Feb. 18, 1947. A. L. FOSTER 2,415,998

COMBINATION PROCESS FOR THE CRACKING AND DESTRUCTIVE HYDROGENATION OF HYDROCARBONS

Filed May 17, 1943 3 Sheets-Sheet 1

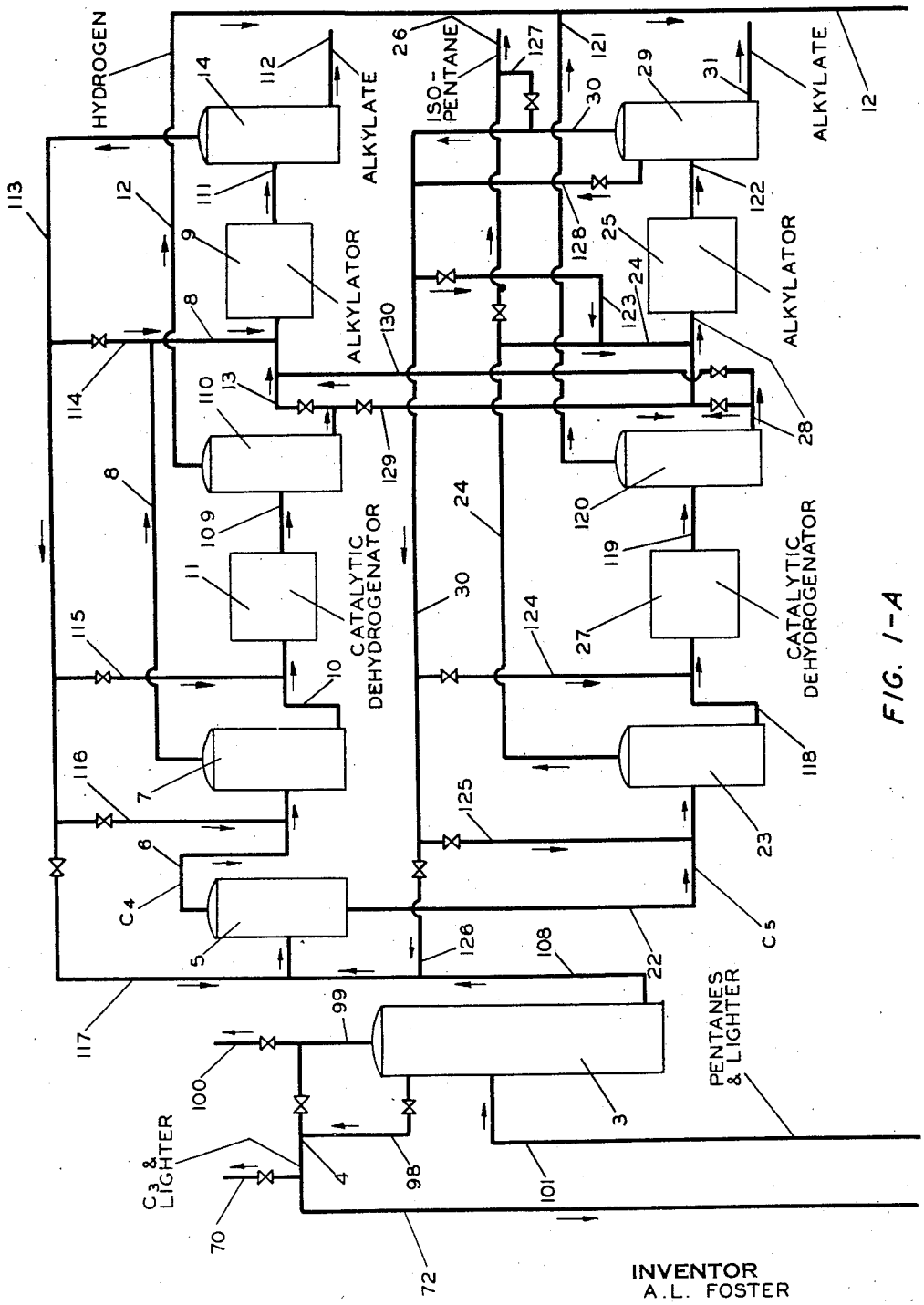


FIG. 1-A

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COMBINATION PROCESS FOR THE CRACKING AND DESTRUCTIVE HYDROGENATION OF HYDROCARBONS

