Feb. 16, 1960 W. G. ANNABLE ET AL 2,925,373

PROCESS FOR ENHANCING THE OCTANE NUMBER OF NAPHTHAS BOILING WITHIN THE GASOLINE RANGE

Filed April 12, 1957 3 Sheets-Sheet 1

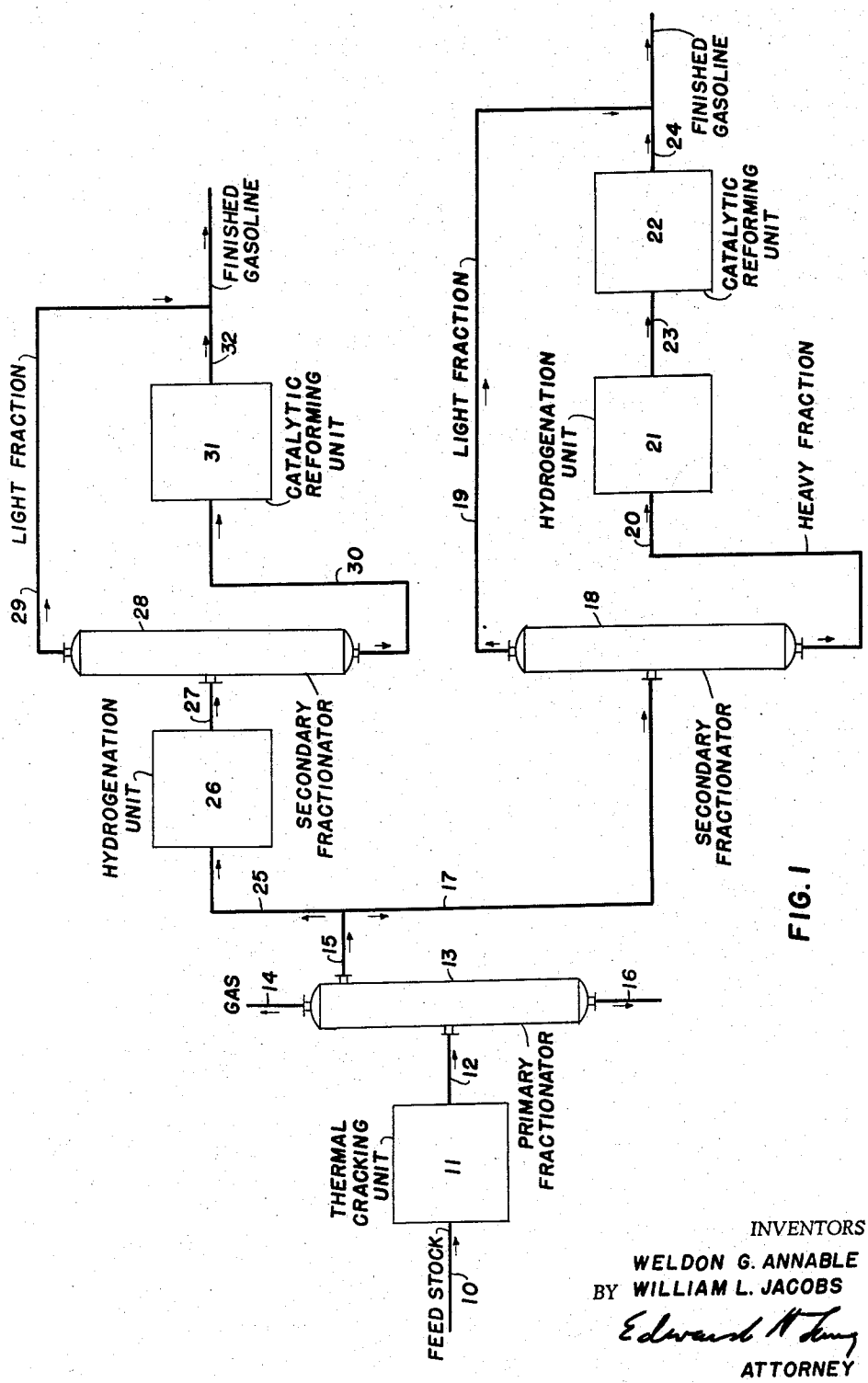


FIG. 1

INVENTORS
WELDON G. ANNABLE
BY WILLIAM L. JACOBS
Edward N. Long
ATTORNEY

Feb. 16, 1960 W. G. ANNABLE ET AL 2,925,373

