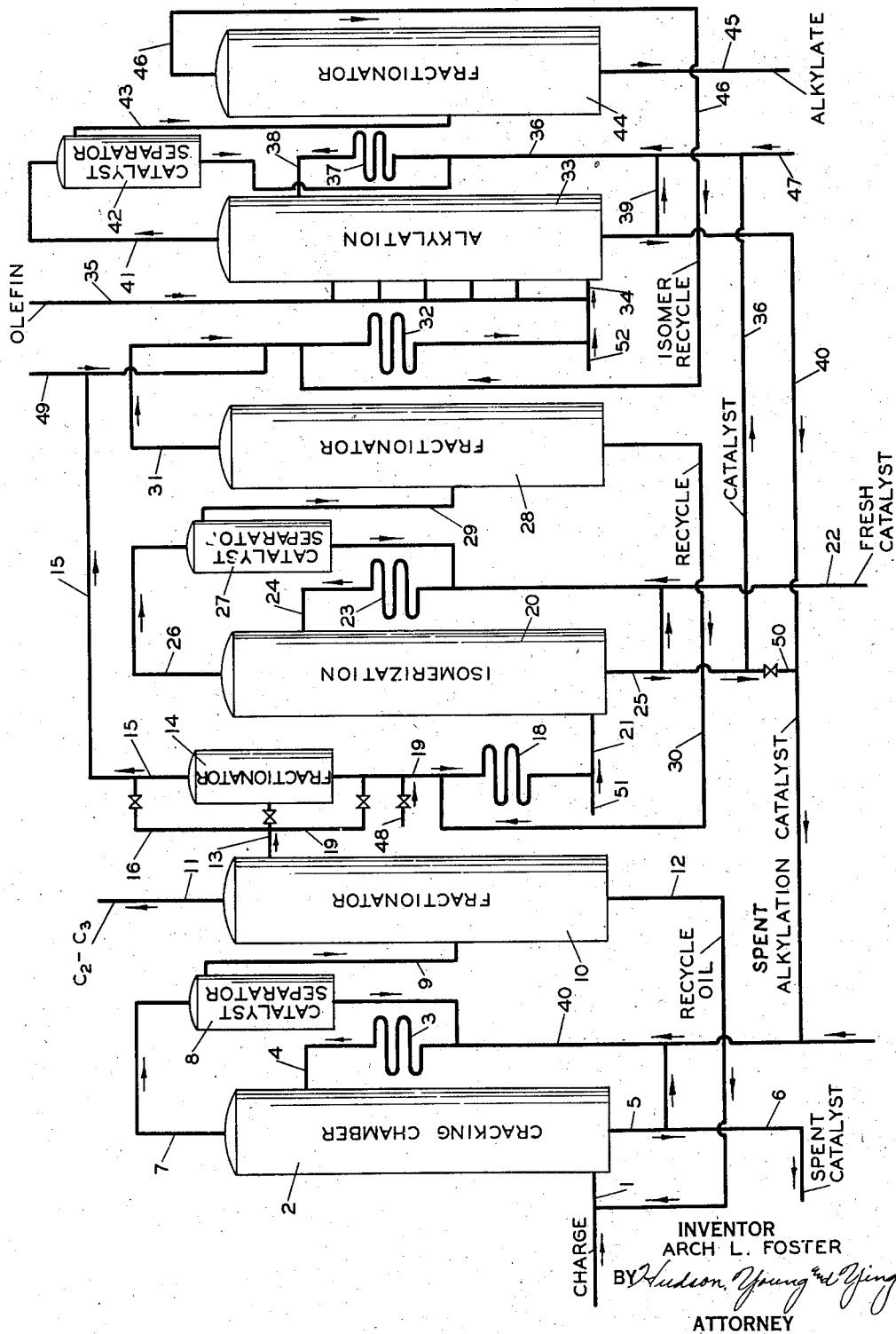


2,385,806

Filed Feb. 16, 1942



UNITED STATES PATENT OFFICE

2,385,806

CATALYTIC CRACKING-ISOMERIZATION
ALKYLATION PROCESSArch L. Foster, Bartlesville, Okla., assignor to
Phillips Petroleum Company, a corporation of
Delaware

Application February 16, 1942, Serial No. 431,174

7 Claims. (Cl. 196—54)

My invention relates to an improved process of hydrocarbon conversion. In a specific aspect it relates to a process of making hydrocarbons boiling in the motor and aviation fuel range. One particular embodiment has reference to a process including the steps of cracking heavy oils, i. e., petroleum oils boiling above the motor or aviation fuel range to produce a maximum of C₂ to C₆ paraffinic hydrocarbons, isomerizing resulting paraffins of four to six carbon atoms per molecule to isoparaffins and alkylating these isoparaffins with olefins from an outside source, and using the same catalyst in the steps of the system in a different sequence from that followed by the charge stock in such manner that it is used in steps of progressively increasing severity.

The production of motor and aviation fuel components in an efficient and economical manner has been a problem of great difficulty. Prior practices have involved the use of a plurality of unrelated steps carried out separately and inefficiently in different plants or in different locations. Costs have been excessive because of the inefficiency and non-unitary nature of previous processes. My process aims to markedly reduce these high costs and increase efficiency by providing a unitary process of obtaining these high octane highly branched paraffin hydrocarbons from crude raw material and in which the several steps are uniquely inter-related in a new and unexpectedly efficient manner, and in which a single catalyst is used in the several different steps of the process without intermediate reactivation or regeneration.

This invention relates generally to the treatment of hydrocarbon oils to produce oils more directly adapted to purposes more useful than those to which the original oil may be applied. More specifically it relates to the conversion of heavy oils or of light fractions of lower molecular weight and anti-knock properties to superior fuels of very high anti-knock characteristics and of the desired volatility and vapor pressure required by modern automotive and aviation engines. These desirable results are obtained by a series of catalytic steps, whereby the desired products are obtained in a new and novel manner and more economically than has been practiced in the art heretofore.

