Oct. 3, 1961 W. W. HAMILTON 3,002,916

TWO-STAGE REFORMING WITH INTERMEDIATE FRACTIONATION

Filed Sept. 6, 1956 3 Sheets-Sheet 1

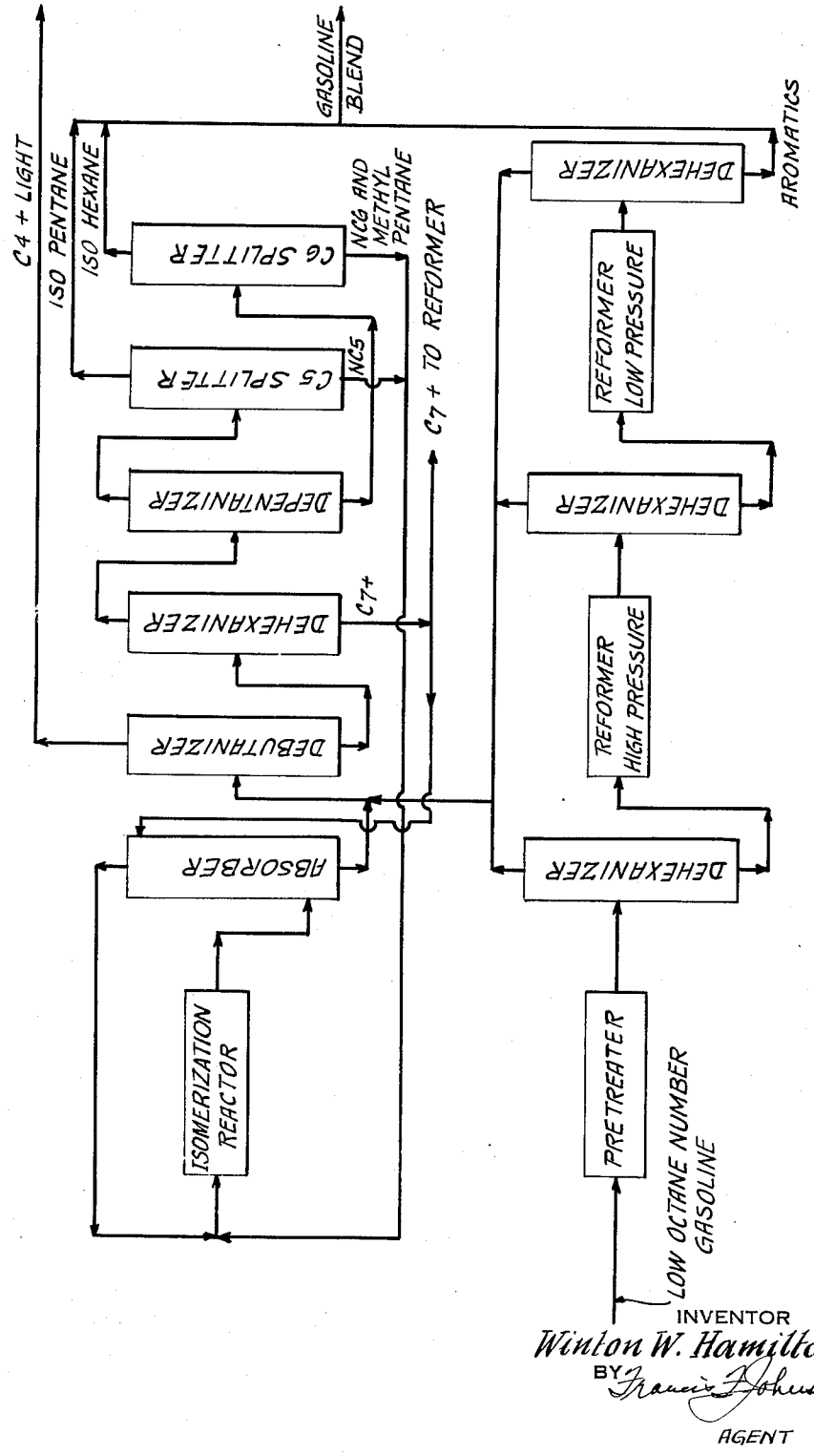


