

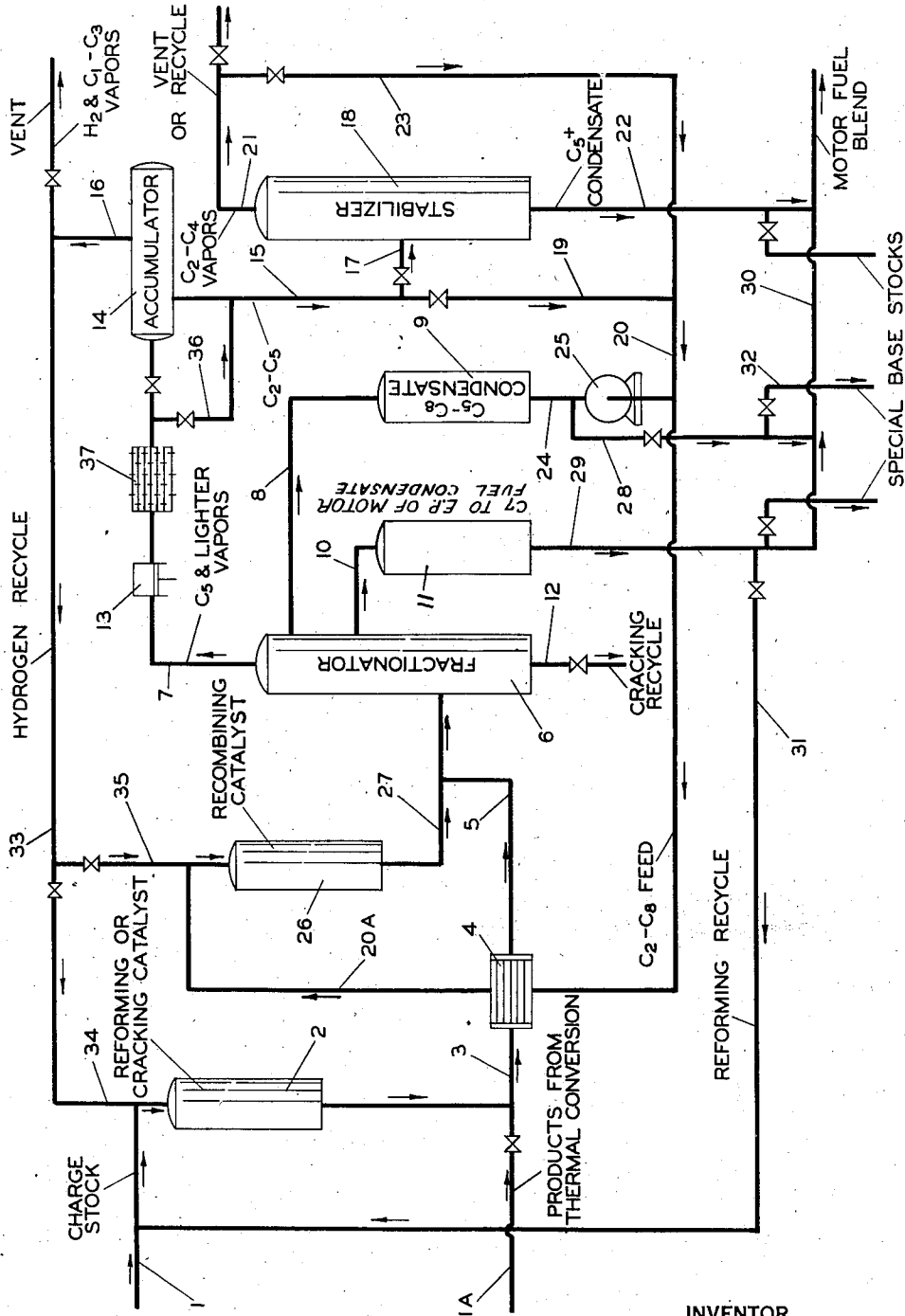
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PROCESS FOR THE CATALYTIC TREATMENT OF HYDROCARBONS

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PROCESS FOR THE CATALYTIC TREATMENT
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This invention relates to the catalytic conversion of hydrocarbons to produce motor fuels. More specifically the invention relates to the catalytic treatment of hydrocarbons ranging from those normally gaseous to liquids higher boiling than gasoline to produce motor fuels of improved quality and in greatly increased yields. While the process of the present invention is applicable to a wide variety of charging stocks, it is of particular value in application to the total or the partially fractionated effluents of cracking and/or reforming operations designed to produce valuable motor fuel components.