PROCESS FOR ENHANCING THE OCTANE NUMBER OF NAPHTHAS BOILING WITHIN THE GASOLINE RANGE

Filed April 12, 1957 3 Sheets-Sheet 2

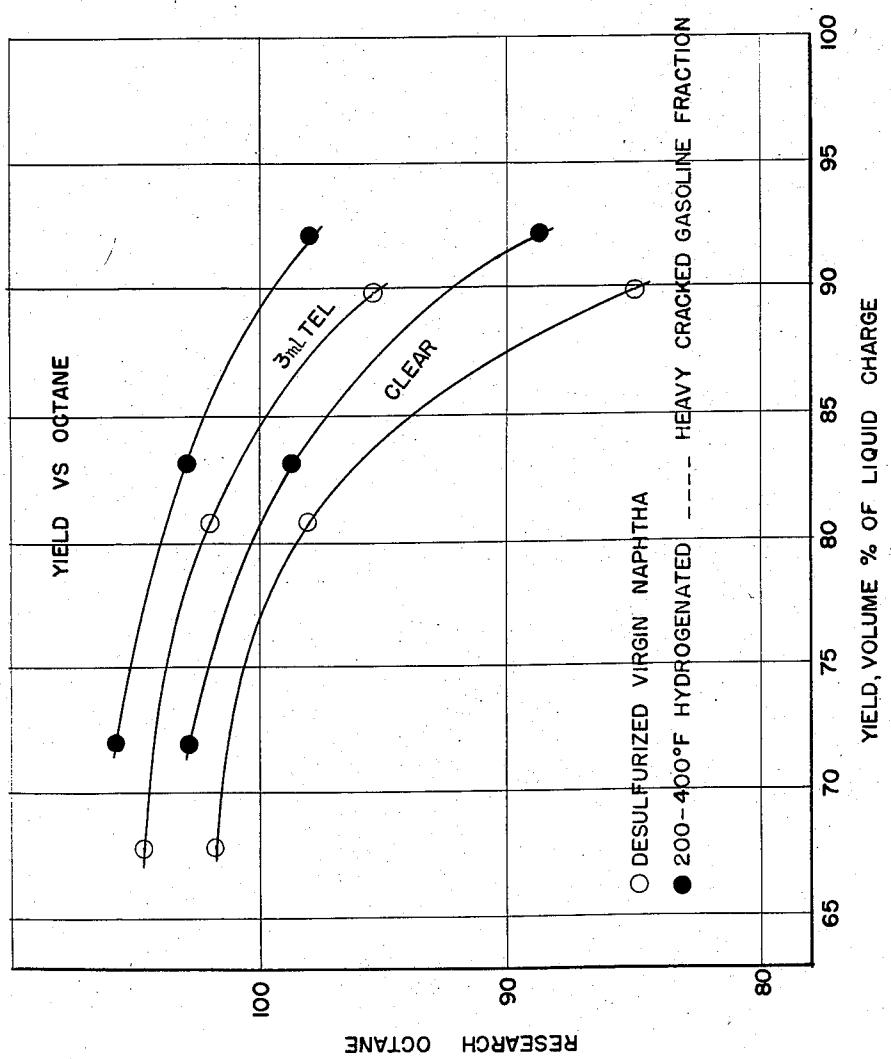


FIG. 2

INVENTORS.
WELDON G. ANNABLE
BY WILLIAM L. JACOBS
Edward A. Tang
ATTORNEY

Feb. 16, 1960 W. G. ANNABLE ET AL 2,925,373
PROCESS FOR ENHANCING THE OCTANE NUMBER OF NAPHTHAS
BOILING WITHIN THE GASOLINE RANGE
Filed April 12, 1957 3 Sheets-Sheet 3