Filed May 17, 1943 3 Sheets-Sheet 2

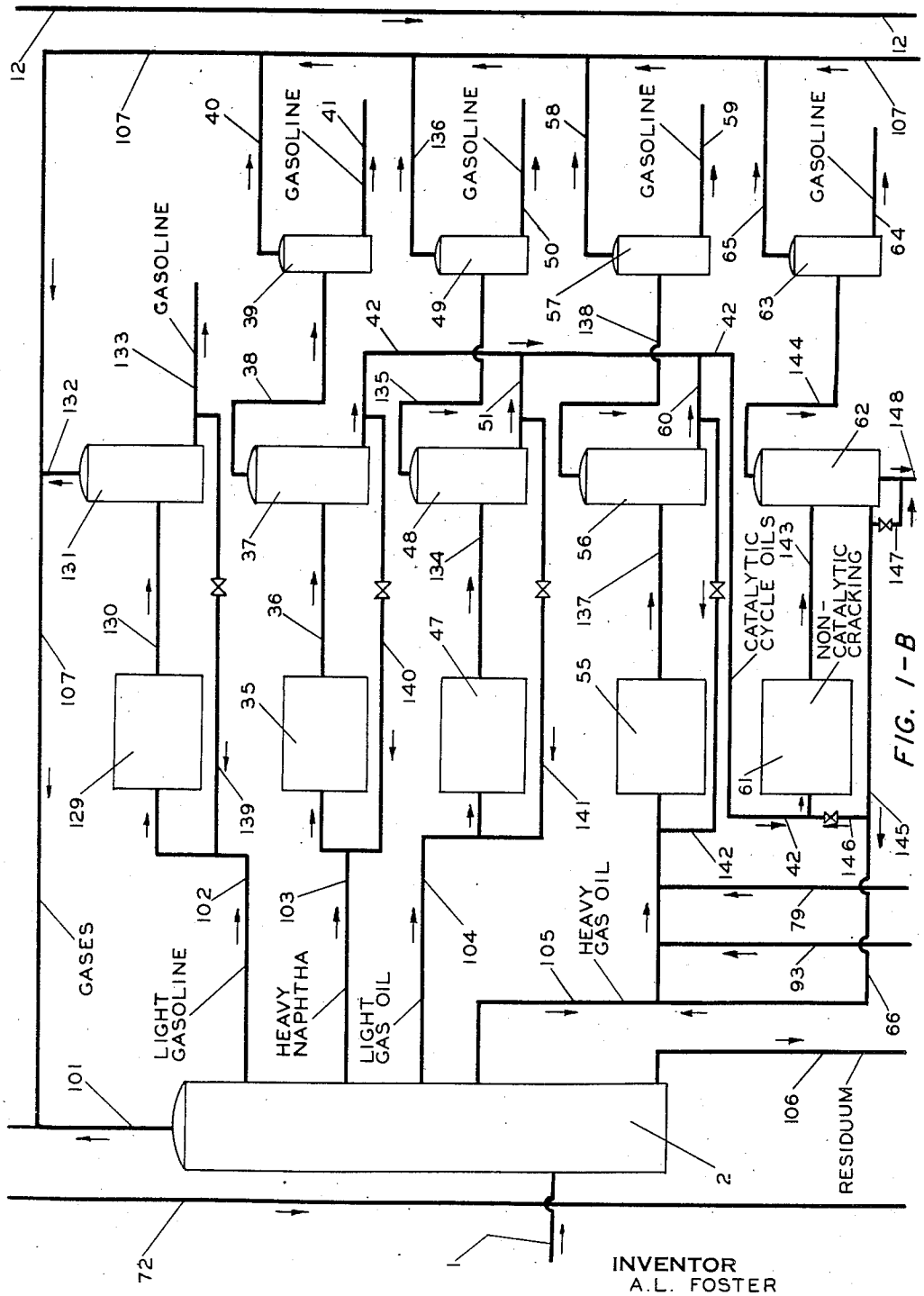


FIG. 1-B

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Filed May 17, 1943 3 Sheets-Sheet 3

