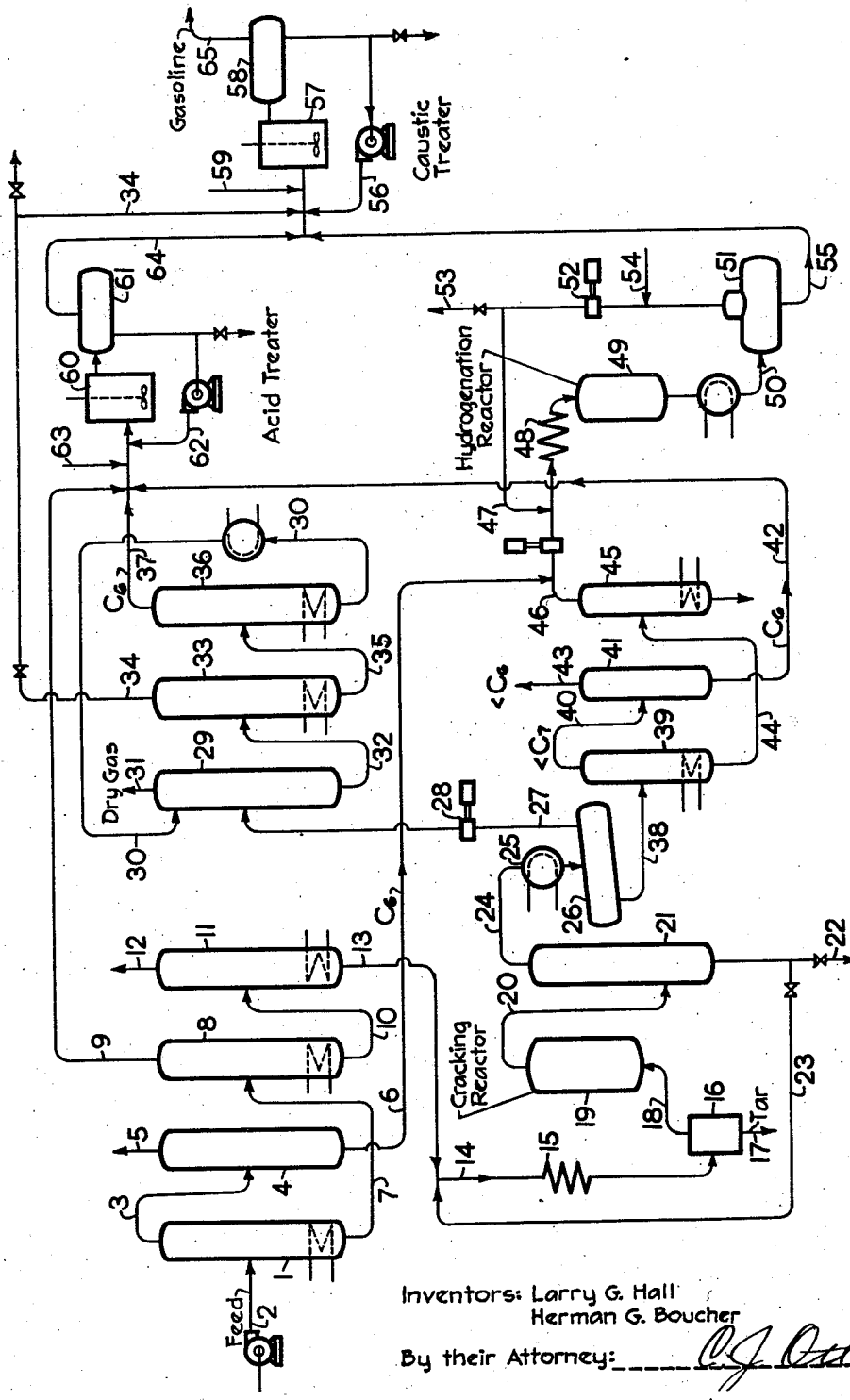
Sept. 10, 1946. L. G. HALL ET AL 2,407,492

PRODUCTION OF GASOLINE

Filed June 11, 1945



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By their Attorney: _____

Patented Sept. 10, 1946

2,407,492

UNITED STATES PATENT OFFICE

2,407,492

PRODUCTION OF GASOLINE

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Application June 11, 1945, Serial No. 598,708

7 Claims. (Cl. 196—50)

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This invention relates to the production of gasoline and especially aviation grade gasoline from petroleums. More particularly the invention relates to a method of treatment whereby increased production of gasoline of any specified quality and comprising straight run gasoline and cracked gasoline may be produced from a given amount of petroleum in a more economical manner.