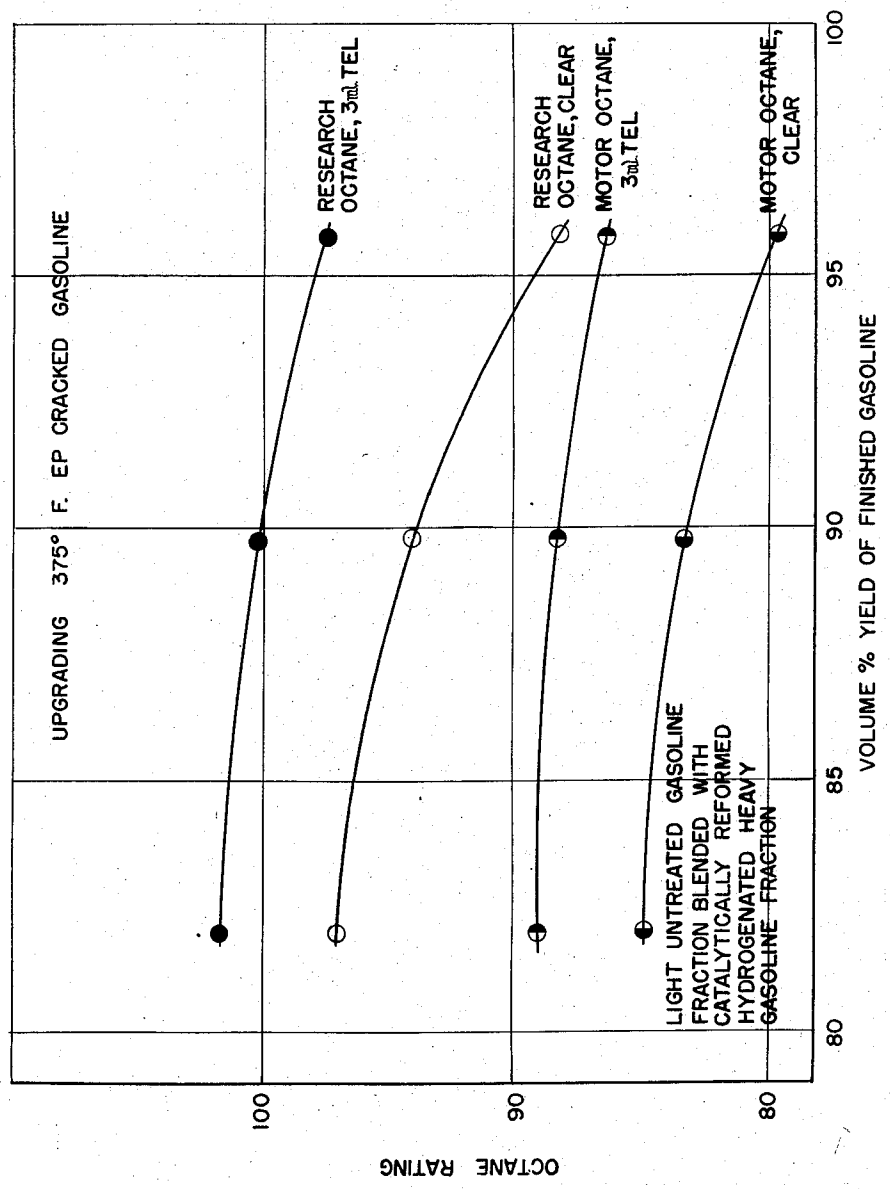


FIG. 3

INVENTORS.
WELDON G. ANNABLE
BY WILLIAM L. JACOBS
Edward H. Kenyon
ATTORNEY

United States Patent Office 2,925,373 Patented Feb. 16, 1960

2,925,373

PROCESS FOR ENHANCING THE OCTANE NUMBER OF NAPHTHAS BOILING WITHIN THE GASOLINE RANGE

Weldon G. Annable, Mundelein, and William L. Jacobs, Crystal Lake, Ill., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

Application April 12, 1957, Serial No. 652,438

7 Claims. (Cl. 208—57)

The present invention relates generally to a process for the preparation of high-octane-number gasolines and, more particularly, to the upgrading of thermally cracked gasoline.

Cracking processes have been the primary sources of materials for producing finished gasolines of high octane number. Such gasolines are in demand today for high-compression, internal combustion engines coupled with automatic transmissions. Although the importance of thermal cracking has diminished as a means of obtaining finished gasolines of high octane rating, thermal cracking still remains as a potential expedient for processing light recycle stock and gas oils of virgin or blended origin. This invention relates broadly to a process for upgrading thermally cracked gasolines by separating such gasolines into a light and heavy fraction, hydrogenating and catalytically reforming the heavy fraction, and blending the resultant catalytically reformed heavy fraction with the untreated light fraction.

The invention is further illustrated by the drawings in which:

Figure 1 is a general flow diagram of the process showing the sequence of steps involved.

Figure 2 is a graph showing the octane-yield relationship for the catalytic reforming of the hydrogenated heavy fraction of thermally cracked gasoline compared with that for reforming a virgin naphtha having a similar boiling range.

Figure 3 is a graph showing the yield of finished gasoline versus octane rating when upgrading debutanized, 375° F. end-point, thermally cracked gasoline by blending the light fraction with the catalytically reformed, hydrogenated heavy fraction.

Referring to Figure 1, the general steps of the process of the invention may be followed. A gas-oil feed stock, from a source not shown, is introduced through line **10** into a conventional thermal cracking process, **11**. The cracked products therefrom pass via line **12** to primary fractionator **13** wherein the C_4 and lighter hydrocarbons are separated and pass off via line **14**, the unstabilized cracked gasoline cut, having an E.P. of about 375° F. is taken off at line **15** and the products boiling above about 375° F. are taken off as bottoms at line **16** for recycle to thermal cracking process **11**. The feed stock entering line **10** may contain from 50–60% of recycle material from line **16**.

In one embodiment of the invention the cracked gasoline cut is sent by line **17** to secondary fractionator **18** wherein a light fraction having a boiling range of about 100° to 185° F., with an end-point no higher than about 200° F. is removed at line **19** and a heavy fraction boiling from about 200° F. to about 375° F., with an end-point no higher than about 400° F. is removed at line **20**. The heavy fraction is hydrogenated in unit **21** under mild conditions to saturate the olefins and to effect desulfurization. The hydrogenated product proceeds, with or without further treatment, directly into catalytic reforming unit **22** via line **23**. In a commercial reforming operation the hydrogenation taking place in **21** is carried out in a "guard case" prior to the reforming step. The light, untreated, cracked fraction in line **19** is blended with the hydrogenated-reformed product in line **24** to form the upgraded high-octane fuel of this invention.

In accordance with an alternate embodiment of the invention, the debutanized, thermally cracked gasoline fraction from line **15** is passed via line **25** to hydrogenation unit **26**. The hydrogenated product passes via line **27** to secondary fractionator **28**. A light fraction having a boiling range of about 100° to 185° F. with an end-point no higher than about 200° F. is removed via line **29** and a heavy fraction boiling from about 200° F. to about 375° F. with an end-point no higher than about 400° F. is removed as bottoms at line **30**. The heavy fraction is sent to catalytic reformer **31** and the reformed products in line **32**, when blended with the light fraction in line **29**, form the upgraded high-octane fuel of this invention.

The invention therefore has as its primary object a process for upgrading thermally cracked gasolines.