The conversion of heavier hydrocarbons of petroleum by thermal means into lighter products having improved volatility and anti-knock tendencies has long been practiced by the industry. More recently several catalytic methods for effecting this conversion have been developed

and are being used in commercial processes. In all these processes, especially in those employing thermal methods alone, a large percentage of the charge stocks is converted to gaseous hydrocarbons and light materials too volatile to be used satisfactorily in motor and aviation fuels. Thermal and catalytic processes as normally operated also form hydrocarbons differing widely in molecular weight and volatility and in degree of saturation of the molecules formed by decomposition of the heavy oils. Rectification of these distillates of wide boiling range and widely varying molecular structure produces motor fuels meeting with more or less exactness the specifications for boiling range of motor gasoline. The anti-knock properties of these distillates, while often greatly improved over those of the straight-run gasoline from the crude are not satisfactory for use in aviation and similar fuels requiring especially high octane number characteristics. The unsaturated nature of these products also makes them unsuitable for aviation fuel purposes. Addition of hydrogen to saturate these molecules is a process well known in the art, but is expensive, and generally reduces the anti-knock tendencies of the hydrogenated product.

Furthermore, in the distillation, cracking and refining of crude petroleum and its fractions varying amounts of saturated and unsaturated light hydrocarbons, including those containing one to six carbon atoms, are formed. Loss of these hydrocarbons or any substantial part of them reduces seriously the efficiency and the yields in refining petroleum, and methods of utilization of these by-products and of converting them to useful materials improves both the economy of refining and the quality of the products made.

The percentage of these waste hydrocarbons is contingent on the conditions of operation of the processes in which they are formed, and the quantity produced in any refinery at different times may vary widely. Operation of a process employing these waste products as raw material would be hindered or made impracticable if dependence for raw materials is placed solely on this source. It is necessary therefore to make certain that the required amount of charge material is available, and to include in such a process means for insuring an adequate supply of such material. The more satisfactory method is to include means in the process which can supply all the raw material required for the capacity of the process unit, and to add to the charge material from this source such light hydrocar-

bons as may be produced by other processes operated nearby, the use of these waste hydrocarbons being in the nature of auxiliary supply relieving the demands on the primary source of charge stock in the process with which this invention deals. Variation in quantity of such auxiliary-produced charge stocks available can thus be smoothed out by varying at will the amounts produced from the primary source, the first or cracking step in the invention discussed below. Variation in composition of such auxiliary charge material may be obviated within reasonable limits by change in the manner and conditions of operation of the step employed as source of the primary supply of raw material for the succeeding steps of this invention. The net result of providing against all such variations in quantity and quality is to insure that the economics and the efficiency of the process of this invention are satisfactory and therefore that its commercial success is assured within any reasonable limits.

Another of the factors on which the technical and commercial success of a catalytic process depends is economy and efficiency in the use of catalysts. Catalysts, such as those mentioned herein, are efficient for a given purpose under the conditions employed for a given throughput or length of time, and then are said to be exhausted, to require regeneration or which must then be discarded as of no further value. However, I have discovered that the catalysts recommended herein, after having spent their effect in one step of the process, are extremely useful and efficient in other steps under different operating conditions and to effect different results. It is therefore practicable to employ these catalysts in successive steps in the process, and by such repeated employment to make each step more efficient than it can be made in any other manner, and to utilize the catalyst to a much higher degree of efficiency than has been heretofore practised in the art. The sequence of steps and of operating conditions to which the catalyst is subjected is so arranged that, when the catalyst's activity is exhausted at one temperature, pressure or contact rate and because of which exhaustion its efficiency in effecting a given reaction is reduced below a satisfactory level, its activity is somewhat restored and it becomes satisfactory for effecting another reaction under different operating conditions when catalyzing another reaction between or upon other charge stocks or raw materials. An efficient arrangement of the sequence of these steps and of the employment of the catalyst in them, arranging the operating conditions so as to promote to the greatest degree the efficiency of the catalyst and of the reactions which are effected by it in turn, are very important factors in the invention and are an essential part thereof.

The essential arrangement of these steps and of the reaction conditions employed in each step in sequence have been so determined that the results obtained in each step and the composite result of the entire process is higher efficiency in product yield and product quality than is obtainable by any other procedure known to the prior art.

One object of this invention, therefore, is to obtain higher efficiency in the use of catalysts than has been obtained heretofore. This higher efficiency is obtained by utilizing the catalyst or catalysts under different conditions in a series of steps which constitute a major part of the

invention, each step so conditioned and operated that the optimum results in that step are obtained, the catalyst is used to the optimum degree and is left in such condition as to be most efficient in the next step of the process. This method insures the greatest economy in operation of the process, in which economy of operation is one of the essentials for its success.

Another object of the invention is to convert heavy oils, unsuitable for fuels in spark-ignition engines of any type commercially operated now, into fuels of lower average molecular weight, higher volatility and of greatly increased anti-knock values by a process of higher technical efficiency and greater commercial economy than any practised in the art at present. Conversion of such oils to products suitable for these purposes has been consummated in numerous ways, such as by thermal cracking, polymerization of unsaturated low molecular weight hydrocarbons with subsequent hydrogenation with or without catalysts, catalytic cracking, etc., but in every case these processes have been attended by serious drawbacks for some of the purposes for which this invention has been developed, either in quality of product, in yield, in number of steps required to obtain the product, in adverse economy results required in the process or a combination of two or more of these disadvantages. This invention obviates these disadvantages in turn, producing a premium quality product from waste and/or low grade raw materials with the best economy, at the same time utilizing one of the most essential elements of the process, the catalyst, to the highest degree of efficiency.

Still another object of this invention is the utilization of otherwise waste or light, normally gaseous hydrocarbons formed in other refinery processes such as thermal or catalytic cracking as intermediates for the manufacture of these super-quality fuels. This object represents a definite conservation of natural resources and an improvement in the overall efficiency of the refining of petroleum. It also increases the amount of these superior fuels produced from any given quantity of raw material.