The primary aim of the petroleum refiner is to produce the maximum amount of best quality gasoline from a given quantity of crude petroleum in the most economical manner. Thus, the criterion of the production obtained is not merely the number of barrels of gasoline produced per barrel of crude, nor the quality of the gasoline, but a combination of these hereinafter referred to as quality-barrel. The term "quality" in this expression is a weighted numerical index of quality such as octane number or such other index as may be suitable. In general the quality of gasoline is fixed by specification and the refiner then strives to produce the maximum amount of material meeting such specifications.

In the usual practice the first step in the production of gasoline from petroleum is to separate gasoline constituents naturally occurring therein. This is effected by a simple topping operation. The product is known as straight run gasoline. Straight run gasoline consists essentially of saturated hydrocarbons and contains only small amounts of impurities which, due to their character, are, furthermore, relatively easily removed. It therefore generally requires and is given only a light acid refining treatment. Straight run gasoline, however, generally has very poor anti-knock characteristics and is consequently of poor quality.

The material remaining after topping to remove straight run gasoline is usually separated somewhat further into one or more such products as kerosene, naphtha, stove oil, gas oil, and reduced crude. One or more of these products is then cracked by various conventional cracking processes to produce additional amounts of gasoline. Any of the conventional cracking processes producing an olefinic high anti-knock gasoline product may be employed. However, in conventional practice, catalytic cracking with clay-type cracking catalysts is preferred since such processes produce gasoline of superior quality.

The cracked gasolines contain appreciable amounts of sulfur compounds, nitrogen compounds, diolefins, acetylenic compounds, and other materials which are difficult to remove by ordinary refining methods without large losses of

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material and considerable depreciation of the anti-knock properties of the gasoline. Refining by conventional acid treating followed by doctor treating and rerunning has the recognized disadvantages of high acid consumption, poor yields and depreciation of the anti-knock properties. In view of these disadvantages such materials are sometimes refined by catalytic methods referred to generally as hydrofining. In this refining method the material is treated under hydrogen pressure in the presence of a suitable hydrogenation catalyst. The chief advantage of hydrofining over conventional acid refining methods is that the material may be refined with less loss of material. However, hydrofining, as practiced at present, is not wholly satisfactory. The process consumes considerable amounts of expensive hydrogen; furthermore, a considerable loss in anti-knock characteristics is usually caused by the saturation of at least part of the olefinic and/or aromatic constituents of the gasoline.

The refined cracked gasoline is then blended with the maximum amount of the refined straight run gasoline that can be tolerated while still maintaining the desired quality of the blend.

It will be appreciated that the refiner usually has at his disposal one or more additives such as alkylate, isopentane, aromatic extract, cumene, xylidine, tetraethyl lead, etc., which are usually added to the blend of cracked and straight run gasoline to produce the final gasoline product. However, the amount of such additives that can be added to the blend of cracked and straight run gasoline (sometimes referred to as base stock) is limited by the limited availability of the additives or by specifications of such factors as heat content, volatility, corrosiveness, and the like. The minimum quality of the blend of cracked and straight run gasoline produced by the refiner is therefore usually below that of the finished gasoline and is determined by the amount of such additives available for use.