It is conventional refining practice to subject low-octane distillates and cracking stocks to high temperature conversion treatments in order to produce motor fuels of improved antiknock characteristics. Thermal cracking and reforming may be thus employed, and more recently catalytic processes for producing and/or improving motor fuels have been emphasized. The products of such conversions comprise, in addition to the desired motor fuel fractions, amounts of lighter and heavier hydrocarbons which vary with the nature of the charging stock and the conditions of conversion. Thus, gasoline or naphtha reforming operations may yield largely gasoline and lighter gases, while cracking operations produce the same materials plus heavy recycle distillates or residual stocks.

Various methods have been proposed for increasing motor fuel yields from such processes and the use of catalysts with generally milder conditions and increased specificity of conversion has been of great economic benefit. However, the lower-boiling fractions, comprising C_5 and lighter hydrocarbons, which often are produced in large quantities by high-temperature conversions can be retained in only limited amounts in the final fuel blends, and thus must be removed by fractionation in the so-called stabilization of said fuels. In this instance, stabilization refers to the adjustment of the vapor pressure and/or volatility of the motor fuel blends. The stabilization thus requires additional fractionation equipment, reduces the volume of product, and simultaneously removes a potential source of additional high-octane liquid products.

It has been proposed to separate the normally gaseous products, which are often rather highly unsaturated and to partially convert these into liquid products of suitable boiling range by thermal and/or catalytic polymerization or alkylation. Such a procedure has ordinarily involved separate facilities for obtaining and treating the feed stock and for fractionating the effluents to

recover the gasoline boiling range material. This separation of the cracking and/or reforming step from the polymerization or recombining step is ordinarily justified on the basis that optimum conditions for each step are quite different and the efficiency of each step is enhanced by the separation. From an operating standpoint, it is desirable that the steps be integrated to utilize common fractionation, stabilization and other processing equipment, but the necessary feed stock segregation and reaction control to avoid under or over conversion have heretofore been lacking.

It is an object of this invention to integrate more closely the operation of a process designed to produce maximum yields of motor fuel components from light or heavy charging stocks.

Another object of this invention is to produce high yields of motor fuel components within a single group of processing units in such a controlled volume ratio that the blends obtainable are substantially balanced with regard to volatility and distillation characteristics and have modified olefin content and improved susceptibility to antidetonants. Often the high octane products of conversion processes must be refractionated to remove valuable light ends or blended with heavy stocks of less desirable quality. The present invention avoids this difficulty by providing for suitable treatment of the said conversion products to revise the distillation curve of a fuel blend without impairing the quality thereof and with appreciable increase in overall yields.

Broadly, the invention embodies a first step wherein a hydrocarbon charge stock undergoes high temperature conversion, preferably in the presence of a catalyst, although thermally converted streams may be handled with somewhat decreased efficiency. The effluent from the high temperature conversion, comprising hydrogen and hydrocarbons ranging from methane through high-boiling liquids, are submitted to fractionation to separate and recover (1) light vapors lower boiling than about C_5 hydrocarbons; (2) a light liquid condensate comprising C_5 to about C_6 hydrocarbons; (3) an intermediate liquid condensate comprising about C_7 and higher boiling hydrocarbons up to the normal end point of the desired motor fuel blends; and (4) one or more heavy distillate or residual stocks which may serve as recycle streams to thermal or catalytic cracking operations.

The vapor stream from the fractionation is submitted to compression to attain the pressure required by subsequent processing steps, and hydrogen-rich uncondensed vapors are removed

from the condensate resulting from compression. This compression condensate is then returned, with or without stabilization to separate essentially C_5 hydrocarbons, to a catalytic treatment at moderately elevated temperature and pressure over a recombining catalyst, being admixed ahead of said catalyst with controlled proportions of the lighter liquid condensate from the primary fractionation zone. A number of reactions may occur in the second catalytic treatment, including alkylation, isomerization, polymerization, and limited hydrogenation when hydrogen is supplied. The net result is an increase in the proportion of high octane normally liquid hydrocarbons within the motor fuel boiling range. The effluents from the recombining catalyst are discharged into the common primary fractionating zone, and the fractionator condensate streams are continuously withdrawn from the system in the desired proportions to produce finished motor fuel blends. Stabilizer bottoms may be produced and added as required to regulate the vapor pressures of said blends.

