying the mixture to a third conversion step, subjecting the same therein to the action of a precalcined solid phosphoric acid catalyst at a temperature not substantially in excess of 600° F. and at sufficient pressure to maintain the reactants in substantially liquid state, to produce a selected fraction rich in aromatics and of materially reduced olefin content, relative to the charging stock supplied to this step, and to convert substantial quantities of the olefins in said charging stock into liquid products boiling above the range of said selected aromatic-rich fraction, recovering the latter and returning higher boiling products formed in said third conversion step to the initial conversion step.

5. A process for converting non-aromatic hydrocarbon oil to form a product rich in low-boiling aromatics and low in olefins which comprises, thermally reforming a hydrocarbon distillate boiling within the approximate range of 200 to 400° F. in an initial conversion step to form aromatics and olefins boiling within the range of gasoline, separating light and heavy gasoline

fractions from the resulting products, supplying said heavy gasoline fractions to a second conversion step, therein subjecting the same to further thermal reforming treatment to form low-boiling aromatics and reduce the olefin content of said heavy gasoline fractions, separating from the resulting products a fraction consisting predominantly of the desired aromatics and other hydrocarbons, including olefins, of corresponding carbon-atom content, commingling the same with said light gasoline fractions formed in the initial conversion step and supplying the mixture to a third conversion step, therein subjecting the same to the action of a silica-alumina type cracking catalyst at a temperature within the range of 600 to 1100° F. with a catalyst:oil ratio, within the range of 5:1 to 30:1, regulated to effect conversion of a substantial portion of the olefins supplied to this step, without substantial conversion of the aromatics, and form said product rich in low-boiling aromatics and low in olefins, the process being further characterized by the formation of liquid products in the third conversion step which boil above the range of said aromatic-rich product, and returning higher boiling fraction formed in the third conversion step to the initial conversion step.

6. A process for converting non-aromatic hydrocarbon oil to form a product rich in low-boiling aromatics and low in olefins which comprises, thermally reforming a hydrocarbon distillate boiling within the approximate range of 200 to 400° F. in an initial conversion step to form aromatics and olefins boiling within the range of gasoline, separating light and heavy gasoline fractions from the resulting products, supplying said heavy gasoline fractions to a second conversion step, therein subjecting the same to the action of an aromatizing catalyst under conditions regulated to convert substantial quantities of the olefins in said heavy gasoline fractions into low-boiling aromatics, separating from the resulting products a selected fraction consisting predominantly of the desired aromatics and other hydrocarbons, including olefins, of corresponding carbon-atom content, commingling the same with said light gasoline fractions formed in the initial conversion step and supplying the mixture to a third conversion step, subjecting the same therein to the action of a precalcined solid phosphoric acid catalyst at a temperature not substantially in excess of 600° F. to produce a selected fraction rich in aromatics and of materially reduced olefin content, relative to the charging stock supplied to this step, and to convert substantial quantities of the olefins in said charging stock into liquid products boiling above the range of said selected aromatic-rich fraction, recovering the latter and returning higher boiling products formed in said third conversion step to the initial conversion step.

7. A process for converting non-aromatic hydrocarbon oil to form a product rich in low-boiling aromatics and low in olefins which comprises, cracking said oil in an initial conversion step to form aromatics and olefins boiling within the range of gasoline, separating light and heavy gasoline fractions from the resulting products, supplying said heavy gasoline fractions to a second conversion step, therein reforming the same under aromatizing conditions to form additional quantities of aromatics and materially reduce the olefin content of said gasoline fractions, separating from the resulting products a selected fraction consisting predominantly of the desired

aromatics and other hydrocarbons, including olefins, of corresponding carbon-atom content, subjecting said selected fraction together with said light gasoline fractions formed in said initial conversion step to the action of a silica-alumina type cracking catalyst in a third conversion step at a temperature within the range of 600 to 1100° F. with a catalyst:oil ratio, within the range of 5:1 to 30:1, regulated to effect conversion of a substantial portion of the olefins supplied to this step into liquid products boiling above the range of the desired aromatics without substantial conversion of the latter, recovering from the resulting products said aromatic-rich fraction of low olefin content, and returning higher boiling fractions formed in the third conversion step to the initial conversion step.