Another object is to provide an integrated, split treatment of a thermally cracked gasoline or fractions thereof to produce a high-octane gasoline.

Still another object of the invention is to provide an integrated split treatment, hydrogenation and catalytic reforming process for thermally cracked gasoline or fractions thereof to produce a high-octane gasoline having a minimum increase in sensitivity.

A further object of the invention is to provide a process for upgrading thermally cracked gasoline by fractionating the 375° F. end-point gasoline into a light and heavy fraction, catalytically reforming the heavy fraction, and blending the catalytically reformed heavy fraction with the untreated light fraction to obtain a high octane product.

Another object of the invention is to upgrade thermally cracked gasoline with a minimum increase in sensitivity by mildly hydrogenating 375° F. end-point, thermally cracked gasoline in a separate hydrogenation unit prior to fractionating it into light and heavy fractions, catalytically reforming the heavy fraction and blending the reformed heavy fraction with the hydrogenated light fraction to obtain a high octane product.

It is generally known that there is a difference between the F–1 or research octane number (CRC designation F–1–545) and the F–2 or motor octane number (CRC designation F–2–545) of spark-ignited fuels for internal combustion engines. The apparent difference between these values as actually found in blend testing, or the so-called "sensitivity" factor, is used herein as an expression of the road performance characteristics of the finished products to give a more realistic approach. The increase in sensitivity of gasoline-type motor fuels is primarily due to the fact that refining techniques generally employed to process crude oil fractions, such as cracking and reforming, are rather limited in their ability to produce gasoline of high F–2 anti-knock quality.

To more specifically illustrate the invention, a feed stock having the following composition and general characteristics was used:

TABLE I

Composition	Vol. Percent	B.R., ° F.	°API Grav.	Total Percent S.
Heavy cycle stock	28	540–725	26.5	0.47
Light cycle stock	29	480–625	29.7	0.19
Kerosene	30	350–525	43.0	0.13
No. 5 Diesel Cut	13	350–590	38.0	0.50

The feed stock shown in Table I was treated to thermal cracking at about 900 to 1000° F., 400–600 p.s.i.g. to produce a thermally cracked 431° end-point gasoline. This product was debutanized to remove about 7.44 vol. percent of C_4 hydrocarbons and lighter, and then was fractionated into a light and heavy fraction. The properties of the thermally cracked stock and the light and heavy fractions produced therefrom are shown in Table II.

TABLE II

Inspection data for light and heavy fractions of thermally cracked gasoline

Fraction	Thermally Cracked Gasoline	Light Fraction	Heavy Fraction
Vol. Percent of Debutanized Thermally Cracked Gasoline		28.8	71.2
Gravity, ° API	56.8	79.3	45.8
ASTM Distillation, ° F.:			
IBP	98	99	210
5%	113	108	226
10%	125	110	238
20%	151	112	251
30%	185	115	263
40%	219	118	281
50%	253	122	301
60%	285	126	324
70%	319	132	348
80%	352	140	370
90%	388	150	393
95%	412	156	409
DP		161	
EP	431	162	436
Rec	98.0	98.0	99.0
Res	1.1	0.6	1.0
Loss	0.9	1.4	0.0
Refractive Index, n^{20}/D	1.4238	1.3802	1.4478
Vol. Percent Naphthenes and Paraffins	50.1	46.4	41.2
Vol. Percent Olefins	33.7	52.3	31.4
Vol. Percent Aromatics	16.2	1.3	27.4
Total Sulfur, Wt. Percent	0.038	0.007	0.042
Research Octane, clear	77.0	85.2	71.2
+1.0 ml. TEL	85.6	93.0	
+3.0 ml. TEL	90.0	96.0	84.8
Motor Octane, clear	70.0	76.1	65.0
+1.0 ml. TEL	76.4	81.9	
+3.0 ml. TEL	80.9	84.6	77.5

The light and heavy fractions were divided into several portions. One portion of each of the light and heavy fractions was subjected to hydrogenation under the operating conditions and material balance data shown in Table III, using Filtrol R–3241 catalyst which comprises 9% molybdenum oxide on alumina.

TABLE III

Hydrogenation of light and heavy fractions of thermally cracked gasoline

OPERATING CONDITIONS AND RESULTS

Run #	HT—77, 78 and 79	HT—80, 81 and 82
Fraction	Light Fraction	Heavy Fraction
Operating Conditions:		
Temperatures, ° F.:		
Preheater	600	644
Block	600	650
Cat. Bed	674	743
Pressure, p.s.i.g	500	500
LVHSV	2.4	2.3
H_2 rate, Ft.³/bbl. (STP)	2048	2177
Material Balance, Percent	99.2	100.1
No-Loss Liquid Recovery:		
Wt. Percent of Liq. Charge	100.4	100.6
Vol. Percent of Liq. Charge	102.2	101.7
Inspection data for Hydrogenated Liquid Products:		
Gravity, ° API	83.2	47.7
ASTM Distillation, ° F.:		
IBP	98	209
5%	106	228
10%	110	238
20%	113	250
30%	116	266
40%	117	283
50%	123	304
60%	127	326
70%	132	348
80%	141	370
90%	153	393