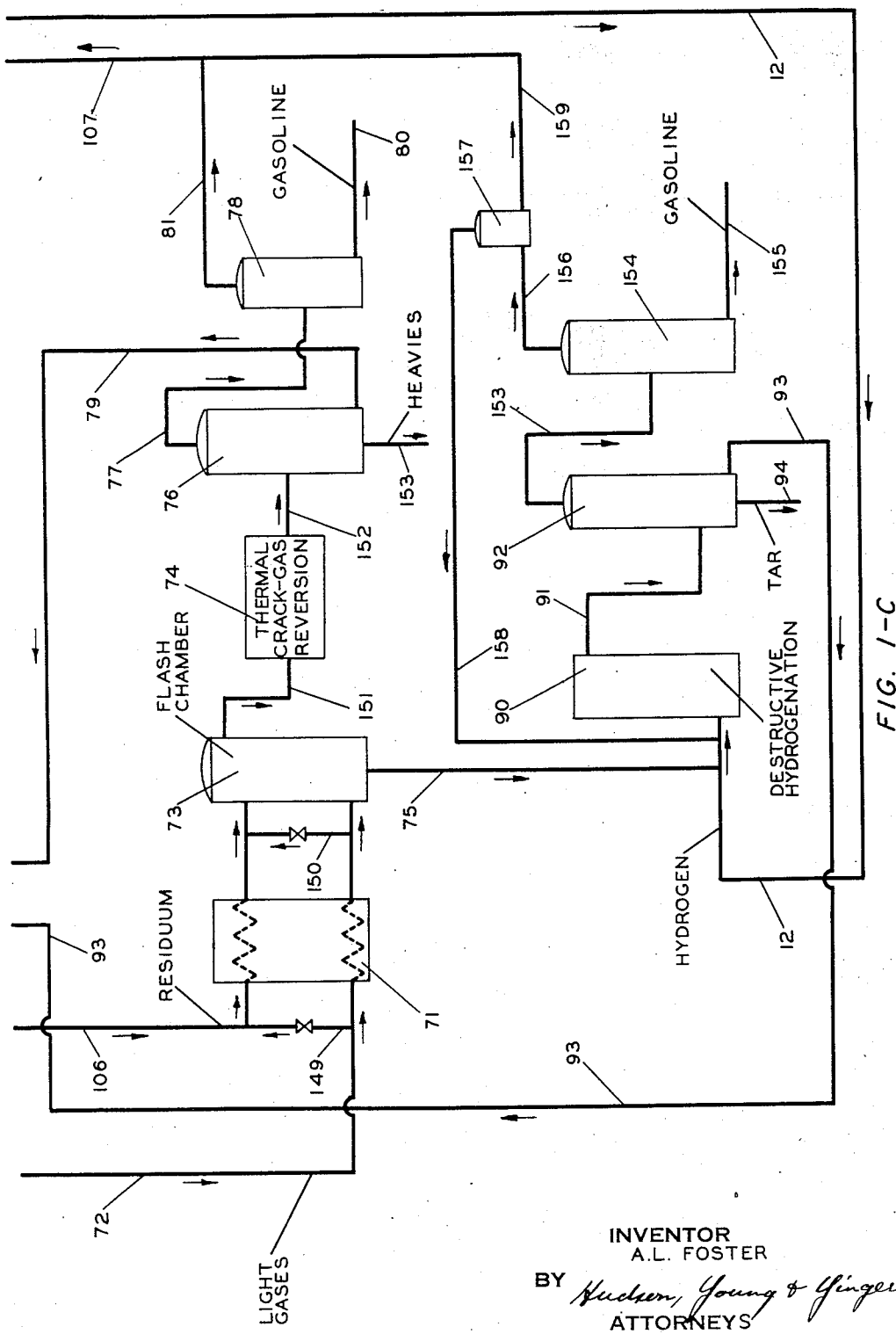


FIG. 1-C

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Patented Feb. 18, 1947 2,415,998

UNITED STATES PATENT OFFICE

2,415,998

COMBINATION PROCESS FOR THE CRACKING AND DESTRUCTIVE HYDROGENATION OF HYDROCARBONS

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Application May 17, 1943, Serial No. 487,364

1 Claim. (Cl. 196—49)

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This invention relates to the treatment of petroleum hydrocarbons for the purpose of converting crude materials into finished products. More specifically it relates to the conversion of hydrocarbons by catalytic and non-catalytic means and to the intercorrelation of particular treatments of definite fractions of crude petroleum to give improved yields of high octane number motor fuel stock.

Modern refinery technology requires that crude petroleum, before being processed further, shall be divided into various fractions suitable for different purposes which may be processed in different ways to yield similar or different products. Furthermore, during the processing of these different fractions, intermediate materials are formed which are ordinarily considered by-products or waste materials, unprocessible for making the main product from the given reaction which, however, may be processed further in a different manner to yield marketable products. In some cases such intermediate or by-products from two or more processes may be combined in such manner as to yield another product otherwise not made, converting a low-grade or waste material into valuable products to improve the efficiency of the process.

A primary object of my invention is to produce high yields of valuable hydrocarbons suitable for use as motor fuel. Another object is to provide increased yields of motor fuel from heavy components of crude oil. Another object is to combine and correlate certain processes and materials in such manner as to produce new materials therefrom, to utilize all waste products to the highest advantage, and to produce large yields of the most valuable products. A further object is to treat together gaseous and heavy residual products obtained by distillation of crude petroleum and from certain catalytic and non-catalytic hydrocarbon conversion processes in such manner as to give optimum yields of high octane number motor fuel stock. Yet another object is to provide a method for the production of motor fuel hydrocarbons from heavier hydrocarbons which are not ordinarily treated to give motor fuel hydrocarbons. Further objects and advantages of the invention will be apparent from the accompanying disclosure and discussion.

In a preferred practice of my invention, a crude petroleum is separated by fractionation into a number of fractions comprising at least (*a*) pentanes and lighter, (*b*) gasoline or naphtha, (*c*) gas oil, and (*d*) residuum. Fraction (*a*) is passed to a second fractionator in admixture with saturated and unsaturated C_5 and lighter hydrocarbons and usually some hydrogen from other conversion steps described below, and the admixture therein separated into fractions including a C_3 and lighter gas. The four- and five-carbon-atom hydrocarbons are recovered together or separately from said fractionator, a portion thereof catalytically dehydrogenated followed by separation of hydrogen and olefins, and said hydrocarbons including said olefins subjected to controlled alkylation which will be described more fully hereinafter. The C_3 and lighter gas mentioned above is heated and admixed with the residuum (*d*) and the mixture flashed, with separation of gas and liquid phases. The gas phase is maintained under reaction conditions such as to effect a non-catalytic gas reversion type of conversion producing light gases, motor fuel, and heavier hydrocarbons. The liquid phase is admixed with hydrogen from the aforementioned catalytic dehydrogenation and subjected to destructive hydrogenation whereby it is converted in large part to motor fuel and hydrocarbons amenable to catalytic cracking. Said hydrocarbons, in admixture with heavier hydrocarbons from said gas reversion and with virgin gas-oil separated from the crude petroleum as fraction (*c*), are subjected to catalytic cracking to give high yields of motor fuel. Light gases produced as by-products are passed to the aforementioned second fractionator. Fraction or fractions (*b*) are subjected to catalytic reforming to give higher octane number motor fuel, and any light gases passed to said second fractionator. Additional features include the non-catalytic cracking of cycle stocks separated from catalytic cracking.

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The accompanying drawing, along with the description thereof, is provided to aid in the understanding of the various aspects and intercorrelations of my invention, and exemplifies a preferred modification thereof. It will, of course, be understood that the invention is not limited to the exact arrangement shown, since various other modifications are indicated herein or will be obvious to one skilled in the art in view of the disclosure herein. The drawing shows diagrammatically an arrangement of apparatus, not necessarily drawn to scale, suitable for carrying out treatment of hydrocarbons in accordance with my invention. The single drawing, for the sake of clarity, comprises three sheets, numbered Figures 1A, 1B, and 1C, with lines interconnecting between the sheets as shown.