Another object of this invention is the utilization of light normally gaseous hydrocarbons which may be obtained in the manufacture of natural gasoline but which possess too high volatility for use as such in motor or aviation fuels in any great amount. Conversion of these hydrocarbons to usable products is also a conservation feature of the process vital to the industry and to economy in the use of natural resources, at the same time contributing to the production of super-fuels highly necessary in our national development.

These several objects of the invention do not exhaust the advantages nor the purposes of it, nor are its purposes and objects confined to those mentioned, which are to be considered as typical examples of its usefulness in application to the technology of the art. Other objects and advantages will become apparent in the specifications and claims which follow.

In accordance with my invention in one form, a catalyst, in slurry or other form which permits it to flow from place to place, is circulated through an individual reaction zone continuously until its reactivity in that step is exhausted; is then transferred to another reaction zone under more severe operating conditions wherein its reactivity is greatly increased for the purpose of the new reaction and is circulated therein until its reactivity for that reaction is exhausted; and is

then transferred to a third reaction zone in which it possesses excellent reactivity for the reaction conducted therein under still more severe operating conditions. Thus, the same catalyst is passed through a series of three steps which make up the process of my invention. These steps, arranged sequentially with respect to path of the hydrocarbon feed, are as follows: (1) heavy oils are cracked catalytically to produce substantially maximum yields of normal and isomeric paraffin hydrocarbons of up to six carbon atoms per molecule. (2) these hydrocarbons are molecularly rearranged to produce isomeric paraffins of more complex structure. (3) the resulting hydrocarbons are alkylated with olefins under optimum conditions for this reaction, to form more complex molecules boiling in the motor and aviation fuel range.

Arranged sequentially with respect to the path of the catalyst, or its use, the steps of my invention are; first the isomerization step wherein temperatures and pressures are the mildest of the three steps, next the alkylation step wherein more severe conditions prevail, and finally the cracking step wherein still more drastic conditions of temperature and pressure are used.

The catalyst need not be in slurry or pumpable form, transferred from zone to zone. On the contrary, it may be a solid, in situ, and by a system of manifolding of the reaction chambers the charge material to each step may be switched so that the same sequence of conditions and reactions are effected in the same tower. Thus the principle of a succession of reactions destined to convert heavy oils into highly branched-chain hydrocarbons of high anti-knock rating and volatilities suitable for motor and aviation fuels, with the same catalyst under conditions suitable for each of the three main reactions is applied in this variation.

The catalyst is employed first in the isomerization step, wherein temperatures and pressures are the mildest used in the process; when its reactivity is exhausted under those conditions, temperatures and/or pressures are increased to values at which its reactivity is somewhat restored and is satisfactory for promoting the alkylation reaction; when its reactivity is exhausted for use in this step, temperatures and/or pressures are raised to values which somewhat restore the reactivity of the catalyst and which are satisfactory for its use in cracking heavy oils to produce paraffin hydrocarbons of two to six carbon atoms per molecule in maximum yield.

I believe that the combination of the steps of cracking, isomerizing, and alkylating in succession in a single closed system with the same catalyst under differing conditions is new. This process enables the operator to effect increases in yields, to pass material from any one step to any other step to produce the maximum yields or maximum conversion with resultant economies in heating, pumping and other attendant steps in the process, and to obtain results, formerly obtained in separate steps at the expense of economies of cost and of production efficiency, at the lowest cost and maximum efficiency in utilization of raw charge stock and of catalyst with a minimum of separate steps. Numerous other advantages of the present invention will be apparent to those skilled in the art from a consideration of the following detailed disclosure.

The purpose of this invention is accomplished by the decomposition, by catalytic means, of

heavy oils to produce a maximum yield of saturated hydrocarbons containing two to six carbon atoms per molecule; by effecting catalytically a rearrangement of the molecular structure of these light hydrocarbons which have at least four carbon atoms per molecule to form branched-chain molecules from normal or straight-chain hydrocarbons and more highly branched structures from the simpler branched-chain types; by combining catalytically these branched-chain hydrocarbons with olefinic light hydrocarbons of the same or a different number of carbon atoms per molecule, to produce still more highly complex branched-chain hydrocarbons of extremely high anti-knock properties and of the desired volatility required in automotive and aviation fuels, or for any other purpose for which these properties are particularly suitable. The terms "heavy oils" as used above is defined to include any hydrocarbon material the lowest molecular weight of the components of which—present in substantial quantities, is greater than the molecular weight desired in the products from the first step in the invention as described below.

It is well known in the art that heavier hydrocarbons under the influence of catalyst suited to the purpose may be decomposed to hydrocarbons of higher and of lower molecular weights. With some catalysts these lighter hydrocarbons so formed will be unsaturated in character, that is, they will contain hydrogen and carbon in a lower hydrogen-carbon ratio than is shown by the type formula C_nH_{2n+2} . Other catalysts form highly saturated products of either normal or straight-chain structure or those of the simpler branched-chain or isometric structure. The catalysts employed in the first step of this invention produce the saturated hydrocarbons under the conditions described and it is to such catalysts that reference is made herein when the term "catalyst" is employed in describing the first step.

It is also known to the art that straight-chain and/or the simpler branched chain hydrocarbons undergo a molecular rearrangement when treated with the proper catalysts, forming hydrocarbons of more intricately branched structures. The second step in this invention accomplishes this molecular rearrangement reaction to prepare the type of highly branched paraffin hydrocarbons required in the third step, from those formed in the first step. These several steps may be accomplished by the use of the same or different catalysts in each reaction step. It is preferable, to obtain the full advantage of this invention, to employ certain catalysts, such as metallic halides in various physical forms, under differing operating conditions, using the same catalyst to effect each of the three steps which constitute this invention.

It is also known that, under suitable reaction conditions and with the necessary catalysts, branched-chain paraffins will unite with either straight- or branched-chain olefins in such manner as to form a larger molecule, chiefly the type of molecule the weight of which is the sum of the molecular weights of the reacting hydrocarbons. By carrying out this reaction in the third step of this invention, a reaction between the branched-chain hydrocarbons obtained as a result of the second step and olefinic hydrocarbons containing two to six or a higher number of carbon atoms per molecule, the final product of this process and invention is composed of hydrocarbons of

complex molecular structure possessing the high anti-knock properties and the range of volatilities which is desired.