In the process of the present invention straight run gasoline and cracked gasoline are produced from petroleum in the above described general manner. The invention lies in the particular method of handling these materials to produce the finished blend. The cracked gasoline may be produced from any portion of the petroleum boiling above the gasoline desired and may be produced by any of the conventional cracking and/or reforming methods which produce a high anti-knock olefinic gasoline. A preferred method is by the catalytic cracking of petroleum oils with clay-type catalyst. Such processes are, for

example, the Houdry process, the Thermofor process, and the fluid catalyst catalytic cracking process. The catalysts used in these processes comprise certain selective natural clays and earths, modified clays, and various synthetic clay-type catalysts. The clays are sometimes used in their natural state but are usually treated and/or modified for instance, by acid washing, removing iron-bearing impurities, leaching out alumina, adjusting the ratio of silica to alumina, and/or by incorporating minor amounts of promoters in order to increase their activity, stability, etc., or to reduce their carbon-forming tendency. Various synthetic clay-type cracking catalysts are also now widely used. These catalysts consist largely of silica and/or alumina and/or magnesia and are often modified by minor amounts of such materials as B_2O_3, AlF_3, $AlPO_4$, ZrO_2, etc. Also certain promoters may be introduced along with the hydrocarbon stream entering the reaction zone. Such promoters include boric oxide, hydrogen, halides, organic halides, etc. The specific catalyst forms no part of the present invention and will not be described in further detail.

In these processes the oil to be cracked is contacted, usually in the vapor phase, with the catalyst under suitable conditions of pressure and residence time at a temperature usually in the order of 750° F. to 1200° F. depending upon the particular hydrocarbon feed, the particular catalyst, and the particular results desired.

According to the process of the present invention there is separated from the cracked gasoline prior to further handling an olefinic fraction consisting largely of C_6 or C_6–C_7 hydrocarbons. Likewise there is separated from the straight run gasoline prior to refining a substantially saturated fraction consisting largely of C_6 hydrocarbons. The separated straight run fraction is blended with the remaining cracked gasoline. Thus, the separated straight run fraction is substituted for the separated cracked fraction in the cracked gasoline. The two materials resulting are separately refined and then reblended. In a preferred embodiment of the invention the separated cracked fraction is also blended with a remaining portion of the straight run gasoline; thus the separated cracked fraction is also substituted for the separated straight run fraction in the straight run gasoline.

The catalytic gasoline containing the separated straight run fraction is mixed with a hydrogen-containing gas and contacted with a hydrogenation catalyst, i. e., hydrofined. The hydrofining treatment may be carried out with any of the catalysts commonly employed and recommended for this process. Examples of suitable catalysts are the oxides and sulfides of V, Cr, Mn, Fe, Co, Ni, Mo and W. Particularly suitable catalysts comprise a sulfide of a metal of the iron group, preferably in combination with a sulfide of a metal of group VI of the periodic system of the elements. Examples of such preferred catalysts are nickel sulfide, iron sulfide, cobalt sulfide, alone and in combination with sulfides of molybdenum or tungsten. These catalysts may generally be used substantially continuously for hundreds of hours without regeneration. The treatment is carried out in the presence of an excess of hydrogen. The amount of hydrogen employed is in general between about 1 and 30 mols per mol of hydrocarbon feed. (Only a portion of this hydrogen is consumed.) The pressure may vary over a wide range. Pressures in the order of 200–2000 pounds per square inch are illustrative. The hydrofining treatment may be advantageously carried out at temperatures ranging from about 400° F. to about 1000° F. When the material treated is high in sulfur (for example containing more than about 0.1% sulfur) low temperatures (below about 850° F.) consistent with the activity of the catalyst and the other treating conditions are generally preferred. If the material treated is low in sulfur (for example containing less than about 0.1% sulfur) higher temperatures (for example, between about 850° F. and 1000° F.) may be preferred. The treatment afforded may be the minimum treatment consistent with the desired degree of refining (as measured by the sulfur content, gum-forming tendency, etc.); this allows the treatment to be effected with a minimum hydrogen consumption and results in the minimum loss of anti-knock properties. In some cases, however, a more thorough treatment to produce a substantially saturated product (particularly when operating at the higher temperature levels) may be more advantageous.

The separated cracked gasoline fraction consisting largely of C_6 hydrocarbons is subjected to a separate non-hydrogenating refining treatment. A preferred treatment is a conventional acid refining treatment, for example, with sulfuric acid or spent alkylation acid (H_2SO_4). The treatment is carried out under conditions of acid concentration, temperature, time, etc., and in the known manner to the extent necessary to provide a suitable refining. The exact strength and/or amount of acid required will depend to a certain extent upon the amount of unsaturated hydrocarbons present in the material treated and to a certain extent upon the conditions employed in the treating step. Any suitable method of contacting the gasoline with the acid may be used and since such methods are well known there is no need to describe them in detail.