One specific application of the process may be further illustrated by reference to the drawing which is a simplified flow diagram showing conventional equipment arranged to perform the basic process steps. In the drawing a preheated hydrocarbon charge stock which may be a heavy gas oil distillate for cracking or a selected naphtha cut for reforming enters by line 1 and is treated over the cracking and/or reforming catalyst in vessel 2. The effluents pass through line 3, heat exchanger 4 and line 5 to fractionator 6 or products from thermal conversion may enter the system through line 1A, pass through said line 3, heat exchanger 4 and line 5 into said fractionator 6. From the fractionator, C_5 and lighter vapors are taken overhead through line 7, while a light liquid condensate is removed as a side-stream through line 8 to vessel 9. This light liquid fraction contains approximately C_5 to C_8 hydrocarbons, the C_7 and C_8 hydrocarbons being present in relatively small amounts resulting from solution and entrapment and partial pressure relations in the fractionator as occasioned by the removal of two side streams from the fractionator and by the non-use of reflux. Refluxing of fractionator 6 is not shown in the drawing nor disclosed in the specification, and since refluxing is not used a given hydrocarbon fraction is contaminated with higher boiling hydrocarbons. It is well known in the art that refluxing controls end points. An intermediate liquid condensate is also withdrawn through line 10 to vessel 11, this condensate containing hydrocarbons from approximately C_7 up to hydrocarbons of boiling points about equal to the end point of motor fuel, and higher boiling liquids nominally heavier or higher boiling than motor fuel are withdrawn through line 12. This last-named stream may be at least partially recycled to the first catalytic zone when cracking is performed therein, although when the original charge stock is a reforming naphtha, the bottoms stream comprises only a small volume of tarry residue and/or polymeric material which may be discarded.

The overhead vapors passing through line 1 are compressed in system 13, cooled in condenser 37, and discharged into accumulator 14 for the separation of uncondensed gases from the compression condensate. The liquid is taken from the accumulator through line 15, while the hydrogen-rich gases pass through line 16 to be vented or recycled as described hereinafter. The liquid com-

prising ordinarily C_2 — C_5 hydrocarbons may then pass through line 17 to stabilizer 18, and/or through line 19 to line 20 which gathers the feed to the second catalytic step. Usually, the condensate stream in line 15 is divided with a portion being fractionated in stabilizer 18 to take C_4 and lighter hydrocarbons overhead through line 21 while the bottoms which are predominantly C_5 boiling range hydrocarbons are removed through line 22 as a blending stock for volatility requirements. The C_2 — C_4 overhead vapors from the stabilizer may be vented, or wholly or partially returned to line 20 through line 23. Usually, the operation is conducted so as to vent continuously a portion of this stream to avoid pyramiding of C_2 — C_4 paraffins within the system.

A secondary stock comprising compression condensate from lines 19 and/or 23 and light side-stream condensate from vessel 9 through line 24 and pump 25 is taken through line 20 to heat exchanger 4 where the necessary heat is ordinarily supplied by the high temperature stream in line 3. Other methods of heating may, of course, be employed. The heated feed then passes through line 20a to catalyst case 26 containing a recombining catalyst capable of promoting the interrelated reactions described above. The treated effluents then pass through line 27 to fractionator 6 for the separation of liquid and normally gaseous products according to the previously-described scheme. As the motor fuel components are thus manufactured and separated, they may be continuously withdrawn and blended in suitable proportions through lines 22, 28 and 29 to blending line 30. Any or all of the designated product streams may also be subjected to clay-treatment or other conventional processing for the removal of color, gum, etc., and if desirable, any of the product streams may be utilized in non-related blends, such as aviation fuel blends for which the light liquid condensate of C_5 — C_8 hydrocarbons may be especially suitable, and for such use is withdrawn through its drawoff line 32.