Raw crude oil or other charge of wide boiling range, heated to the desired temperature in any

convenient manner not shown in the drawing, enters through line 1 and is flashed in crude fractionator 2. By methods well known to the art the charge is divided into a plurality of overhead, side, and bottom streams, such as the six shown in the figure: line 101 carries pentanes and lighter hydrocarbons, line 102 carries a light gasoline fraction of up to 275–300° F. end point, line 103 carries a heavy naphtha boiling up to 450° F. or higher, line 104 carries a kerosene-light gas oil fraction with, for example, a 550–600° F. end point, line 105 carries a heavy gas oil fraction, and line 106 carries a medium or heavy residuum of any desired specifications. The crude or other charge may be sub-divided into any desired combination of fractions to meet the requirements of the operations without departing from the principles of the invention.

The C_5 and lighter stream passes from fractionator 2 via line 101 into an efficient fractionator 3, and is joined via line 107 by the lighter saturated and unsaturated hydrocarbons, preferably C_5 and lighter, and some hydrogen, separated in various other fractionators in the system from the different conversion steps, as will appear more fully hereinafter. In fractionator 3, an overhead cut is obtained comprising methane, ethylene, ethane, propylene, and propane, and usually some hydrogen, and this C_3 and lighter cut is passed via line 4 to further use as will be explained later. Any portion not required for such use may be withdrawn through line 70 for use as fuel. A portion of the C_3 and lighter stream may be continuously bled off, as by line 70 or line 109, to avoid pyramiding of hydrogen and/or methane in the system. It may sometimes be desirable to separate a lightest fraction comprising hydrogen and which also may comprise methane, via lines 99 and 100, a portion of which may be passed to line 4 if desired, with another fraction comprising C_2 and C_3, and also methane if desired, being separated via lines 98 and 4. The kettle product from fractionator 3 is passed via line 108 to fractionator 5, wherein C_4's are separated from C_5's.

The butane-butene fraction is carried overhead through line 6 into fractionator 7 wherein isobutane and at least part, and preferably substantially all, of the isobutylene and butene-1, are separated as an overhead product which is carried through line 8 to alkylation unit 9. The normal butane together with butenes-2 and any other butenes not taken off overhead are withdrawn as kettle product from column 7 via line 10 and passed to a catalytic dehydrogenation system indicated diagrammatically at 11. This system comprises the usual furnaces, catalyst chambers, catalyst regeneration means, and other equipment well known to the art, which need not be recited here in detail. The dehydrogenation may be carried out without the aid of catalysts, but this is generally less desirable, in that a greater variety of products and poorer efficiency is obtained. The hydrocarbons to be dehydrogenated are preferably passed at the desired temperature, generally in the range of 950 to 1150° F., and flow rate, such as space velocities from 50 to 2000, over an efficient dehydrogenation catalyst, such as one of the chromia-alumina catalysts now widely used for this purpose, and the dehydrogenation products are introduced via line 109 into fractionating system 110, from which hydrogen is separated via line 12 to be used in the destructive hydrogenation step of the process as described below. System 110 ordinarily comprises a single- or multiple-stage scrubbing, combined with fractionation in one or more conventional columns. The butenes formed in the dehydrogenation, plus any butenes fed thereto, are passed from unit 110 via line 13 to alkylator 9. These butenes may be separated in unit 110 from any undehydrogenated normal butane which is recycled to the dehydrogenation unit 11. Ordinarily, however, this is not done, the entire C_4 hydrocarbon content of the dehydrogenation effluents being passed to the alkylation step, wherein the normal butane may take part in the alkylation reaction, although more often, and preferably, it acts merely as a desirable or at least innocuous diluent.

In alkylation unit 9, the isobutane is alkylated by the butenes in any manner known to the art, to give a very high octane number substantially saturated motor fuel blending stock. Preferably a liquid catalyst such as sulfuric acid, or especially hydrofluoric acid, is used, at atmospheric or near-atmospheric temperatures, and with sufficient pressure to maintain the entire reaction mixture in liquid phase. The ratio of isoparaffin to olefin is kept at a value well above 1:1, and frequently as high as 100:1 or even higher, depending upon the particular method of contacting hydrocarbons with acid and upon other characteristics of the alkylation system. The art of alkylation is now well developed and accordingly the various details for carrying out the alkylation itself need not be discussed further. Hydrocarbons effluent from the alkylation are passed via line 111 to fractionator 14, wherein a separation is made between the alkylate product, comprising C_5 and heavier, which leaves through line 112, and C_4 hydrocarbons, generally consisting entirely of iso- and normal butane, which are recycled by means of line 113 to one or more desired points in the fractionation and alkylation system just described. According to the composition of the stream in line 113 and of the other streams, a portion or all may be reintroduced through line 114 for introduction to alkylator 9, line 115 for dehydrogenation in unit 11, or line 116 for separation into iso- and normal components in fractionator 7, from which it again is passed along with other hydrocarbons for dehydrogenation and/or alkylation as described.

It is to be understood that throughout the process disclosed herein various auxiliary steps of intermediate or secondary fractionations or separations other than those described may be employed, such as settling and recycling of mobile catalyst, separation of catalyst from hydrocarbons, separating reacted product from unreacted material which may be recycled, separating by-products from other desired products, and other similar steps which may be required in practice to promote efficiency and increase yields of primary products. All of such steps are not shown herein, their use being indicated by, or being obvious to one skilled in the art in view of, the disclosure herein.

A pentane-pentene fraction is obtained as bottom product from fractionator 5 through line 22, and is subjected to the same type of treatment as that just described for the butane-butene fraction obtained as top product from fractionator 5, but under conditions chosen as optimum for the particular C_5 hydrocarbons being treated, which are generally different from the optimum conditions for the same operations on C_4 hydrocarbons. Material flows from line 22 into fractionator 23, iso-C_5's, particularly isopentane, are taken off overhead via line 24 and passed to alkylator 25, higher boiling C_5's, particularly normal pentane,

are taken as kettle product from 23 via line 118 and passed to catalytic dehydrogenation 27. Effluents from unit 27, comprising principally pentenes, undehydrogenated n-pentane, and hydrogen, are passed to separator 120 via line 119, and separated into hydrogen, which is taken off through line 121 to join the hydrogen in line 12 for further use as later described, and a pentene fraction which is passed via line 28 to alkylator 25.