The separated cracked gasoline fraction may, in general, be more advantageously treated in a blend with a remaining portion of the straight run gasoline. Thus, according to a preferred embodiment of the invention the separated cracked fraction is blended with a portion of the remaining straight run gasoline (such portion being the remaining tolerable straight run material above the separated straight run fraction blended with the remaining cracked gasoline) and the blend is subjected to the described refining treatment.

After acid treating the material is usually neutralized by washing with an alkaline reagent such as a caustic solution. This treatment may or may not be followed by rerunning, i. e., cutting to the desired end-point.

The hydrofined blend and the acid treated product are blended together in substantially their entirety to produce the desired blend of cracked gasoline and straight run gasoline (base stock) having the necessary quality. To the base stock blend there is usually then added various amounts of one or more additives in accordance with their availability and with due regard to specifications to produce the final gasoline of the specified quality.

Although the novel features which are believed to be characteristic of the process of the invention are mentioned above and are particularly pointed out in the claims appended hereto, the process may perhaps be better understood by referring to the following more detailed descrip-

tion in which specific preferred embodiments are set forth. To assist in this description reference is had to the attached drawing wherein there is shown by conventional figures a simplified flow diagram of a typical application of the process of the invention.

Referring to the drawing, the feed entering via line 2 is topped in topping column 1 to recover overhead a light straight run fraction containing substantially all of the C_5 hydrocarbons and if desired a portion of the C_7 hydrocarbons. This overhead fraction is passed via line 3 to fractionating column 4 wherein it is separated into a lower boiling overhead fraction containing substantially all of the constituents up through pentane which is withdrawn via line 5, and a higher boiling fraction consisting largely of the straight run C_6 hydrocarbons which is withdrawn via line 6. The lower boiling material withdrawn via line 5 may be treated and/or utilized in any desired manner. The straight run fraction withdrawn via line 6 is combined with the dehexanized cracked gasoline as hereinafter described.

The topped feed removed from column 1 via line 7 is passed to a fractionating column 8 wherein a further portion of straight run gasoline is separated. The amount of straight run gasoline separated and removed overhead via line 9 is preferably adjusted with respect to the maximum tolerable amount of straight run gasoline to be included in the finished gasoline. Thus, for example, in a typical operation the material removed from fractionating column 8 via line 9 may have an end-point of, for instance 185° F. This material is combined with the cracked C_6 fraction as hereinafter described.

The bottom product from fractionator 8 is passed via line 10 to a further fractionating column 11 to remove additional material such as naphtha, kerosene, or the like. Such materials are removed overhead via line 12 and may be treated and/or used in any desired manner. The higher boiling residue from fractionator 11 (reduced crude) is passed via lines 13 and 14 to a suitable heater 15 and tar separator 16. Heavy residue or tar is removed via line 17. Vaporized material is then passed via line 18 to a cracking reactor 19 wherein it is cracked in the conventional manner with one of the conventional clay-type cracking catalysts. The cracked product leaves the cracking reactor via line 20 and passes to a fractionating column 21 wherein the converted products are separated from unconverted and insufficiently converted material. This latter material may be withdrawn via line 22 or recycled in whole or in part via line 23 to the cracking reactor. The converted products consisting essentially of gasoline and gases passes overhead from fractionator 21 via line 24 to a cooler 25 and separator 26.

The vaporous product from separator 26 is withdrawn via line 27, compressed by compressor 28, and passed to a typical adsorption system. Thus, this vaporous product is contacted under pressure in absorber 29 with a suitable naphtha or oil fraction recirculated via line 30. Dry gas is removed from the absorber via line 31. The absorber liquid containing the absorbed hydrocarbons passes via line 32 to a stripping column 33. The conditions in stripping column 33 are adjusted to remove as an overhead product substantially all of the absorbed material up through normal pentane, which product is removed via line 34. The absorber oil then passes via line 35 to a further stripping column 36. The conditions

in stripping column 36 are adjusted to remove as an overhead product a cracked gasoline fraction consisting largely of C_6 hydrocarbons which is removed via line 37. The stripped absorber oil is recycled to the absorber via line 30.