Example

As an example of my invention the following data are taken as illustrative of the application of my invention when treating a thermally converted, stabilized gasoline. The stabilized gasoline from a deep thermal conversion, after removal of the recycle stock, had the following characteristics:

A. P. I. gravity	76.7
R. V. P.	11.0
10% ————— ° F.	112
50% ————— ° F.	129
90% ————— ° F.	201
Per cent evap. at 212° F.	92.2
Sulfur ————— per cent.	0.113
Bromine number	66
A. S. T. M. octane number	71.4
A. S. T. M. octane number plus 1 cc. TEL	77.9

When separated in a tower similar to fractionator 6, the stream obtained from line 8 had the following characteristics:

A. P. I. gravity	83.7
R. V. P.	15.3
10% ————— ° F.	101
50% ————— ° F.	109
90% ————— ° F.	136
Bromine number	72
A. S. T. M. octane number	73.7

Stream 8 was then passed through the recombining catalyst chamber 26 along with the recycle gases as from line 36—15—19 to yield the following product:

A. P. I. gravity	73.2
R. V. P.	13.4
10% °F	102
50% °F	120
90% °F	495
Per cent evap. at 212° F	73
Bromine number	17
A. S. T. M. octane number	74.0
A. S. T. M. octane number plus 1 cc. TEL	83.5

The liquid volume recovery was in excess of 98 per cent.

When recombined with stream 10 the following product was obtained and compared with the original charge:

	Product	Charge stock
A. P. I. gravity	69.2	76.7
R. V. P.	9.3	11.0
10% °F	116	112
50% °F	151	129
90% °F	335	201
Per cent evap. at 212° F	74.0	92.2
A. S. T. M. octane number	72.4	71.4
A. S. T. M. octane number plus 1 cc. TEL	81.3	77.9
Bromine number	27	66
Sulfur	0.021	0.113

The outlined operation is obviously capable of various modifications depending on the nature of the charge stock, the catalysts employed, and the type of product which is desired. Thus, the hydrogen-rich gas in line 16 may be recycled to the initial catalytic treatment in chamber 2 through lines 33 and 34 and, utilized to control the olefin content of the products and to prolong the catalyst life. Such recycled hydrogen should not be allowed to pyramid in the first catalytic zone to the extent that the conversion is adversely affected. Also, this hydrogen-rich gas may be added in the second catalytic step by injection through line 35 to chamber 26. Alternately, hydrogen for the second step may be provided by taking a portion of the total overhead stream, after compression in system 13, through lines 36, 15, 19 and 20a to the catalyst chamber 26.

When it is desired to produce larger volumes of the light condensate indicated at vessel 9, a portion or all of the intermediate condensate from vessel 11 may be recycled through line 31 to a reforming catalyst. This intermediate condensate fraction of rather narrow boiling range and relatively free of refractory light hydrocarbons may be an excellent recycle feed stock for continuation of the dehydrogenation, alkylation, isomerization, cyclization and other reactions which may take place in the two successive catalytic zones.

In some types of operation involving catalytic cracking of selected fractions with hydrogen recycle and relatively long contact time, it may be found that the intermediate condensate from vessel 11 is rich in aromatics such as benzene, toluene and homologues. In this case the condensate may be withdrawn and processed by precise fractionation, solvent extraction or other suitable means for segregation of aromatics. Or the condensate may be employed as a high octane base stock in the production of special fuel blends. In this type of operation the initial separation of the light and intermediate condensates is of benefit in avoiding possible excessive formation

of heavy products boiling above the motor fuel range in the second catalytic stage.

While the present process is not limited to any particular high temperature cracking or reforming step, it is preferred to employ catalysts in order to have a more selective conversion and to produce larger amounts of unsaturates in the light gas fractions for recombination in the second step. For example, the first step may employ a catalyst of known activity in cracking and/or reforming conversions such as bauxite, active natural silicates, synthetic silica-alumina combinations, or the like. These catalysts may also be promoted with minor quantities of active metal oxides such as those of chromium, nickel, zinc, manganese, cobalt, etc. The conversion step over these catalysts will ordinarily be conducted at temperatures in the range of about 850° to about 1150° F. and at pressures ranging from about atmospheric to about 500 pounds gage or even higher. The particular combination of operating conditions will be determined by the nature of the charge stock and the depth and type of conversion desired.