TABLE III—Continued

Run #	HT—77, 78 and 79	HT—80, 81 and 82
Fraction	Light Fraction	Heavy Fraction
Inspection data for Hydrogenated Liquid Products—Continued		
ASTM Distillation, ° F—Continued		
95%	156	411
DP	163	
EP	166	445
Rec	98.0	99.0
Res	0.5	1.0
Loss	1.5	0.0
Refractive Index n^{20}/D	1.3705	1.4401
Vol. Percent Naphthenes and Paraffins	99.0	76.5
Vol. Percent Olefins	0.2	0.5
Vol. Percent Aromatics	0.8	23.0
Total Sulfur, Wt. Percent	0.004	<0.03
Research Octane, clear	68.0	54.0
+1.0 ml. TEL	80.2	
+3.0 ml. TEL	89.1	
Motor Octane, clear	66.2	
+1.0 ml. TEL	81.8	
+3.0 ml. TEL	84.9	

In order to demonstrate the effect of the hydrogenation process on the sensitivity before further processing, the octane numbers of various blends of untreated and hydrogenated light and heavy fractions were determined. The results are shown in Table IV.

TABLE IV

Effect of hydrogenation on blends of light and heavy fractions of thermally cracked gasoline

	Composition			
Blend No.	1	2	3	4
Materials:				
Untreated Light Fraction	28.8		28.5	
Untreated Heavy Fraction	71.2	70.7		
Hydrogenated light fraction		29.3		29.0
Hydrogenated heavy fraction			71.5	71.0
Vol. percent of thermally cracked gasoline	100.0	100.6	101.2	101.8
Octane Nos:				
Res. Octane, Clear	74.8	68.0	65.1	59.0
+3.0 ml. TEL	88.0	85.0		
Motor Octane, clear	69.0	65.2		
+3.0 ml. TEL	79.9	79.4		
Sensitivity	8.1	5.6		

The results in Table IV show that hydrogenating all or part of thermally, cracked gasoline decreases its octane rating and reduces its sensitivity. However, when the hydrogenated heavy fraction is subsequently catalytically reformed, a high-octane product is obtained.

In order to demonstrate the effect of catalytically reforming the hydrogenated heavy fraction of the cracked gasoline, a series of experiments were carried out with three comparative runs conducted at reactor inlet temperatures of 900° F., 950° F. and 1000° F. using a desulfurized virgin naphtha and a portion of the hydrogenated, heavy, cracked gasoline described in Table III. Table V gives the operating conditions and results of these experiments which were conducted in the presence of a platinum catalyst.

Referring to Table V, it is pointed out that the liquid product from the mild hydrogenation of the heavy fraction of the cracked gasoline was fractionated to recover 83.9 vol. percent overhead material before the experiments were conducted. This overhead material had a boiling range similar to that of the desulfurized virgin naptha which was used for comparison. Inspection data for the liquid products obtained in the experiments indicated by Table V are shown in Table VI. These indicate that less hydrocracking occurs when reforming the hydrogenated heavy fraction of the cracked gasoline than is evidenced in reforming the desulfurized virgin naphtha. Analysis of the product gas for these experiments was found to substantiate this finding. Also, the overall

TABLE V

Catalytic reforming of desulfurized virgin naphtha and hydrogenated heavy fractions of thermally cracked gasoline

OPERATING CONDITIONS AND RESULTS

Run #	CR-1	CR-2	CR-3	CR-4	CR-5	CR-6
Charge Stock	Desulfurized Virgin Naphtha			200–400° F. Hydrogenated Heavy Fractions of Cracked Gasoline.		
Operating Conditions:						
Temperatures, ° F.:						
Preheater	904	954	995	902	948	996
Block	893	944	1002	901	944	998
Cat. Bed	835	888	935	848	889	945
Pressure, p.s.i.g	500	500	500	500	500	500
LVHSV	1.9	1.8	1.9	1.8	1.8	1.7
H_2 Rate, Ft.³/bbl. (STP)	2572	2755	2478	2803	2665	2743
Material Balance, Percent	99.3	99.8	97.5	99.1	98.8	98.4
No Loss Liquid Recovery:						
Wt. Percent of Liq. Charge	92.3	82.5	71.4	93.5	85.0	75.4
Vol. Percent of Liq. Charge	89.9	81.0	68.1	92.3	83.5	72.2

product distribution upon comparison showed that less hydrocracking took place when the 200–400° F. boiling range, hydrogenated, heavy fraction of cracked gasoline was reformed as compared with the reforming of the desulfurized virgin naphtha. These results are shown graphically in Figure II.

cracked gasoline as a starting material, are also shown in Table VII. The data show that thermally cracked gasoline can be upgraded to a high octane level without serious losses in yield. Although various proportions of the light and heavy fractions may be used in blending up the products produced by the process of the invention to

TABLE VI

Catalytic reforming of desulfurized virgin naphtha and hydrogenated heavy fraction of thermally cracked gasoline