The liquid hydrocarbon from separator 26 is passed via line 38 to a fractionating column 39. The conditions in fractionating column 39 are adjusted to remove as an overhead product substantially all of the material up through normal hexane. This overhead product removed via line 40 is passed to a second fractionating column 41 wherein it is separated into a lower boiling fraction consisting of products boiling up through normal pentane which is removed via line 43 and a higher boiling fraction consisting largely of C_6 hydrocarbons which is removed via line 42. This C_6 fraction is combined with the cracked C_6 fraction removed from the stripper 36 via line 37. The combined fractions are blended with the straight run material and separately treated as hereinafter described.

The cracked gasoline from which the C_6 hydrocarbon fraction has been removed is withdrawn from fractionating column 39 via line 44. This material may be cut to a desired end-point in fractionating column 45. The overhead product from fractionator 45 withdrawn via line 46 is the cracked gasoline fraction from which the C_6 hydrocarbons have been substantially removed. The C_6 hydrocarbon fraction removed from the cracked gasoline as hereinbefore described is substituted or replaced by the straight run fraction separated as hereinbefore described. Thus, the straight run fraction withdrawn from fractionating column 4 via line 6 is blended with the overhead product from fractionating column 45. This blend is mixed with an excess of hydrogen (with respect to that required for complete saturation of the gasoline) entering via line 47. For example, the amount of hydrogen introduced via line 47 may be 6 mols per mol of hydrocarbon feed. The mixture is preheated to a suitable reaction temperature (for example 850° F.) in a suitable preheater 48 and passed to catalytic reactor 49. Reactor 49 contains a suitable hydrogenation-dehydrogenation catalyst such, for example, as a pelleted mixture of nickel sulfide-tungsten sulfide. The conditions of pressure and contact time may be adjusted to effect a substantially complete hydrogenation of the olefins. Under such conditions the sulfur compounds and/or nitrogen compounds will be largely removed or decomposed and also dehydrogenation of naphthenic constituents of the feed may take place. Typical conditions are, for example, a pressure of about 850 p. s. i. and a liquid hourly space velocity of about 4. The product withdrawn via line 50 is passed to a conventional separating and recovery system illustrated diagrammatically in the drawing by a single separator 51. Gas rich in hydrogen is withdrawn from the separator 51 and recycled via pump 52 and line 47. In order to maintain a suitable concentration of hydrogen in the recycle gas some of this gas may be withdrawn from the system via line 53 and make-up hydrogen may be added via line 54. The hydrofined blend of cracked and straight run gasoline withdrawn from separator 51 via line 55 is blended with the acid treated blend or straight run gasoline and cracked gasoline as hereinafter described and treated by suitable means to remove hydrogen sulfide formed in the hydrofining treatment. Thus, the hydrofined gasoline is mixed with caustic solution entering via line 56 and passed to a

caustic treater 57. The product is withdrawn to a settler 58. Caustic solution is recycled via line 56. Make-up caustic is added via line 59.

The straight run gasoline from which the C_6 hydrocarbons, and if desired also some of the C_7 hydrocarbons, have been removed as hereinbefore described (withdrawn from fractionating column 8 via line 9) is blended with the combined catalytic C_6 fractions separated as hereinbefore defined (entering via lines 37 and 42). This blend passes via line 37 to an acid treater 60 wherein it is contacted with sulfuric acid, spent alkylation acid, or other suitable acid under conditions chosen with respect to the particular feed to afford the degree of refining required for the particular gasoline being produced. In the production of automotive gasoline, for example, a very mild refining treatment at low temperature and with relatively dilute acid may be sufficient. In the production of certain types of aviation gasoline, on the other hand, a relatively severe treatment with a more concentrated acid may be required. The acid treated material is withdrawn to a separator 61. Acid is recycled via line 62. Make-up acid is added via line 63. The acid treated material is withdrawn from the separator via line 64. This material is combined with the hydrofined blend of cracked and straight run material from line 55 and is neutralized in the caustic scrubber 57. The finished blend or base stock consisting of straight run gasoline and cracked gasoline properly refined and in the desired proportions is withdrawn via line 65. In general a portion of the cracked C_5 fraction is included in the finished gasoline. This material requires a caustic treatment to remove mercaptans and hydrogen sulfide. This material, withdrawn via line 34, may be blended with the gasoline entering the caustic treater.