In producing improved yields of high octane catalytic gasolines by this process, i. e., by proportioning and blending the three product streams illustrated above, the stabilization load may be limited to values producing suitable vapor pressure in the final blends. This method of operation involves direct feeding of most of the compression condensate to the second catalytic step and/or controlling the light vapor recycle by venting from the accumulator 14. Alternately, a somewhat more selective feed to the second step may be produced by a relatively complete depentanization of most of the compression condensate and return of the predominantly C₃ and C₄ vapors to the recombining catalyst. The process steps employed will again depend on the related catalytic treatment and the products which are desired.

The second catalytic step in which recombination of the light products occurs is ordinarily operated at moderately high superatmospheric pressures in order to promote the recombining reactions. However, the conditions employed, particularly with respect to pressure and temperature, will depend on the activity and nature of the catalyst, the composition of the feed stock and the desired products. In general, pressures in the range of about 100 to about 1000 pounds gage are suitable even with catalysts of restricted activity, while temperatures range from about 200 or somewhat less to about 600° F. Higher temperatures may be desirable in certain instances, but are usually not as favorable to the class of reactions which are promoted in this second catalytic treatment.

The flow rates of the feed stock to the second catalytic zone and the time of contact of reactants with the catalyst may be adjusted to conform to the operating temperature and pressure and the catalyst activity. It is considered important in this operation to employ catalysts of relatively moderate activity and hence to provide ample reaction time for the recombination reactions. At the elevated pressures and moderate temperatures employed, part or all of the hydrocarbons passing through the catalyst are in liquid phase, and the contact time even at rather high liquid through-put is satisfactorily long. In this liquid or mixed liquid-vapor phase treatment, both the catalyst life and the degree of conversion are much improved over those ob-

tained in a treatment conducted in vapor phase.

The catalysts which are useful in this recombining treatment are selected carefully on the basis of activity and the desired depth of conversion of the secondary feed stock. Obviously over-conversion with the consequent production of large amounts of heavy tarry residues is not desirable and the catalyst activity is an important factor in controlling the boiling range and quality of the liquid products from this catalytic zone. It is preferred to employ contact catalysts which combine mild activity for promoting alkylation, polymerization and hydrogenation reactions so that ultimate process control will lie in the proportioning of the feed streams and the zone pressure and temperature.

Especially suitable for the recombining step are bauxite catalysts used in natural form or modified by treatment with metal salts or oxides which may affect the rate of one or more of the catalytic reactions. Thus polymerization may be promoted with iron, aluminum or zinc chlorides while chromium, nickel and iron salts may be employed to promote polymerization and hydrogenation. Instead of natural minerals, synthetic combinations of silica, alumina, zirconia and other metal oxides may be used to promote recombination of the low-boiling unsaturates in the secondary feed stream. Highly active and non-selective polymerization catalysts such as various phosphoric acid catalysts with or without metal salt promoters may also be employed in certain instances, although they are not preferred in most applications of the process. Also specific catalysts for promoting isomerization of hydrocarbons, particularly the mono-olefins, may be used in the second catalytic zone to promote re-arrangement prior to or simultaneous with the recombining reactions.

It has been noted that the unsaturation of the products of the second catalytic treatment may be altered appreciably by the inclusion of varying amounts of hydrogen in the secondary feed stream. This function of the recombining catalyst may be of great benefit in the production of high octane products of greatly reduced olefin content from treatment of both the light condensate and the normally gaseous mixtures separated from the compression and/or the stabilization operations of the present process. The advantages peculiar to the present invention are that over-conversion is avoided by the combination of the feed streams ahead of the catalyst, and the integration of the steps which produce and utilize both feed and product streams.

The products of the second catalyst step comprise liquid hydrocarbons resulting from the possible catalytic recombinations of (a) low-boiling olefins in the primary reaction gases and (b) low-boiling olefins in said gases with liquid components of the light condensate. A portion of unreactive components of the gas streams must of course be continuously removed from the system by venting at the fractionator and/or the stabilizer. When only a controlled portion of the compression condensate stream is fed to the stabilizer, this removal of C_2-C_4 paraffins may be accomplished by venting the overhead vapors from the stabilizer.