It is obvious to one skilled in the art that the composition of the charge stocks employed in this invention, and the operating conditions in the different steps may be varied over a wide range of combinations. These conditions may be changed or varied at will within the limits of the process and of the properties of charge stock, catalyst, etc., either for reasons of the nature of the products desired or of the properties of the raw materials most easily or economically available, for both or for other reasons. Differences in the characteristics of charge stocks, in the nature of the catalyst or in its mode of preparation or use, or in the composition of the product from any step in the process as may be desirable, or in the composition desired in the finished product, and in any or all of these considerations may dictate changes in conditions or vice versa. Changes in any or all of these factors will effect changes in the results obtained. The effect of variations in process details will be apparent to those skilled in the art, and experience in operation of a given unit for the application of this process to any desired purpose or with any combination of raw materials will inform the skilled operator of the effect different conditions will have upon the products made and on the economy of the process. Nor under any circumstances are the examples here given of the operation of the process to be considered as exhausting the possibilities or setting exact limits to the invention. These examples are for the express purpose of showing how the principles on which the invention is based may be applied to the preparation of superior products by the most novel and economical process included in the invention.

Following is a description of how the principles of this invention may be applied in practice. Many variations of this method of application may be used to obtain the desired results. Differences in the nature and properties of the raw material and differences desired in the finished products will dictate changes in operating conditions which will be well within the limits of the invention and which will apply the principles set forth herein.

In accordance with my invention, in its broadest aspect, a petroleum hydrocarbon raw material is subjected to at least two different catalytic conversion operations of fundamentally different type in sequence, in which reaction conditions of substantially differing severity are maintained, such as for example; cracking and isomerization; cracking and alkylation; isomerization and alkylation; cracking, isomerization and alkylation; etc. The same metal halide catalyst, preferably anhydrous aluminum chloride, is used in the different operations, being used first in the less severe or more mild operation, usually until its reactivity for that reaction is substantially spent, and is then used in the more severe operation. By using the same catalyst in conversion steps in which progressively more severe conversion conditions are maintained, the catalyst which is spent for a preceding conversion step is rendered sufficiently active for the next conversion step and great economies are effected.

In a more specific aspect, my invention comprises subjecting a petroleum oil ranging from naphtha to heavy gas oil to cracking over a metal halide catalyst preferably aluminum chloride in anhydrous form which has been spent for

the subsequent alkylation step in the process, under relatively severe conditions to form substantial quantities of C_4 to C_6 paraffin hydrocarbons, and alkylating said C_4 to C_6 paraffins either as such, or the highly branched content thereof, or preferably after a catalytic isomerization step to convert the normal paraffin content thereof and/or the less highly branched paraffin content thereof to the most highly branched isomers which are most desirable for alkylation. The same metal halide catalyst is used in the alkylation step, it being used for the cracking step after it has become spent for said alkylation step. Reaction conditions for the alkylation step which are substantially less severe than those in the cracking step are maintained, and although the catalyst be substantially spent for the alkylation step the more severe cracking conditions cause it to be highly active for the cracking step.

In another embodiment, my invention may comprise subjecting a petroleum oil ranging from naphtha to heavy gas oil to cracking over a metal halide catalyst preferably aluminum chloride in anhydrous form which has been spent for a subsequent isomerization step, under relatively severe conditions to form substantial quantities of C_4 to C_6 paraffin hydrocarbons, and isomerizing the normal paraffin content of said C_4 to C_6 paraffin hydrocarbons and/or the less highly branched paraffin content thereof to the most highly branched isomers.

The same metal halide catalyst is used in the isomerization step, it being used for the cracking step after it has become spent for said isomerization step. Reaction conditions for the isomerization step which are substantially less severe than those in the cracking step are maintained, and although the catalyst is substantially spent for the isomerization step the more severe conditions maintained for the cracking cause it to be highly active for said cracking step.

In a still more specific embodiment the present invention comprises subjecting a petroleum oil ranging from naphtha to heavy gas oil to cracking over a metal halide catalyst, such as anhydrous aluminum chloride which has been spent for a subsequent alkylation step, under relatively severe conditions to form substantial quantities of C_4 to C_6 paraffin hydrocarbons, subjecting to catalytic isomerization the normal paraffin content of said C_4 to C_6 paraffin hydrocarbons and/or the less highly branched paraffin content thereof to form the most highly branched isomers, under relatively mild conditions with fresh solid metal halide catalyst which is the same as that used in the cracking step, and subjecting the most highly branched isomers to alkylation under conditions more severe than for said isomerization and less severe than for said cracking step using as catalyst the spent catalyst from said isomerization step.

The cracking step may be conducted by preheating the cracking feed in suitable equipment up to a temperature of from about 600° to about 800° F. and passing it at this temperature in either the liquid or vaporized form depending upon the feed, the temperature and the pressure, and at a pressure of from about 200 to about 500 pounds per square inch, through a suitable reaction vessel where it intimately contacts the metal halide catalyst. Sufficiently drastic cracking conditions, i. e. temperature, pressure and contact time, are employed to give the desired cracking reaction with the spent catalyst from the alkylation step or the isomerization step. The selection

of pressure, temperature, and contact time will depend upon the specific charge stock being treated and the specifications of the products desired from the cracking step, and will be obvious to those skilled in the art in the light of this disclosure. The metal halide catalyst may be employed either as a slurry, or sludge as obtained from the second or third main steps of my process or may be in situ in the tower in solid form and on any convenient supporting means if desired.