8. A process for converting non-aromatic hydrocarbon oil to form a product rich in low-boiling aromatics and low in olefins which comprises, cracking said oil in an initial conversion step to form aromatics and olefins boiling within the range of gasoline, separating light and heavy gasoline fractions from the resulting products, supplying said heavy gasoline fractions to a second conversion step, therein reforming the same under aromatizing conditions to form additional quantities of aromatics and materially reduce the olefin content of said gasoline fractions, separating from the resulting products a selected fraction consisting predominantly of the desired aromatics and other hydrocarbons, including olefins, of corresponding carbon-atom content, subjecting said selected fraction together with said light gasoline fractions formed in said initial conversion step to the action of a precalcined solid phosphoric acid catalyst in a third conversion step at a temperature not substantially in excess of 600° F. to convert substantial quantities of the olefins in said selected fraction into liquid products boiling above the range of the desired product rich in aromatics and low in olefins, recovering the latter from the resulting products and returning higher boiling products formed in said third conversion step to the initial conversion step.

9. A process such as defined in claim 7, wherein said initial conversion step comprises a catalytic cracking operation employing a silica-alumina type cracking catalyst.

10. A process such as defined in claim 8, wherein said initial conversion step comprises a catalytic cracking operation employing a silica-alumina type cracking catalyst.

11. A process such as defined in claim 7, wherein said second conversion step employs an aromatizing catalyst and is conducted in a system of the fluid bed type.

12. A process such as defined in claim 8, wherein said second conversion step employs an aromatizing catalyst and is conducted in a system of the fluid bed type.

13. A process such as defined in claim 4, which includes the additional steps of separating 4 carbon atom fractions from lighter normally gaseous

products of said conversion steps, subjecting said C₄ fractions to catalytic alkylation to chemically combine iso-butane with butylenes and form a substantially saturated alkylmer gasoline rich in iso-octane, and returning the higher boiling products of the alkylating step to the initial conversion step.

14. A process such as defined in claim 4, which includes the additional steps of separating 4 carbon atom fractions from lighter normally gaseous products of said conversion steps, subjecting said C₄ fractions to catalytic alkylation to chemically combine iso-butane with butylenes and form a substantially saturated alkylmer gasoline rich in iso-octane, returning the higher boiling products of the alkylating step to the initial conversion step, and returning unconverted normal butane from the alkylating step to the first conversion step.

15. A process such as defined in claim 4, which includes the additional steps of separating 4 carbon atom fractions from lighter normally gaseous products of said conversion steps, subjecting said C₄ fractions to catalytic alkylation to chemically combine iso-butane with butylenes and form a substantially saturated alkylmer gasoline rich in iso-octane, returning the higher boiling products of the alkylating step to the initial conversion step, and returning unconverted normal butane from the alkylating step to the second conversion step.

16. A process such as defined in claim 4, which includes the additional steps of separating 4 carbon atom fractions from lighter normally gaseous products of said conversion steps, subjecting said C₄ fractions to catalytic alkylation to chemically combine iso-butane with butylenes and form a substantially saturated alkylmer gasoline rich in iso-octane, returning the higher boiling products of the alkylating step to the initial conversion step, and returning unconverted normal butane from the alkylating step to the first and second conversion steps.

17. A process such as defined in claim 7, which includes the additional steps of separating 4 carbon atom fractions from lighter normally gaseous products of said conversion steps, subjecting said C₄ fractions to catalytic alkylation to chemically combine iso-butane with butylenes and form a substantially saturated alkylmer gasoline rich in iso-octane, and returning the higher boiling products of the alkylating step to the initial conversion step.

18. A process such as defined in claim 8, which includes the additional steps of separating 4 carbon atom fractions from lighter normally gaseous products of said conversion steps, subjecting said C₄ fractions to catalytic alkylation to chemically combine iso-butane with butylenes and form a substantially saturated alkylmer gasoline rich in iso-octane, and returning the higher boiling products of the alkylating step to the initial conversion step.

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