The volatility of the motor fuel products of the process may be further controlled within the desired range by varying the proportions of light condensate which are withdrawn through line 28 to blending operations. Thus, treatment of a major proportion of this light condensate through

the second catalytic zone tends to produce a heavier product of high octane number but very low volatility. On the other hand, withdrawal of larger amounts of the condensate for blending purposes may lower the average boiling range of liquid products from the second catalytic zone and at the same time directly increase the volume of a low-boiling blending component. In any case, two distinct but related catalytic processes may be operated with the use of only one fractionator and one stabilizer, and the load on the latter is greatly reduced through partial separation of the lower-boiling constituents of the fractionator feed at the indicated side streams and in the compression operation on the overhead vapors.

The process of the present invention is of particular value in such operations as the catalytic reforming of gasoline or naphtha stocks and the catalytic cracking of heavier distillates. The flexibility and economy of operation and the improved yields obtained permit, for example, a reforming treatment in which the depth of conversion is much greater in the first catalytic zone because the normally gaseous products and the low-boiling liquid products are at least partially recombined to produce high octane liquids of suitable boiling range. The overall motor fuel yield of such a process may thus be increased by as much as about 5 to about 10 or more per cent of the charge, and with an appreciable improvement in the quality and lead susceptibility of the product. The net effects therefore may include increased liquid recovery, controlled olefin content and improved response to antidetonants.

In catalytic cracking, the improved yields attributable to recombination of the light products to liquid products of controlled olefin content is also obtained, and the depths of per pass cracking may be economically increased. In fact, it may be desirable to increase conversion in the first step far beyond that producing maximum yield of gasoline boiling range material, and to employ the flexibility of this invention to recombine and/or reconstitute both the normally gaseous and the light condensate fractions. As an example of this type of operation, it is possible to crack gas oil with controlled hydrogen recycle to produce varying amounts of unsaturates in the gaseous and light liquid fractions and substantial amounts of aromatics in the intermediate condensate fraction. From this application of the process it is possible to obtain stocks of high octane number due in one case to aromatics and in the other case to recombined or reconstituted branched chain structure. These stocks are suitable with a minimum of treatment for use as special base stocks in aviation fuels.

In the operation of this invention, it will be understood that various modifications may be made. For example, the catalyst in both catalytic zones will become spent in use, thus requiring replacement or reactivation. In such case, in order to obtain continuous operation, as many catalyst cases may be provided as are required. Also, the products of the process, whether blended or utilized separately may receive any conventional treatment which improves gum or color characteristics or minimizes deterioration in storage.

The preceding disclosure has included specific descriptions and diagrams of preferred operations in order to explain the functioning of the elements of the process and their cooperative features. However, it is intended that all modifi-

cations involving the substitution of obvious and equivalent elements for the specifically described means or equipment are included within the scope of the disclosure. No limitations are, therefore, implied except as defined in the appended claims.

I claim:

1. A process for the production of high quality motor fuel which comprises catalytically cracking a hydrocarbon oil charge stock, passing the effluent of the catalytic cracking step into a fractionating zone and therein separating a vaporous fraction containing predominantly hydrocarbons, and hydrogen, said hydrocarbons being of C_5 and lighter; a light liquid fraction containing approximately C_5 to C_8 hydrocarbons; an intermediate liquid fraction containing hydrocarbons from approximately C_7 up to hydrocarbons of boiling points approximately equivalent to the normal end point of motor fuel; and a bottoms fraction boiling higher than the normal end point of motor fuel; stabilizing said vaporous fraction to remove C_4 and lighter hydrocarbons and hydrogen from the C_5 hydrocarbons; withdrawing as motor fuel blending stocks said C_5 hydrocarbons, a portion of the intermediate liquid fraction and a portion of the said light liquid fraction; passing the stabilizer vapors containing the C_4 and lighter hydrocarbons and hydrogen in admixture with another portion of the said light liquid fraction through a catalytic recombining zone at a temperature of approximately 200° to 600° F. and at such a pressure that said mixture is maintained at least in part in the liquid phase in said recombining zone, passing the effluent of said recombining zone into said fractionating zone in admixture with the first-named effluent, and recycling another portion of the said intermediate liquid fraction into the original charge stock previous to the catalytic cracking step.