INSPECTION DATA FOR LIQUID PRODUCTS

Run #	Charge	CR-1	CR-2	CR-3	Charge	CR-4	CR-5	CR-6
Charge Stock	Desulfurized Virgin Naphtha				200–400° F. Hydrogenated Heavy Fraction of Cracked Gasoline			
Gravity, °API	54.5	50.0	50.9	45.7	51.7	49.0	48.2	43.9
ASTM Distillation, ° F.:								
IBP	210	102	80	85	208	102	85	80
5%	254	156	108	107	225	158	124	109
10%	263	196	129	124	231	186	149	130
20%	273	234	168	169	241	217	186	178
30%	280	258	210	230	249	232	218	230
40%	288	271	248	262	259	245	238	250
50%	296	284	274	276	270	259	260	263
60%	304	295	290	287	282	274	278	273
70%	314	308	306	302	300	293	296	289
80%	325	324	322	319	317	316	318	308
90%	339	347	361	349	340	340	352	353
95%	349	375	----------	----------	351	370	----------	----------
EP	375	413	424	362	366	419	435	485
Rec	99.5	97.2	93.0	92.0	98.0	97.9	94.5	94.0
Res	0.4	1.4	1.0	1.5	1.5	0.9	1.3	1.2
Loss	0.1	1.4	6.0	6.5	0.5	1.2	4.2	4.8
Reid Vapor Pressure	----------	9.9	17.0	18.8	----------	7.3	13.9	16.7
Refractive Index n^{20}/D	1.4230	1.4390	1.4410	1.4552	1.4290	1.4435	1.4470	1.4590
Vol. Percent Naphthenes and Paraffins	91.8	58.5	43.4	28.6	80.5	53.4	43.6	25.3
Vol. Percent Olefins	1.0	0.8	0.7	0.6	1.6	0.7	0.4	0.3
Vol. Percent Aromatics	7.2	40.7	55.9	70.8	17.9	45.9	56.0	74.4
Wt. Percent Total Sulfur	0.009	0.013	0.017	0.021	<0.003	0.004	<0.01	<0.01
Vol. Percent C_3's and Lighter	----------	0.6	1.4	2.1	----------	1.1	1.8	1.7
Vol. Percent C_4's	----------	3.2	7.8	10.7	----------	2.8	6.6	8.4
Vol. Percent C_5's and Heavier	----------	96.2	90.8	87.2	----------	96.1	91.6	89.9
Molecular wt. (C_5's+)	----------	110	110	103	----------	107	101	102
Spec. Gravity (C_5's+)	----------	0.7860	0.7972	0.8256	----------	0.7914	0.8035	0.827
Research Octane, clear	39.0	85.0	98.0	102.1	52.0	88.7	98.6	103.6
Research Octane, +3.0 ml. TEL	----------	95.5	102.5	106.8	----------	97.9	103.8	108.6

Following these experiments, a number of blends of the untreated light fraction of thermally cracked gasoline (Table II) with the three products obtained in the catalytic reforming of the 200–400° F. hydrogenated heavy fraction of the thermally cracked gasoline were prepared and their octane ratings determined. In addition, blends of the hydrogenated light fraction of cracked gasoline (Table III) with these same reformed products were prepared and their octane ratings tested. The results are shown in Table VII.

The yields of finished gasoline, based on the 375° F. prepare finished gasolines of particular octane levels, it is most desirable to use all of each component produced.

Referring to the graph, Figure III, there is shown a plot of the octane ratings against the yields of finished gasolines for upgrading the 375° F. end-point cracked gasoline. The curves are based on blending the light, untreated fraction of thermally cracked gasoline with the catalytically reformed, 200–400° F., hydrogenated heavy fraction of the cracked gasoline. According to the graph, 100 research octane (3 ml. TEL) gasoline can be produced from 375° end-point cracked gasoline with a 90 vol. per-

TABLE VII

Upgrading 375° F. E.P. thermally cracked gasoline octane ratings of blends of finished products

A. UNTREATED LIGHT FRACTION AND REFORMED HEAVY FRACTION

Catalytic Reforming Run #	CR-4	CR-5	CR-6
Composition:			
Vol. Percent Light fraction	34.0	36.3	39.7
Vol. Percent Heavy fraction	66.0	63.7	60.3
Yield of Finished Gasoline, Vol. Percent	95.8	89.8	82.0
Research Octane, clear	88.0	94.1	97.0
+3.0 ml. TEL	97.3	100.1	102.1
Motor Octane, clear	79.4	83.2	84.8
+3.0 ml. TEL	86.2	88.2	89.0
Sensitivity	11.1	11.9	13.1

B. HYDROGENATED LIGHT FRACTION AND REFORMED HEAVY FRACTION

Composition:			
Vol. Percent light fraction	34.5	36.8	40.3
Vol. Percent heavy fraction	65.5	63.2	59.7
Yield of Finished Gasoline, Vol. Percent	96.5	90.5	82.7
Research Octane, clear	82.3	88.9	-------
+3.0 ml. TEL	95.1	98.1	100.3
Motor Octane, clear	76.9	81.9	-------
+3.0 ml. TEL	86.9	89.6	90.8
Sensitivity (Leaded)	8.2	8.5	9.5

cent yield of finished product. Similar curves can be shown for the blends prepared using the hydrogenated light fraction.