In unit 25, isopentane is alkylated by the pentenes, preferably through the aid of a suitable alkylation catalyst as described above with reference to the C_4 alkylation step, and effluent hydrocarbons are then passed via line 122 to fractionator 29. The alkylate, a high octane number saturated motor fuel stock particularly suited for use in aviation fuels, is withdrawn via line 31. All or a part of the unreacted C_5's, which are usually substantially free from olefins, may be withdrawn as part of the alkylate to give a desired volatility thereto, and/or may be separated overhead, as by line 30, for recycle in a manner similar to the C_4 recycle from line 113 as heretofore explained. For this purpose lines 123, 124, and 125 are provided, leading from line 30 to alkylator 25, dehydrogenator 27, and fractionator 23, respectively.

Frequently it is desirable to separate out a substantially pure isopentane fraction for use as a blending agent for aviation fuels inasmuch as isopentane has a high octane number and at the same time is highly volatile. Such a fraction may be separated out via line 26. When the pentene content of the feed to fractionator 23 is sufficiently low, or such that pure, olefin-free isopentane can be separated therefrom, such isopentane may be taken off overhead through line 24, with part being diverted to line 26 for the purpose stated. More often, however, such olefin-free isopentane blending stock is best obtained from the alkylation effluents by fractionation in column 29, the alkylation thus serving to remove pentenes from admixture with the isopentane. In this instance, isopentane may be taken as a top product through line 30, with part or all passing via line 127 to line 26, while normal pentane is separated from fractionation system 29 via line 128 and recycled via line 30 to one or more desired points either alone or in admixture with some isopentane. The relative amounts of isopentane used up in the alkylation step or separated as blending agent will of course depend upon the available supply thereof from the crude oil or other charge stock and from the various conversions soon to be described, as well upon the properties desired of the finished motor fuel blend or blends produced by my invention.

A modification of the alkylation steps just discussed which is sometimes preferred because of the relative amounts of the various hydrocarbons available, other uses to which certain of the hydrocarbons may be put, or certain properties of alkylate which it is desired to obtain, involves the alkylation of isobutane with pentenes and/or the alkylation of isopentane with butenes. For this purpose, line 129 is provided for passing butenes to alkylator 25 for reaction therein with isopentane, and line 130 is provided for passing pentenes to alkylator 9 for reaction therein with isobutane. In this manner, instead of obtaining one alkylate which is predominantly C_8 and another alkylate which is predominantly C_{10}, one may obtain a single alkylate which is predominantly C_9 if desired. Another instance in which this modification may be taken advantage of is when butenes are needed for another use, such as a dehydrogenation feed for the production of butadiene to be used in producing a synthetic rubber or the like, and when isopentane is more valuable as an aviation fuel blending stock than as alkylation feed. In this case, only alkylation unit 9 is operated, on a butane-pentene feed, while butenes and isopentane are sent to their respective utilizations instead of being subjected to alkylation. Furthermore, when one or the other of the two alkylation systems is overloaded or underloaded due to a particular manner in which the various conversions are being operated, a portion of fresh charge or recycle charge or both, comprising paraffins and/or olefins, may be diverted through lines shown and/or by means not shown, from one system to the alkylation unit of the other system, and the two charges may thus be at least partially comingled with the production of a mixed alkylate. This type of operation may be utilized over a wide range of concentrations without departing from the limits of the invention as described and claimed, and allows a very desirable flexibility in carrying out the over-all operations. When any of these various modifications are practiced it may be desirable to recycle streams of unconverted hydrocarbons containing both 4- and 5-carbon atom hydrocarbons back to fractionator 5 for separation into the two families of C_4 and C_5 hydrocarbons prior to further treatment, and for this purpose lines 117 and 126 are provided.

While I have referred primarily to alkylation of isoparaffins, it should be understood that I may also alkylate normal paraffins under some circumstances, by either catalytic or non-catalytic means known to the art. Conditions necessary are usually more severe than with isoparaffin alkylation, and the choice will depend upon the relative availability of the various C_4 and C_5 hydrocarbons. Furthermore, while I have shown specific steps for separation of paraffins from olefins and the like, other steps, including those such as selective solvent extraction and the like as well as conventional fractionation, may be utilized, depending again upon the relative proportions of the various hydrocarbons, and on the particular fractions it may be desired to separate out for a certain alkylation or other conversion or utilization. In some cases a portion of the C_3 hydrocarbons comprising propylene may be passed to alkylation along with butenes and/or pentenes. The extent to which dehydrogenation will be used to provide olefin feed for the alkylations is indirectly at least a function of the conversions of heavier hydrocarbons effected in other portions of the system. Generally these conversions are such that, although highly olefinic gases are formed, there is still an excess of paraffins available for alkylation feed stock, thus making possible the use of catalytic dehydrogenation of the same to increase the ultimate yield of alkylate.

Turning now to the hydrocarbons in the crude oil having more than five carbon atoms to the molecule, it will be seen from the drawing that each of the fractions 102, 103, 104, and 105 is treated separately in a catalytic conversion step to produce optimum yields of desired hydrocarbons, usually those boiling in the motor fuel range. Much higher ultimate yields of desired products are obtainable through catalytic treatment of these fractions than would be obtain-

able if they were treated by non-catalytic conversion processes exclusively.