If the slurry or sludge form of catalyst is employed, it is pumped into the cracking tower at a point below the top of the tower and preferably below the point of exit of the charge stock if the latter is in the liquid state. The catalyst is also preheated to the reaction temperature and the tower is heated by external means to maintain the desired temperature or temperature gradient throughout the reaction zone. The tower may also be equipped with perforated or solid baffles set at any convenient angle up to 45 to 60° below the horizontal. The catalyst may be discharged from the bottom of the tower as spent or preferably is recycled, a portion being discharged from the effluent equivalent to the amount of catalyst added to the cracking system.

Temperatures, pressures, and flow rates of charge and of catalyst are so controlled as to produce the maximum yield of C_4 to C_6 paraffin hydrocarbons. Formation of any one or more of these may be increased or decreased by change in operating conditions. The operating conditions to yield the desired type of product may easily be determined by the skilled operator for any given charge stock or combination of stocks. If desired the lighter products formed during the reaction may be vaporized and freed from liquid or solid matter in the upper part of the tower, which space is maintained as a flash space free of liquid or solid material and in which a suitable baffle arrangement may be placed to knock back any solid or liquid entrained material. The effluent will contain the C_2 to C_6 hydrocarbons as well as any lighter and heavy material which may be vaporized at the temperatures and pressures employed and any solid, liquid or vaporized catalyst. These vapors after separation of entrained catalyst are rectified in conventional fractionating equipment, the lighter products going to the plant vapor recovery unit or to any other desired point such as a dehydrogenating unit. The heavier incompletely cracked material is recycled to the cracking step mixed with the fresh charge for further reduction in molecular weight.

If the charge is introduced in vapor form no charge liquid will be present to be discharged from the cracking tower. If in liquid form the residue of the charge is drawn off, the vapor is passed into a knock-out box to remove any entrained or volatilized catalyst and discharged into the fractionating tower. If the same fractionating tower is used for both overhead vapors and liquid residue the liquid may enter the tower at a point below that where the vapors enter. In the latter case the liquid residue is stripped of desirable lighter components, and withdrawn from the tower bottom. Recycle stock may be drawn from a point higher in the same tower as a side stream. The rectified vapors pass overhead from this tower, are preheated if necessary and enter the second step of the process.

Another variation of this part of the process is that fractionation tower conditions of reflux,

temperature, etc. may be varied so that the product is obtained in two or more streams. For example, by the employment of one or more additional fractionating towers, individual hydrocarbons may be isolated and in turn each may be fed to individual separate units in the next step in the process. Or, for example, the C_3 to C_4 fraction may be taken overhead from the main tower, while the C_5 to C_6 fraction may be drawn off as a side stream and fed to the next step in the process separately from the lighter fraction.

In a modification, the fractionation of the cracking effluent may be so conducted as to yield two separate fractions of C_4 to C_6 hydrocarbons, one of which consists of the most highly branched paraffins which may be passed around the isomerization step to the alkylation step, and the other of which consists of the less highly branched and straight chain paraffins which may be passed into the isomerization unit. In this way more effective isomerization is effected since the presence of the most highly branched isomers in the isomerization feed would tend to prevent conversion of less highly branched forms to such isomers by reason of their already high concentration, in consequence of the law of mass action.

Another variation of the process is the use of the catalyst in solid form. In this case the catalyst may be pelleted, briquetted with or without an inert carrier or deposited on a solid inert carrier. Thus the catalyst may be placed in the reaction towers, supported in any convenient manner, as on wire screens, perforated plates or merely stacked in the towers to the desired level.

Cracking conditions are so maintained with any given charge that the total conversion to lighter hydrocarbons is not less than about 10 percent to not more than about 50 percent of the charge. Percentage of the different hydrocarbons vary with varying reaction conditions, but a typical composition of the effluent vapors from the reaction zone is: ethane, 2-5%; propane, 4-15%; butanes, 20-50%; pentanes, 12-30%; hexanes, 5-20%; small amounts of heavier material to be recycled; and also small amounts of methane. Still more severe temperatures and pressures tend to produce larger proportions of the lighter hydrocarbons of relatively simple structure. More rapid throughput and shorter contact time, with less severe temperatures and pressures produce a larger proportion of the pentanes and hexanes with somewhat more branched-chain structure.

The products from the cracking step are highly saturated in character, containing little if any olefins and are chiefly normal and simpler branched-chain products. The ethane and propane in the exit vapors are segregated by fractionation in a suitable low temperature tower from the remainder of the vapors, which latter preferably are at the same time separated into individual hydrocarbon streams, or may be removed in a single fraction for further treatment as described later. In the event that multiple streams of product are obtained by multiple fractionation to segregate hydrocarbons of essentially the same molecular weight in individual streams, it is practicable to further fractionate each of these streams to separate the normal from the branched-chain paraffins in each stream. The branched-chain fraction of each stream may then by-pass the second or isomerization step, described below, and may be used directly as part of the charge to the third or alkylation step, also described below, either blended into one stream or treated in individual reaction vessels as desired.

Generally, however, it is preferable to transfer the entire product from the first step (i. e., the entire C₄ to C₆ paraffin portion) directly to the second or isomerization step, either in a single composite stream or in two or more streams as desired. In this second step the normal hydrocarbons are converted to branched-chain isomers and the simpler branched-chain hydrocarbons are converted to more complex branched-chain isomers, resulting in a final product more complex in molecular structure and higher in anti-knock properties.

Normal and/or isomeric paraffins of C₄ to C₆ may be added to the stream or streams at this point in the system, such as paraffins derived from other sources such as refinery vapor recovery products or those from natural gasoline recovery plants. These outside hydrocarbons may be concentrated to the same degree as the streams from the cracking or decomposition reaction and correspond to their qualitative composition.

The vapor and/or liquid stream or streams from the cracking step are now introduced into an isomerization unit where fresh catalyst either in slurry or solid form is encountered. If in slurry form the catalyst may be made up in any convenient manner as with oil from the charge stock to the first step or with a portion of the charge of C₄ to C₆ paraffins to the isomerization step itself. If solid it may be in any form such as indicated above for the first or cracking step or in any other form convenient or efficient for the purpose. The step described here will include only that variation employing the slurry catalyst form, but the principle of the invention is applied as easily and efficiently when using solid catalyst or a combination of solid and liquid catalyst, and these other modifications are included in the scope of this invention.