The foregoing examples are to be considered as non-limiting and other manipulative techniques may be employed in carrying out the operations of this invention; for example, in determining the cut-point for separating the low-boiling fraction and the high-boiling fraction in the initial fractionation, the proportion of the full-boiling-range gasoline which is to be catalytically reformed may be determined experimentally. The selected low-boiling fraction will be generally characterized by a boiling range of 100–185° F. with an end-point no higher than 200° F. The clear research octane rating should be 85 or higher and the leaded (3 ml. TEL) research octane rating should be 96 or higher. The remaining material comprises the high-boiling fraction and is generally characterized by a boiling range of 200–375° F. with an end-point no higher than 400° F.

The feed stocks to which the present invention is applicable comprise gas oils broadly having initial boiling points of about 400° F. and end-points ranging from about 600–1000° F. These materials may contain portions of cracked cycle stock and various fractions of virgin gas oil, such as kerosene and diesel cuts. It is recommended that about 40 to 50% of the feed stock comprise virgin material.

The general conditions for the thermal cracking step are as follows:

Conditions	Range	Preferred
Temperature, ° F	800–1,200	900–1,000
Pressure, p.s.i.g	300–1,000	400–600

The fractionation step may be carried out in any type of equipment which is capable of separating a low-boiling fraction boiling in the range of about 100 to 185° F., with an end-point no higher than about 200° F., and a heavy fraction boiling in the range of about 200 to 375° F., with an end-point no higher than about 400° F. The fractionation is conducted so that substantially all of the thermally cracked gasoline is recovered in the light and heavy fractions, there being substantially no heavy material remaining. The small amount of C_4 and lighter hydrocarbons are, of course, removed prior to the fractionation.

The hydrogenation of the heavy fraction is conducted by the use of conventional techniques. The operating conditions which may be employed are as follows:

Conditions	Range	Preferred
Temperature, ° F	600–800	750
Pressure, p.s.i.g	300–600	500
LVHSV	1.0–10.0	2.5
H_2 rate, ft.³/bbl. (STP)	1,500–5,000	2,000

The catalyst to be used in the hydrogenation step comprises those commonly used in hydrogenation reactions involving these types of hydrocarbon feed stocks. It is preferred that oxides and salts or free metals of groups VI and VIII of the periodic table be used. These oxides, salts, or free metals may be used alone or supported on a suitable carrier such as silica-alumina, alumina, silica-alumina-manganese, kieselguhr, etc. As examples, without limitation on the type of catalyst, may be cited nickel, platinum and copper in the form of chromites, sulfites, etc., and also oxides of nickel, molybdenum, cobalt and tungsten used singly or in admixture. A preferred catalyst for the hydrogenation step comprises molybdena on alumina, which is described in our copending application, Serial Number 593,821, filed June 26, 1956.

Similarly, the catalytic reforming operation which is applied to the hydrogenated, high-boiling fraction employs customary procedures known to the art. The catalyst for this operation may be a group VIII noble metal catalyst comprising platinum and palladium used alone or deposited upon a suitable inert carrier, preferably one containing silica. A number of catalyst compositions are available and known to the art for use as reforming catalyst. Those catalyst compositions described in U.S. Patents 2,479,109; 2,478,916; 2,550,531; 2,589,189; and 2,750,329 may be used. A preferred form of catalyst for the reforming is a platinum catalyst containing about 0.2 to 0.6 wt. percent of platinum on a highly extended alumina base having a surface area in excess of 350 square meters per gram. The catalyst may be in an extruded form, or pellets having diameters of about 3/32".

The reforming operating conditions that may be used are as follows:

Conditions	Range	Preferred
Temperature, ° F	900–1,050	1,000
Pressure, p.s.i.g	300–600	500
LVHSV	1–3	2
H_2 rate, ft.³/bbl. (STP)	1,500–5,000	2,500

The foregoing illustrative examples and process conditions of this invention are merely illustrative and are non-limiting. The conditions used to hydrogenate the heavy fraction in unit 21 may be used to hydrogenate the entire cracked products in unit 26. For practical reasons, the "guard case" technique is used in unit 21 because better temperature control during reforming is obtained and the sulfur-sensitive reforming catalyst used in reforming is protected. The cut-point between the low- and high-boiling fractions may vary somewhat from 185°–200° F. where feed hydrocarbons of different characteristics are to be treated.

The thermally cracked gasoline to be upgraded may be any type of feed hydrocarbon or mixture which is amenable to producing a good grade of gasoline and may be produced by any of the known methods of thermal cracking. The charge stock to the thermal cracking operation should contain about 40% to 50% of virgin material with the balance being recycle stock or other extraneous feeds suitable for producing gasoline. The boiling range of this initial charge stock may be about 350° to 900° F. or as high as 1000° F.

The data presented shows that by means of the integrated hydrogenation-fractionation-reforming process or the integrated fractionation-hydrogenation-reforming process of this invention, the thermally cracked gasoline can be upgraded to yield on subsequent blending of products a high-octane-number product with no appreciable increase in sensitivity. The invention is subject to various obvious modifications and the only limitations attaching thereto appear in the appended claims.