The light gasoline fraction separated from still 2 via line 102 is heated by means not shown to a reforming temperature such as 900 to 1050° F., and passed into unit 129 at a flow rate preferably in the range of 10 to 20 barrels of liquid charge per hour per ton of catalyst over a suitable reforming catalyst such as bauxite, alumina having a small proportion of chromium oxide associated therewith, or others such as those well known to the art, whereby an appreciable improvement in octane number of the gasoline may be obtained while suffering comparatively small loss in yield of gasoline. Reforming effluents are passed via line 130 to stabilizer 131 wherein light gases, primarily hydrogen, are separated overhead via line 132 for passage to line 107 and thence to fractionator 3, while the reformed gasoline product is taken via line 133 for blending with other gasoline products produced elsewhere in the system. Ordinarily no appreciable amount of material heavier than gasoline is formed, and thus no provisions need be made for separating out such material.

The heavy naphtha fraction obtained through line 103 is subjected in known manner to catalytic treatment in unit 35, conditions preferably being such that an effect somewhat intermediate simple non-destructive reforming and cracking is obtained. The catalyst may be primarily a reforming catalyst similar to that used in unit 129, or it may be primarily a cracking catalyst similar to that used in units 47 and/or 55 to be described, or it may be a mixture of such catalysts or any other catalyst composition producing the desired results, the choice being within the skill of the art in view of the instant disclosure. The reaction may be such as to produce a desirable quantity of aromatic hydrocarbons. Reaction effluents pass from unit 35 via line 36 into separator 37, ordinarily a single fractionator, wherefrom material boiling below a desired motor fuel end point, such as 325 to 425° F., is taken overhead via line 38 to fractionator 39, while heavier material is passed via line 42 to unit 61 for non-catalytic pyrolytic treatment, since this material is more amenable to such non-catalytic treatment than it is to a recycling operation to the catalyst over which it has already been passed. A reformed or cracked gasoline is separated from column 39 via line 41, while light gases, comprising C_4 or C_5 and lighter hydrocarbons, generally along with some hydrogen, are passed via line 40 to line 107 and fractionator 3.

The light virgin gas oil separated from other constituents of the crude oil is passed by way of line 104 into catalytic cracking unit 47, wherein it is contacted with a suitable cracking catalyst at an elevated temperature generally in the range of 750 to 1100° F., at a low superatmospheric pressure ranging up to 50 or 100 pounds per square inch gage, and at a flow rate and other reaction conditions usually chosen for optimum production of motor fuel hydrocarbons. The catalyst is preferably one of the so-called silica-alumina type, either synthetic or natural, characterized by the presence of silica along with usually relatively minor amounts of alumina, zirconia, and/or other metal oxides, and typified by silica gel activated with adsorbed alumina on the one hand and acid-washed bentonite clay, such as "Super-Filtrol," on the other. If the production of more isoparaffins and less olefins is desired, a metal halide cracking catalyst such as aluminum chloride may be used in this and/or other cracking units.

It may be mentioned here that the catalytic reforming and/ or cracking units 129, 35, 47, and 55, are merely illustrated diagrammatically in the drawing, and that in general any of these units may be of the fixed catalyst bed type, of the moving catalyst bed type, as typified by the so-called "TCC" process, or of the powdered catalyst type typified by the so-called "fluid catalyst" systems, or of any other design which the economics of a particular situation indicate to be most desirable. While the results obtained from these various types of systems on a given charging stock may vary to a limited extent, it may be said that a given general result may be obtained from any of these systems, and the precise operating details for any such catalytic system will be readily supplied by one skilled in the art, based on the disclosures herein of the materials treated and the results desired. It is to be further understood that all of the necessary equipment for effecting catalyst reactivation, as by burning with air or other oxygen-containing gas, is included in the diagrammatic representation, since such equipment and the operation thereof are now well understood, and accordingly do not of themselves form part of the present invention. To show such equipment further would merely complicate the drawing without contributing appreciably to the teachings of this disclosure.

Returning to the catalytic cracking system 47, reaction products, including unconverted gas oil, pass via line 134 to fractionator 48, from the kettle of which is drawn cycle oil which is passed in whole or in part via line 51 into line 42 for treatment in unit 61. Cracked products are taken overhead through line 135 into fractionator 49 from which a cracked gasoline product of high antiknock value is removed through line 50 while light gases, comprising predominantly olefins and isoparaffins of five and/or four carbon atoms and lighter olefins, and usually very minor quantities of hydrogen and/or methane, are sent via lines 136 and 107 to fractionator 3 for separation into components and utilization as specified elsewhere herein.

Heavy virgin gas oil is passed via line 105, in admixture with material from lines 66, 79, and 93 prepared as hereinafter described, into catalytic unit 55, wherein cracking is effected to produce motor fuel stock of good antiknock value. The catalyst in this case is again preferably of the silica-alumina type, and will generally be derived from a natural clay rather than being synthetically produced, since the life of the catalyst in this step is frequently not so long as in the other cracking units shown, and the cost of synthetic catalyst is likely to exceed its value in obtaining any increased efficiency. Reaction conditions are similar to those used in unit 47. Ordinarily, with catalyst of equal activity, a lower temperature may be utilized in cracking the heavier hydrocarbons. However, with a less active catalyst the temperature in unit 55 may be as high as, or even higher than, that in unit 47. Cracked and unconverted hydrocarbons pass via line 137 into fractionation system 56 wherein residue higher boiling than gasoline is separated as kettle bottoms and passed via line 60 to line 42 where it is intermingled with other charge stock passing to non-catalytic unit 61, while gasoline and lighter fractions are taken overhead from 56 via line 138 to fractionator 57. In this latter

fractionator, the desired high octane number motor fuel stock is obtained as kettle product, which is withdrawn through line 59, and light gases somewhat similar in composition to those obtained from fractionator 49 are taken through line 58 to line 107 for admixture and subsequent separation and treatment with other light gases.