The charge stock to the second or molecular rearrangement step is heated if necessary to from about 75° to about 425° F. and pressures from substantially atmospheric to about 350 pounds per sq. in. are employed. The charge may enter the isomerization tower. If a plurality of streams are treated, in separate reaction towers, more severe temperatures and pressures may be maintained for the more refractory streams than for the less refractory in order to obtain a satisfactory conversion rate for all streams. Fresh catalyst may enter near the top of tower or towers continuously, mixed with any slurry which may be recycled, where it meets the ascending charge vapors, and is withdrawn from the bottom of the tower. A portion of the effluent catalyst equal to the amount of fresh catalyst added may be continuously drawn off and transferred to the third step in the process. An auxiliary catalyst or catalyst promoter, such as a hydrogen halide such as anhydrous hydrogen chloride, to the extent of from 1 to about 10% by weight based on the weight of the charge is preferably admixed with the incoming vapors immediately prior to their entrance into the reaction tower. Recycle containing normal hydrocarbons recovered from the isomerization effluent may also be mixed with the fresh charge. The reaction tower may be equipped with a series of horizontal perforated plates, or other means for breaking up the stream of incoming vapor to prevent its passing up through the catalyst in large unbroken volumes, or channeling with consequent poor contact with the catalyst. The time of contact may be varied at will by regulating the rate of introduction of charge. If the requirements of the final product

necessitate a longer contact time than is practicable in one tower, a number of such towers may be operated in series to extend the reaction time to any desired length. The catalyst is preheated to the reaction temperature desired and the isomerization tower is also heated to maintain the required temperature or temperature gradient to achieve optimum results. If a plurality of streams is treated in the isomerization step the operation of each follows essentially the principles outlined above.

Treated vapors from the isomerization unit enter a fractionating tower or towers, after passing through one or more knock-out boxes to remove entrained or volatilized catalyst. In the fractionating system the hydrocarbons of more complex (more highly branched) structure are passed overhead while the normal, straight-chain hydrocarbons are recovered from the bottom of the tower and returned as recycle to be mixed with the fresh charge.

Operating conditions in the isomerization system are maintained such that from about 20 to about 90% of the charge is converted per pass to hydrocarbons of more complex structure, the optimum conversion rate per pass being determined by the requirements of the final or end products and by the composition of the charge.

The branched-chain hydrocarbons overhead from the isomerization step fractionator system pass to the third or alkylation step of the process, being preheated, preferably without prior condensation to a temperature of from about 300° to about 600° F. under pressure of from about 15 to about 500 pounds per sq. in. prior to entry into the alkylation unit which may be operated under said conditions of temperature and pressure. The charge may enter the bottom of the alkylation tower. Where a plurality of streams of C₄ to C₆ iso-paraffins are being alkylated, separate alkylation towers and separate auxiliary equipment may be used for each stream.

Catalyst slurry from the isomerization unit may be circulated through the alkylation unit at a rate not exceeding 100% of the volumetric capacity of the tower per hour and at an actual rate to be determined for each type of charge stock and the type of alkylated product desired.

Olefin hydrocarbons from any convenient source are introduced into the alkylation tower, preferably at a plurality of points. The proportion of olefins introduced into the tower at any instant should not exceed about 10% of the isoparaffin present. The olefins are introduced at intervals spaced so that the olefin-paraffin ratio is so small that polymerization of the olefin is substantially precluded and the desired alkylation reaction between isoparaffin and olefin is promoted to the optimum degree. The olefins are preheated to some temperature not higher than the reaction temperature in the tower but below the temperature where appreciable polymerization takes place. Preferably a small increment of the olefin is mixed with the isoparaffin charge immediately prior to its entrance into the tower.

In addition it is desirable to introduce a small amount of anhydrous hydrogen halide such as hydrogen chloride to the alkylation unit. For example, from about 1 to about 10% by weight based on the weight of the charge may be admixed with the incoming vapors immediately prior to their entrance into the alkylation tower.

Catalyst may be circulated continuously through the alkylation tower, entering at the top and making exit at the bottom, a portion of the

exiting used catalyst being withdrawn continuously and a corresponding amount of spent isomerization catalyst being added to maintain the system constant. The tower may be fitted with a system of horizontal or sloped baffles, either perforated or solid, to insure more intimate and uniform contact between catalyst and reactant vapors. The time of contact may be varied over wide limits by varying the rate of charge input, the height of the tower and of the catalyst column and by the number and design of the baffles. The catalyst is preferably in the form of a slurry as received from the isomerization unit. The catalyst is heated by auxiliary means before entrance to the reaction zone, and the tower is also heated, or insulated, in any suitable manner to maintain the desired temperature or temperature gradient in the reaction zone. This temperature may be varied within the above limits depending on the feed, the specific properties of the desired product and the other operating conditions employed.

The olefin material employed in the alkylation may be obtained from any convenient source, and this source may be varied at the will of the operator. Olefins may be derived from cracked still gases, concentrated to obtain adequate amounts of olefins from ethylene to hexylenes or any desired mixture of these hydrocarbons. Olefins may be derived from the thermal or catalytic dehydrogenation of paraffin hydrocarbons obtained from a source outside my process. A portion of the normal paraffins produced in the cracking step of my process may be diverted to a dehydrogenation step instead of being passed to the isomerization unit. Hydrocarbons of the required number of carbon atoms may be obtained from a source such as refinery or natural gas or gasoline and dehydrogenated to give the necessary olefins.

In the alkylation zone operating conditions are so maintained that no substantial amount of olefins remain unreacted as the vapors exit from this zone. The various control means available to maintain this condition of substantially complete reaction of the olefins introduced to the alkylation unit are obvious to those skilled in the art.

The alkylation reaction vapors are led through a knock-out box for removal of entrained or volatilized catalyst and then to a fractionator where unreacted hydrocarbons are separated from the alkylate and are returned as recycle to be blended with the fresh charge. The alkylate, being high-boiling, is drawn off either at the bottom of the tower as a single stream or as one or more side streams in addition to a bottom stream, and is removed from the system for any further desired treatment or to storage.