What is claimed is:

1. A process for enhancing the octane number of a full-boiling-range gasoline produced in the thermal cracking of a petroleum gas oil having a total sulfur content of not more than about 0.3 weight percent which comprises fractionating said gasoline to provide a low-boiling fraction having an ASTM end-point of about 200° F. and a consecutive high-boiling-range fraction, catalytically hydrogenating said high-boiling fraction at a temperature of about 600–800° F. at 300–600 p.s.i.g. of hydrogen using a liquid-volume-hourly-space-velocity between about 1.0 and 10.0 and a hydrogen flow rate of about 1500 to 5000 cubic feet per barrel of feed at standard temperature and pressure, reforming said hydrogenated high-boiling fraction at a temperature of about 900–1050° F., at 300–600 p.s.i.g. of hydrogen using a liquid-volume-hourly-space velocity of about 1.0–3.0 and a hydrogen flow rate of about 1500–5000 cubic feet per barrel of feed at standard temperature and pressure, and blending said reformed high-boiling fraction with said untreated low-boiling fraction to provide a full-boiling-range gasoline.

2. The process in accordance with claim 1 in which said thermally cracked gasoline has the following approximate physical properties:

Gravity, ° API	56.8
ASTM distillation, ° F., I.B.P.–E.P.	98–431
Rerfactive index, n^{20}/D	1.4238
Vol. percent naphthenes and paraffins	50.1
Vol. percent olefins	33.7
Vol. percent aromatics	16.2
Total sulfur, wt. percent	0.038
Research octane No., clear	77.0
+1.0 ml. TEL	85.6
+3.0 ml. TEL	90.0
Motor octane No., clear	70.0
+1.0 ml. TEL	76.4
+3.0 ml. TEL	80.9

3. The process in accordance with claim 1 in which the low-boiling fraction has the following approximate physical properties:

Gravity, ° API	79.3
ASTM distillation, ° F., I.B.P.–E.P.	99–162
Refractive index, n^{20}/D	1.3802
Vol. percent naphthenes and paraffins	46.4
Vol. percent olefins	52.3
Vol. percent aromatics	1.3
Total sulfur, wt. percent	0.007
Research octane No., clear	85.2
+1.0 ml. TEL	93.0
+3.0 ml. TEL	96.0
Motor octane No., clear	76.1
+1.0 ml. TEL	81.9
+3.0 ml. TEL	84.6

4. The process in accordance with claim 1 in which said consecutive high-boiling fraction before hydrogenation has the following approximate physical properties:

Gravity, ° API	45.8
ASTM distillation, ° F., I.B.P.-E.P	210–436
Refractive index, n^{20}/D	1.4478
Vol, percent naphthenes and paraffins	41.2
Vol. percent olefins	31.4
Vol. percent aromatics	27.4
Total sulfur, wt. percent	0.042
Research octane No., clear	71.2
+3.0 ml. TEL	84.8
Motor octane No., clear	65.0
+3.0 ml. TEL	77.5

5. The process in accordance with claim 1 in which the hydrogenated and reformed heavy fraction has the following range of physical properties:

Gravity, °API	43.9–49.0
ASTM distillation, I.B.P.-E.P	80–485
Refractive index, n^{20}/D	1.4435–1.4590
Vol. percent naphthenes and paraffins	25.3–53.4
Vol. percent olefins	0.3–0.7
Vol. percent aromatics	45.9–74.4
Wt. percent sulfur	<0.01
Research octane No., clear	88.7–103.6
Research octane No. +3.0 ml. TEL	97.9–108.6

6. The process in accordance with claim 1 in which the total production of liquid products from said fractionation, hydrogenation and reforming processes are blended to form a full-boiling range gasoline having an enhanced octane number.

7. A process for enhancing the octane number of a full-boiling range gasoline produced in the thermal cracking of a petroleum gas oil having a total sulfur content of not more than about 0.3 weight percent which consists in fractionating said gasoline to provide a low-boiling fraction having an ASTM end-point of about 200° F. and a total sulfur content of about 0.007 weight percent and a consecutive high-boiling-range fraction having an ASTM end-point of about 400° F. and a total sulfur content of about 0.042 weight percent, catalytically hydrogenating said high-boiling fraction at a temperature of about 600 to 800° F. at 300–600 p.s.i.g. of hydrogen using a liquid-volume-hourly-space velocity of between about 1.0 and 10.0 and a hydrogen flow rate of about 1500 to 5000 cubic feet per barrel of feed at standard temperature and pressure to produce a hydrogenated product having a total sulfur content of less than about 0.03 weight percent, reforming said hydrogenated product at a temperature of about 900° to 1050° F. at 300–600 p.s.i.g. of hydrogen using a liquid-volume-hourly-space velocity of about 1.0 to 3.0 and a hydrogen flow rate of about 1500–5000 cubic feet per barrel of feed at standard temperature and pressure, recovering a reformed high-boiling fraction and blending said reformed high-boiling fraction with said untreated low-boiling fraction to produce a full-boiling gasoline of increased octane number and decreased lead sensitivity.

References Cited in the file of this patent

UNITED STATES PATENTS

2,025,255	Taylor	Dec. 24, 1935
2,367,527	Ridgway	Jan. 16, 1945
2,389,713	Atwell	Nov. 27, 1945
2,413,312	Cole	Dec. 31, 1946
2,463,741	Byrns	Mar. 8, 1949
2,642,381	Dickinson	June 16, 1953