It will be seen from the above discussion that various cuts are separated from the crude petroleum charged to the system, and those cuts ranging from light gasoline to heavy gas oil are separately treated over catalysts to give the desired yields of high octane number motor fuel. This separate treatment makes possible the choice of operating conditions and catalysts optimum for each particular cut. In cracking unit 55 last described, not only is heavy virgin gas oil treated, but also in admixture therewith products obtained from three other stages in the process, which are now to be discussed in detail.

After each of the catalytic treatments referred to, a separation is made, whereby light gases are separated and sent to a common fractionator 3 in admixture with light material obtained from the crude, motor fuel is taken out, and heavy "cycle stock" is obtained. These cycle stocks are all shown as passing into line 42 for subsequent treatment in thermal cracking unit 61. It is to be understood that I may alternatively use a single, common fractionator for separating each of the streams 130, 36, 134, and 137 into the desired light gas, gasoline, and heavier cuts, rather than using the separate fractionators shown in the drawing, and when the catalytic units are each operated on a high conversion per pass, or once-through type of operation, I prefer to pass the effluents therefrom to a common fractionation system. However, it is sometimes more efficient to catalytically reform and crack at a relatively low percentage conversion per pass, with recycle of at least a portion of the unconverted material to the catalyst for additional treatment to obtain a desired overall yield. For this purpose lines 139, 140, 141, and 142 are provided. When this type of procedure is used, it is preferable to use the separate fractionators with each catalytic unit as shown, so that the proper cycle stock for each treatment will be more readily obtained.

In all cases, however, I pass at least a portion of the cycle stock, or partly converted or unconverted materials, to unit 61 for further, non-catalytic cracking. Recycle stocks from catalytic cracking operations are rich in relatively saturated types of hydrocarbons, which are more amenable to purely pyrolytic cracking than to further catalytic treatment, and thus the pyrolytic cracking of the cycle stocks referred to provides a more efficient operation and higher ultimate yield of final product than otherwise obtainable. Such cracking is effected by passing hydrocarbons from line 42 into thermal cracking unit 61, which is constructed and operated in a manner now well known to the art. Generally the hydrocarbons are cracked under pressures of above 200 pounds per square inch, ranging on up to 2000 pounds, and at temperatures of the order of 900 to 1000° F. on up to as high as 1200° F. as may be desired. Light gases from line 4 may be introduced by means not shown into the cracking coils or reaction zone or elsewhere in the cracking unit 61 as desired to promote vaporization of the heated charge, to superheat the charge, and/or to promote gas reversion reactions.

Effluents from unit 61 are passed via line 143 to fractionator 62, from which gasoline and lighter products are passed overhead via line 144 to column 63, while cycle stock is separated via line 145. This cycle stock may in part be returned via line 146 to unit 61 for further cracking in conventional manner, particularly when a relatively low per pass conversion is being obtained therein. However, since the cycle stock is relatively unsaturated and thus more susceptible to catalytic than to further thermal cracking, a portion or all is passed via line 66 to catalytic unit 55, and/or units 35 or 47, to be cracked therein with heavy virgin gas oil and other hydrocarbons as previously described. If this recycle of thermally cracked stock to catalytic cracking, and of catalytically cracked stock to thermal cracking were to be continued indefinitely, the cycle stocks would become more and more refractory due to the build-up of aromatics and other hydrocarbons which are not readily cracked. Accordingly, a portion of stream 145 is withdrawn from the system through lines 147 and 148. Heavy residues from the non-catalytic cracking are also withdrawn from fractionation system 62 through line 148. From fractionator 63 light gases, highly olefinic in character, are taken off overhead through line 65 for passage via line 107 to fractionator 3 in admixture with other light gases, while cracked gasoline product is separated through line 64. This product may be utilized as such, blended with other stocks, or subjected to catalytic aromatizing or other treatment designed to impart particular properties thereto.

Turning now to the residuum from crude fractionator 2, this material passes through line 106 to heater 71 and is heated to such temperature as may be desired, up to that causing some cracking. Light gases separated via line 4 from fractionator 3 as heretofore described, and including both paraffinic and olefinic gases having three and less carbon atoms per molecule, and which also may include some hydrogen, although this is generally not preferred, are introduced via line 72 into a separate coil in heater 71 and/or via line 149 into the liquid charge line 106 prior to entry into a common heating coil. If heated in a separate coil the gases may be brought up to any desired temperature higher or lower than that employed for the liquid reduced crude charge, a temperature as high as 1200° F. being employed in some cases where the maximum vaporization of charge is desired. Both streams, or the streams commingled through use of lines 149 or 150, are flashed in a vaporizing chamber 73, and all vapors pass therefrom via line 151 to the non-catalytic cracking and gas reversion reaction zone 74. The gases serve to superheat the liquid charge before or during flashing, to act as sweeping agent in the vaporization thus giving maximum vaporization of volatile components of the residuum, and to take part in the combined cracking-gas reversion reaction in unit 74. Charge to this unit may be introduced at any desired pressure and temperature, but preferably between about 500 and 1500 pounds per square inch gage and about 850 to 1000° F. A complex series of reactions takes place which may be regarded as a combination of cracking of heavy constituents and of light saturated constituents, along with polymerization of light olefins.