The yield of total alkylate from a given stream may be from about 125 to about 200% or more based on the weight of olefin charged to the system. The final product is practically sulfur-free, has an extremely low content of gum-forming materials and is usually ready for incorporation in a finished aviation or motor fuel without further treatment.

The spent alkylation catalyst drawn continuously or intermittently from this step is transferred to the first or cracking step where it mingles with the catalyst in that step, completing the catalyst cycle. The catalyst discharged as spent from the cracking step may be sent to any suitable regeneration means or discarded as desired.

As the catalyst used in carrying out the present

invention I generally use aluminum chloride as most effective and economical. However, I may use anhydrous metal halides generally such as the chloride, bromide or iodide of such amphoteric metals as aluminum, zinc, tin (stannic), titanium (tetrachloride), antimony (antimonic), iron (ferric), etc. While the catalysts enumerated, with the exception of titanium tetrachloride, are solid at normal temperatures, they may be in liquid and/or vapor state under the conditions encountered in my process. Generally however I prefer to use such pressures that substantial vaporization of the catalyst is precluded. Under some circumstances however the catalyst may be largely or entirely vaporized in one or more steps in my process.

It is to be understood that a solid or in situ type of catalyst may be employed in which the catalyst remains in situ in the reaction zone, and liquid or vapor charge is passed through the zone. If the catalyst used is volatile at the temperatures and pressures employed, any portion of it so removed from the reaction zone may be trapped out in the same way as that described for a slurry type catalyst. This recaptured catalyst may be in the form of a slurry and may be discarded but is preferably recirculated to the step from which it escaped. Or it may be commingled with any other slurry type catalyst from any other part of the system and thereafter used in slurry form. Any combination of solid-type and slurry-type catalyst may be used in the same or separate steps of my process. For example, the slurry formed by volatilization and condensation of solid catalyst in one or in two steps of the process may be employed exclusively in one or more steps. Also, the charge stocks to any step of my process may be brought into contact with either slurry or solid catalyst first and then for further reaction introduced to a reaction zone containing the alternate type of catalyst. Thus, vapors entering the isomerization step may be introduced into an isomerization reaction zone in contact with slurry catalyst after which these vapors enter a second zone in which a solid type catalyst is maintained, the slurry employed in the first zone being made up of the catalyst volatilized from the second or solid catalyst zone.

Referring now to the accompanying drawing, cracking stock such as a medium petroleum distillate such as kerosene, gas oil, solar oil or the like is preheated to a temperature of say 750° F. to vaporize it and is admitted via line 1 to the cracking tower 2. Through the tower 2 is circulated a cracking catalyst such as a metal halide in the form of a slurry or sludge derived from the alkylation unit 33 via line 40, the slurry passing through the preheater 3 into the tower 2 near its top via line 4. The catalyst passes downward and exits from the tower via line 5 and is returned to the heater and to the tower to complete the cycle, a portion of it being removed continuously as spent via line 6.

The hydrocarbon vapors are cracked while passing through the reaction zone, which in practice may be one or a series of towers, and the cracked and uncracked vapors leave the tower via line 7, pass through the catalyst "knock-out" box 8 where any volatilized catalyst is condensed and returned to the catalyst system. The vapors enter the fractionator 10 via line 9. From this tower 10 the ethane and propane are drawn off via line 11, the uncracked and partially cracked hydrocarbons are drawn off and returned via line 12 to mingle with the charge stock entering tower 2,

while the butanes, pentanes and hexanes are taken off as a sidestream via line 13. A portion of recycle stock may be discarded from the system by means of a branch from line 12, not shown in the drawing.

This sidestream may now be passed to a fractionating tower 14 wherein iso-paraffins are separated from normal paraffins and pass as overhead via line 15 to the feed to the alkylation unit 33.

Where the sidestream in line 13 is sufficiently high in iso-paraffins, tower 14 may be by-passed by means of line 16 and the entire sidestream fed directly to alkylation unit 33 via line 15. Or the entire sidestream may be by-passed around fractionator 14 to the heater 18 by means of line 19.

In the heater 18 the sidestream in line 13 or the normal paraffin bottom product leaving tower 14 via line 19 is preheated to a temperature between about 75° and about 425° F. and enters the isomerizing reaction zone, tower 20, at a point near its bottom, via line 21. Fresh catalyst slurry is pumped to this system via line 22, is preheated to essentially the same temperature as that of the incoming charge, in the heater 23, and enters the tower 20 near its top via line 24, leaving the tower via line 25 for recycling by mixing with the fresh incoming catalyst.

The isomerized hydrocarbons are transferred through vapor line 26 to the catalyst knock-out box 27, and thence pass via line 29 to the fractionation unit 28 which may be one or a series of towers, where the lower boiling isomers are separated from the high boiling straight-chain hydrocarbons, the latter being returned as recycle via line 30 to the line 19.

The isomerized product passes via line 31 to preheater 32 and thence enters the alkylation tower 33 at the point 34 after being mixed with a small proportion of olefins. The incoming olefins are admitted via line 35 to the tower 33 at a plurality of vertically-spaced points.

Used catalyst from the isomerization system is pumped continuously from line 25 via line 36 through preheater 37 and thence via line 38 into the upper portion of the alkylation tower 33, passes down through the tower and is returned for recycle through line 39. A portion of this catalyst is withdrawn continuously through line 40 and pumped to the cracking system to replace the spent catalyst withdrawn via line 6.

The alkylate formed in tower 33 passes through line 41, catalyst knock-out box 42, and line 43 to fractionator 44 where it is separated from the unreacted material and is removed from the system through the line 45. Unreacted stock is returned to recycle through the alkylation tower through line 46 to re-enter the alkylation unit 33.

Where the isomerization step in unit 20 is omitted or by-passed, the fresh catalyst may be fed into the alkylation unit 33 via line 47 and the rest of the operation may be substantially as shown.