It will be appreciated that the system described above and illustrated in the drawing is merely a typical example of the process of the invention and may be modified in various particulars. For example, the hydrofined blend and the acid treated blend may be caustic treated separately and each or both of them may be cut to the desired gasoline end-point (rerun) prior to the final blending. Also, for example, in actual practice the separation and recovery system illustrated by the simple separator 51 may be complicated by a system for removing hydrogen sulfide from the recycled hydrogen stream and/or by the utilization of multiple compression and cooling steps. Also, the combinations of fractionating equipment and method of handling to recover and separate the specified fractions may be altered without departing from the spirit of the invention. It is not essential that the cracked gasoline and straight run gasoline be derived from the same petroleum. The straight run fraction, for example, may be derived from any, preferably naphthenic, petroleum while the cracked gasoline may be derived from the cracking or reforming of any feed stock. Also, the separation of the respective C_6 fractions may be altered or adjusted to afford the optimum production of gasoline according to the circumstances. For example, the straight run fraction containing C_6 hydrocarbons may be cut to include a considerable portion of C_7 hydrocarbons and may be cut in such a manner as to be relatively concentrated in C_6 and C_7 naphthenes. When the straight run gasoline contains appreciable amounts of naphthenic hydrocarbons (and most straight run gasolines do) this is a very desirable and most advantageous method of operation.

The principal advantage of the process of the invention is that it allows the production of gasoline of any specified quality (in which a blend of straight run gasoline and cracked gasoline can be used—and this is in nearly every case) to be appreciably increased without increasing the hydrogen requirement. Thus, for example, in a typical plant producing, for instance, about 9,000 B./D. of aviation base stock with a consumption of 1.57 million cubic feet hydrogen the production may be increased between about 100 and 400 B./D. In many instances the increased production may also be obtained with decreased operating expenses. If for some reason increased volume production is not desired the advantage of the process of the invention may be realized either in the production of an equal volume of gasoline of improved quality or in the production of an equal volume of gasoline of equal quality with decreased consumption of more costly additives.

The advantage of the described method of operation in a typical case is illustrated in the following example in which it is assumed that a refiner with the following materials available desires to produce the maximum amount of ANF–28 aviation gasoline:

Example I

Material	Available B./D.
Depentanized straight run base stock	4,000
Catalytic cracked depentanized base stock	5,160
Catalytic cracked C_5 fraction	900
Isopentane (95%)	1,840
Debutanized C_4–C_5 alkylate	6,450
Cumene	1,000
Hydrogen (million cubic feet)	1.57

In normal operation (case 1) 4000 B./D. of depentanized catalytic cracked base stock is hydrofined, 1000 B./D. of depentanized catalytically cracked base stock is acid treated, 1621 B./D. of depentanized straight run base stock is acid treated. The products are then blended. The maximum production of ANF–28 aviation gasoline is 15,265 B./D. When operating according to the process of the invention (case 2) the catalytically cracked C_6 fraction and the straight run C_6 fraction are exchanged as described. A blend of 4,500 B./D. of dehexanized catalytically cracked base stock and 1,000 B./D. of the straight run hexane fraction is hydrofined. A blend of 254 B./D. of catalytically cracked C_6 fraction and 1,150 B./D. of hexanized straight run base stock is acid treated. The materials are then blended. The maximum production of ANF–28 aviation gasoline is 15,625 B./D. Thus, case 2 affords an increased production of 360 B./D.