Hot products from unit 74 pass via line 152 to fractionator 76, and vapors boiling in the gasoline range and below pass overhead therefrom through line 77 to stabilizer 78. The stabilized gasoline passes to blending or storage

or for further treatment through line 80, while light overhead gases pass through line 81 to mingle with similar gases from other units in line 107 for passage to fractionator 3. The gasoline thus produced is highly olefinic and possessed of a high antiknock value. In case it is desired to produce maximum yields of aviation gasoline stocks, this particular gasoline is especially suited for use as feed stock to a catalytic treatment which will effect ring closure and other aromatizing reactions, whereby an aromatic stock very useful for increasing the antiknock value and rich mixture performance of aviation fuels is obtained. Recycle oil and insufficiently cracked material, being olefinic to a marked extent, are taken from fractionator 76 through line 79 to catalytic cracking unit 55 where they are subjected to catalytic cracking in admixture with heavy virgin gas oil, cycle oil from non-catalytic cracking unit 61, and the material as described above. Heavy refractory material unsuited for cracking in unit 55 is withdrawn as bottoms from fractionator 76 through line 153 and discarded, although a portion thereof may sometimes be advantageously recycled to line 106 or flash unit 73 by means not shown.

The heavy residual material from the bottom of flash chamber 73 is taken through line 75 to hydrogenation unit 90, wherein it is commingled with hydrogen from line 12, obtained as hereinbefore specified, in contact with an efficient hydrogenation catalyst such as metallic oxides, sulfides, silicates, or any suitable type known to the art, under elevated pressures and temperatures. Pressures may be 500 pounds per square inch or higher and temperatures may be employed up to 1200° F. or even higher; conditions are so chosen that a substantial portion of the heavy material undergoes what is termed "destructive hydrogenation" to produce hydrocarbons saturated in character and of lower boiling range. Reaction products pass through line 91 and are flashed and fractionated in tower 92 wherein heavy tarry material is removed from the system as bottoms through line 94, light gases and gasoline are taken overhead via line 153 to fractionator 154, and material boiling above the gasoline range and suitable for cracking charge is separated out via line 93 to commingle with other stocks passing to catalytic cracking unit 55. A portion or all of this material may if desired be passed to non-catalytic cracking unit 61. From fractionator 154 is produced a gasoline product through line 155, and a light gas fraction which is partially condensed and passed via line 156 to accumulator 157. The gas phase in accumulator 157, composed predominantly of hydrogen, may be compressed and returned to destructive hydrogenation unit 90 through line 158, while the liquid phase is taken via lines 159 and 107 to fractionator 3 for separation and subsequent utilization.

While the invention has been described in some detail with reference to the specific example illustrated by the drawing, it will be appreciated that many variations may be practiced within the limits of the invention. For example, the light and heavy virgin oil in lines 104 and 105 respectively may be treated together in a single catalytic cracking unit; the same is true of the light gasoline and heavy naphtha in lines 102 and 103 respectively, and of the heavy naphtha and light gas oil in lines 103 and 104 respectively, etc. Furthermore, the cycle oils or other products passing through lines 66, 79, and 93 may first be separated into light and heavy fractions, which are subsequently treated separately as in units 47 and 55 for the light and heavy respectively. While maximum yields of motor fuel hydrocarbons are generally sought and obtained through use of my invention, it will be seen that other products may be obtained in increased yields at the expense of motor fuel production when economic conditions so demand. The various gasoline and other products will frequently be blended together to give a final composite motor fuel, but in many cases one or more of the products may be utilized separately. Also, many of the products and intermediate streams will receive additional treatment, such as clay treating, desulfurization, etc., not described or shown, since the application of such treatment is well understood in the art. Obviously many auxiliary and minor steps have been omitted from this description, since they are well known in the art and simply constitute good practice known to any qualified designer or operator. Various pieces of equipment, including reflux condensors and accumulators, reboilers, valves, pumps, compressors, heating and cooling means, heat exchangers, and the like have not been shown in the drawing for the sake of simplicity. A few valves have been indicated where obviously alternative flows might be used, but it will be understood that no attempt has been made to show all pressure reducing or other valves.

I claim:

A process for the production of motor fuel stock from heavy components of crude petroleum which comprises separating from said crude petroleum a virgin gas oil and a residuum consisting of hydrocarbons higher boiling than said gas oil, flashing said residuum in admixture with a light gas comprising hydrocarbons of more than one carbon atom per molecule at an elevated temperature whereby a gas phase is produced comprising said light gas and volatile constituents of said residuum and a liquid phase is produced comprising heavier constituents of said residuum, said light gas comprising paraffinic and olefinic gases produced in first, second, and third conversion steps hereinafter described, separating said gas phase and maintaining the components thereof in a first conversion step under elevated temperature and pressure and for a sufficient time in a non-catalytic reaction zone to effect substantial production of motor fuel hydrocarbons, separating said motor fuel hydrocarbons as a product of the process, separating a fraction of heavier hydrocarbons so produced and substantially free from constituents boiling in the range of said residuum and passing the same in admixture with said virgin gas oil and a hydrogenated material of similar boiling range produced as hereinafter described in a second conversion step in contact with a cracking catalyst at cracking conditions to effect substantial production of motor fuel hydrocarbons, separating said motor fuel hydrocarbons as a product of the process, subjecting said liquid phase produced by said flashing of said residuum and light gas to destructive hydrogenation in a third conversion step in admixture with hydrogen in the presence of a hydrogenation catalyst at elevated temperatures and pressures to produce substantial quantities of hydrocarbons lower boiling than said residuum, separating motor fuel hydrocarbons so produced as a product of the process, and subjecting to cracking as hereinbefore specified

hydrogenated hydrocarbons so produced higher boiling than said motor fuel hydrocarbons but lower boiling than said residuum.

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