Normal and isomeric paraffins of C₄ to C₆ from an outside source may, if desired, be introduced to the isomerization unit via line 48. Also iso-paraffins of C₄ to C₆ may be fed into the alkylation unit from an extraneous source via line 49.

If desired, although less preferably, spent catalyst sludge or slurry leaving the isomerization unit 20 may be passed directly into the cracking unit by means of line 50 connecting line 36 to line 40.

If desired, appropriate quantities of anhydrous hydrogen chloride or other halide may be in-

troduced into the isomerization unit 20 via line 51 and into the alkylation unit 26 by the line 52 for expediting the reactions therein.

Fresh metal halide catalyst may be introduced via line 22 or line 47 in the form of a slurry containing up to 80 percent of the metal halide, an oil similar to that being treated in isomerization unit 15 or alkylation unit 26 respectively being used to make up the pumpable slurry. Likewise a slurry of fresh metal halide catalyst in the cracking feed may be introduced via line 40 to cracking unit 1 if desired. Also, oil similar to the cracking feed may be used in making up the fresh catalyst slurry introduced to the isomerization or alkylation units.

Preferable methods of carrying out this invention are described herein to produce new and novel results and the invention is shown in sufficient detail to enable one skilled in the art to practice it. It will be appreciated that in connection with the actual operation of any modification of my process much conventional equipment not shown in the flow diagram of the drawing may need to be used and may be readily supplied by one skilled in the art. Such equipment will include pumps, heaters, coolers, catalyst chambers, fractionating columns, reflux lines, temperature controllers, and the like. Such equipment may be adapted in any particular case by one skilled in the art with the benefit of the discussion and disclosures of the operating conditions and material flows given herein. It will be appreciated that various modifications may be included without departing from the spirit of the invention. It is emphasized, however, that this description is purely illustrative and that the invention is not limited thereto, but only by the terms and the spirit of the appended claims.

I claim:

1. A process which comprises subjecting a petroleum oil ranging from naphtha to heavy gas oil to cracking with a metal halide catalyst which has been spent for a subsequent alkylation step, under relatively severe conditions to form substantial quantities of C₄ to C₆ paraffin hydrocarbons, catalytically isomerizing a substantial portion of said C₄ to C₆ hydrocarbons to the iso-paraffin form, alkylating the C₄ to C₆ iso-paraffin hydrocarbons derived from said C₄ to C₆ paraffin hydrocarbons with low molecular weight olefins in the presence of a metal halide catalyst, the same metal halide catalyst being used in turn in said isomerization, alkylation and cracking steps, said isomerization step being conducted under substantially less severe conditions than said alkylating step and said alkylating step being conducted under substantially less severe conditions than said cracking step, and transferring said catalyst after it is substantially spent for said isomerization step to said alkylating step and after it is substantially spent for said alkylating step to said cracking step.

2. A process which comprises subjecting a petroleum oil ranging from naphtha to heavy gas oil to cracking with a metal halide catalyst which has been spent for a subsequent alkylation step, under relatively severe conditions to form substantial quantities of C₄ to C₆ paraffin hydrocarbons, subjecting to catalytic isomerization the content of said C₄ to C₆ paraffin hydrocarbons which is capable of forming more highly branched iso-paraffins under relatively mild conditions using a fresh metal halide catalyst which is the same as that used in the cracking step,

and alkylating the C₄ to C₆ iso-paraffins with low molecular weight olefins under conditions more severe than said conditions for said isomerization but less severe than for said cracking using as catalyst the spent catalyst from said isomerization step.

3. The process of claim 1 wherein said catalyst is anhydrous aluminum chloride.

4. The process of claim 2 wherein said catalyst is anhydrous aluminum chloride.

5. The process of claim 2 in which the cracking effluent is fractionated in such manner as to form separate fractions of the most highly branched C₄ to C₆ paraffins and of the less highly branched C₄ to C₆ paraffins, said second-named fraction is subjected to said isomerization step, and said first-named fraction and the most highly-branched C₄ to C₆ paraffin content of the isomerization effluent are subjected to said alkylation step.

6. The process of claim 2 in which said cracking step is conducted at a temperature of from about 600° to about 800° F. and at a pressure of from about 200 to about 500 pounds per square inch gauge, said isomerization step at a temperature of from about 75° to about 425° F. and at a pressure of from substantially atmospheric to about 350 pounds per square inch gauge, and said alkylation step at a temperature of from about 300° to about 600° F. and at a pressure of from about 15 to about 500 pounds per square inch gauge.

7. A process for producing saturated hydrocarbons of high antiknock value and boiling in the motor fuel range from a heavier hydrocar-

bon material, which comprises subjecting such a hydrocarbon material to catalytic cracking in the presence of a spent metal halide alkylation catalyst from a subsequent alkylation step at a cracking temperature between about 600 and 800° F. and higher than said subsequent alkylation step for a period of time such as to produce a maximum of C₂ to C₆ paraffinic hydrocarbons, separating from effluents of said cracking an isoparaffinic fraction of four to six carbon atoms per molecule and a normal paraffinic fraction of four to six carbon atoms per molecule, subjecting said normal paraffinic fraction to catalytic isomerization in the presence of a fresh metal halide isomerization catalyst at an isomerization temperature between about 75 and 425° F. for a time sufficient to effect substantial isomerization of normal paraffins contained in said fraction forming isoparaffins of four to six carbon atoms per molecule, recovering from effluents of said isomerization isoparaffins of four to six carbon atoms per molecule so produced and passing same together with the aforesaid isoparaffinic fraction to an alkylation step, subjecting said isoparaffins to catalytic alkylation with added olefins in the presence of spent metal halide catalyst from said isomerization at an alkylation temperature to effect alkylation of said isoparaffins to form higher boiling isoparaffins boiling in the motor fuel range, passing spent metal halide catalyst from said alkylation to said catalytic cracking, and recovering from effluents of said alkylation isoparaffins boiling in the motor fuel range so produced.

ARCH L. FOSTER.