Example II

Petroleum was topped to recover a straight run gasoline fraction and various intermediates. Catalytically cracked gasoline was produced from various heavy petroleum products by the fluid catalyst cracking process using the present commercial silica-alumina composite cracking catalyst. The straight run gasoline was fractionated to recover separately a fraction consisting essentially of C_6 hydrocarbons and then rerun to an end-point of about 185° F. The catalytically cracked product was treated to recover catalytically cracked C_5 hydrocarbons and catalytically

cracked C_6 hydrocarbons separately and topped to produce a dehexanized catalytically cracked gasoline having an end-point of about 325° F. The dehexanized catalytically cracked gasoline was blended with the straight run C_6 fraction to produce a feed blend having the following properties:

	Feed	Product
Gravity, API	55.5	56.6
ASTM distillation:		
IBP	142	152
10%	170	172
50%	208	204
90%	278	280
E. P	312	315
Sulfur, % w	.088	.010
Unsaturates, % w	38.5	5.8
Aromatics, % w	30.4	34.5
BON, + 4.6 cc. TEL	----------	93.0
Index No. + 4.6 cc. TEL	----------	117

This blend was hydrofined with a nickel sulfide-tungsten sulfide catalyst under the following approximate conditions:

Temperature, °F	900
Pressure, p. s. i	840
Liquid hourly space velocity	4
Mol ratio of hydrogen to hydrocarbon	6:1

The product had the properties specified in the above table. The catalytically cracked fraction consisting essentially of C_6 hydrocarbons was blended with the straight run gasoline remaining after the separation of the C_6 fraction. This blend was treated with about 20 pounds per barrel of spent alkylation acid, caustic washed and rerun. The losses were about 18%. The acid treated blend was then blended with the hydrofined blend to produce the final blend or base stock.

We claim as our invention:

1. In the production from petroleum of gasoline comprising straight run gasoline and cracked gasoline, the improvement which comprises separating from a cracked gasoline an olefinic fraction consisting largely of C_6 hydrocarbons, replacing said separated olefinic fraction with a saturated straight run gasoline fraction consisting largely of C_6 and C_7 hydrocarbons, subjecting the thus produced blend of said dehexanized cracked gasoline and straight run gasoline fraction to a hydrofining treatment under hydrogen pressure in the presence of a hydrogenation catalyst, subjecting said separated olefinic fraction to an acid refining treatment, and recombining the acid refined material with the hydrofined blend.

2. In the production from petroleum of gasoline comprising straight run gasoline and cracked gasoline, the improvement which comprises separating from a cracked gasoline an olefinic fraction consisting largely of C_6 hydrocarbons, replacing said separated olefinic fraction with a saturated straight run gasoline fraction concentrated in C_6 and C_7 naphthenes, subjecting the thus produced blend of said dehexanized cracked gasoline and straight run gasoline fraction to a hydrofining treatment under hydrogen pressure in the presence of a hydrogenation catalyst, subjecting said separated olefinic fraction to an acid refining treatment, and recombining the acid refined material with the hydrofined blend.

3. In the production from petroleum of gasoline comprising straight run gasoline and cracked gasoline, the improvement which comprises separating from a cracked gasoline an olefinic fraction consisting largely of C_6 hydrocarbons, separating from straight run gasoline a saturated fraction consisting largely of C_6 hydrocarbons, blending said latter fraction with the remainder of the cracked gasoline, subjecting the blend to a hydrofining treatment under hydrogen pressure in the presence of a hydrogenation catalyst, blending said olefinic fraction separated from the cracked gasoline with the remainder of the straight run gasoline, subjecting this latter blend to an acid refining treatment, and blending the two thus-treated gasolines.

4. In the production from petroleum of gasoline comprising straight run gasoline and cracked gasoline, the improvement which comprises separating from a cracked gasoline an olefinic fraction consisting largely of C_6 hydrocarbons, separating from straight run gasoline a saturated fraction relatively concentrated in C_6 and C_7 naphthenes, blending said latter fraction with the remainder of the cracked gasoline, subjecting the blend to a hydrofining treatment under hydrogen pressure in the presence of a hydrogenation catalyst, blending said olefinic fraction separated from the cracked gasoline with the remainder of the straight run gasoline, subjecting this latter blend to an acid refining treatment, and blending the two thus-treated gasolines.

5. Process according to claim 1 in which the cracked gasoline is a catalytically cracked gasoline obtained by cracking a hydrocarbon oil with a clay type cracking catalyst.

6. Process according to claim 1 in which the hydrofining treatment is carried out with a hydrogenating metal sulfide catalyst at a temperature of about 850° F. and 1000° F.

7. Process according to claim 1 in which the acid refining treatment is carried out under mild conditions to leave the major portion of the olefine intact.

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