2. A process for the production of high quality motor fuel which comprises thermally cracking a hydrocarbon oil charge stock, passing the effluent of the cracking step into a fractionating zone and therein separating a vaporous fraction containing predominantly hydrocarbons, and hydrogen, said hydrocarbons being of C_5 and lighter; a light liquid fraction containing approximately C_5 to C_8 hydrocarbons; an intermediate liquid fraction containing hydrocarbons from approximately C_7 up to hydrocarbons of boiling points approximately equivalent to the normal end point of motor fuel; and a bottoms fraction boiling higher than the normal end point of motor fuel; stabilizing said vaporous fraction to remove C_4 and lighter hydrocarbons and hydrogen from the C_5 hydrocarbons; withdrawing as motor fuel blending stocks said C_5 hydrocarbons, a portion of the intermediate liquid fraction and a portion of the said light liquid fraction; passing the stabilizer vapors containing the C_4 and lighter hydrocarbons and hydrogen in admixture with another portion of the said light liquid fraction through a catalytic recombining zone at a temperature of approximately 200° to 600° F. and at such a pressure that said mixture is maintained at least in part in the liquid phase in said recombining zone, passing the effluent of said recombining zone into said fractionating zone in admixture with the first-named effluent, and re-

cycling another portion of the said intermediate liquid fraction into the original charge stock previous to the cracking step.

3. A process for the production of high quality motor fuel which comprises cracking a hydrocarbon oil charge stock, passing the effluent of the cracking step into a fractionating zone and therein separating a vaporous fraction containing predominantly hydrocarbons, said hydrocarbons being of C_5 and lighter; a light liquid fraction containing approximately C_5 to C_8 hydrocarbons; an intermediate liquid fraction containing hydrocarbons from approximately C_7 up to hydrocarbons of boiling points approximately equivalent to the normal end point of motor fuel; and a bottoms fraction boiling higher than the normal end point of motor fuel; stabilizing said vaporous fraction to remove C_4 and lighter hydrocarbons and hydrogen from the C_5 hydrocarbons; withdrawing as motor fuel blending stocks said C_5 hydrocarbons, a portion of the intermediate liquid fraction and a portion of the said light liquid fraction; passing the stabilizer vapors containing the C_4 and lighter hydrocarbons in admixture with another portion of the said light liquid fraction through a catalytic recombining zone at a temperature of approximately 200° to 600° F. and at such a pressure that said mixture is maintained at least in part in the liquid phase in said recombining zone, passing the effluent of said recombining zone into said fractionating zone in admixture with the first-named effluent, and recycling another portion of the said intermediate liquid fraction into the original charge stock previous to the cracking step.

4. A process for the production of high quality motor fuel which comprises cracking a hydrocarbon oil charge stock, passing the effluent of the cracking step into a fractionating zone and therein separating a vaporous fraction containing predominantly hydrocarbons, and hydrogen, said hydrocarbons being of C_5 and lighter; a light liquid fraction containing approximately C_5 to C_8 hydrocarbons; an intermediate liquid fraction containing hydrocarbons from approximately C_7 up to hydrocarbons of boiling points approximately equivalent to the normal end point of motor fuel; and a bottoms fraction boiling higher than the normal end point of motor fuel; stabilizing said vaporous fraction to remove C_4 and lighter hydrocarbons and hydrogen from the C_5 hydrocarbons; withdrawing as motor fuel blending stocks said C_5 hydrocarbons, a portion of the intermediate liquid fraction and a portion of the said light liquid fraction; passing the stabilizer vapors containing the C_4 and lighter hydrocarbons in admixture with another portion of the said light liquid fraction through a catalytic recombining zone at a temperature of approximately 200° to 600° F. and at such a pressure that said mixture is maintained at least in part in the liquid phase in said recombining zone, passing the effluent of said recombining zone into said fractionating zone in admixture with the first-named effluent, and recycling another portion of the said intermediate liquid fraction and hydrogen into the original charge stock previous to the cracking step.

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