Fig. 1

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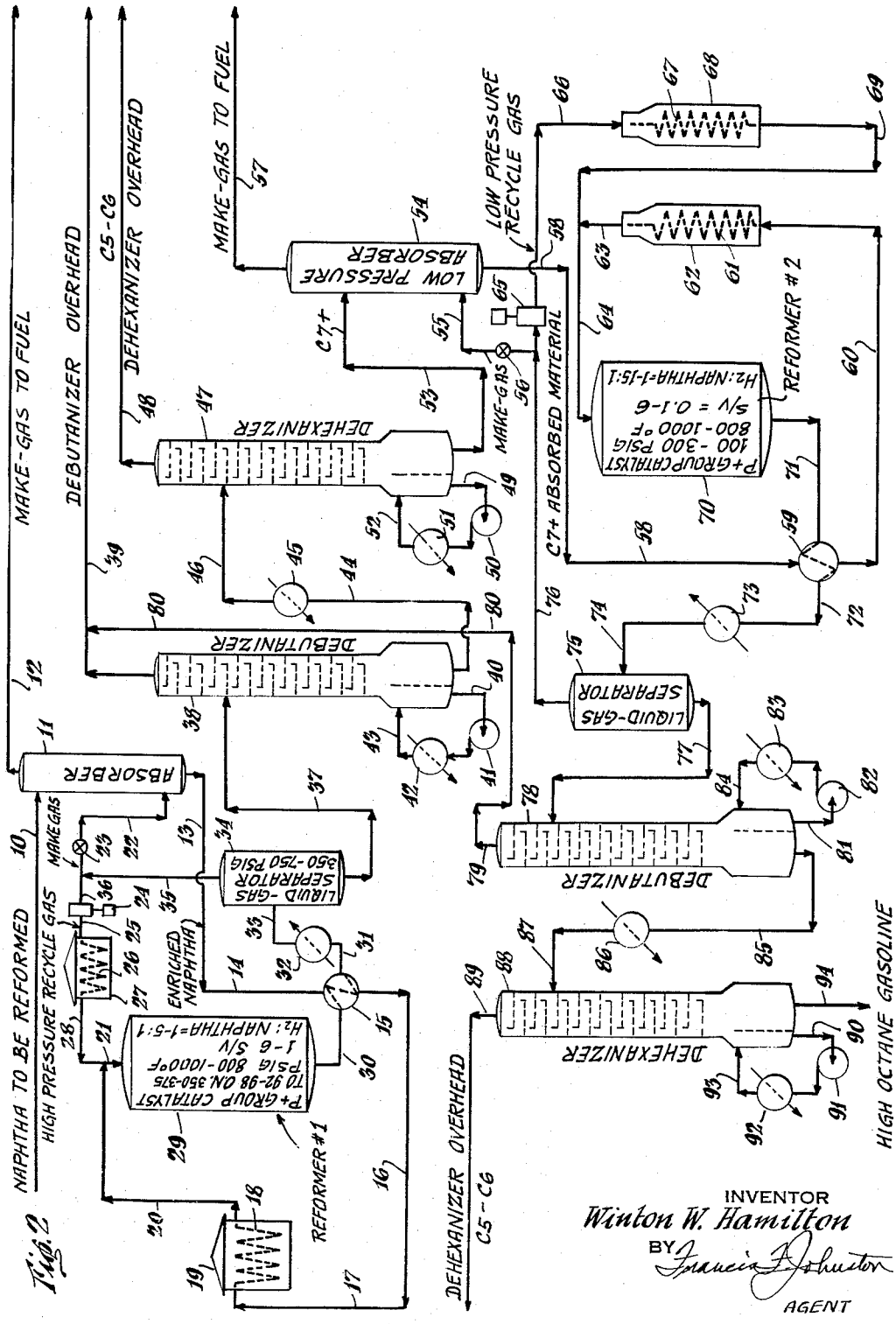


Fig. 2

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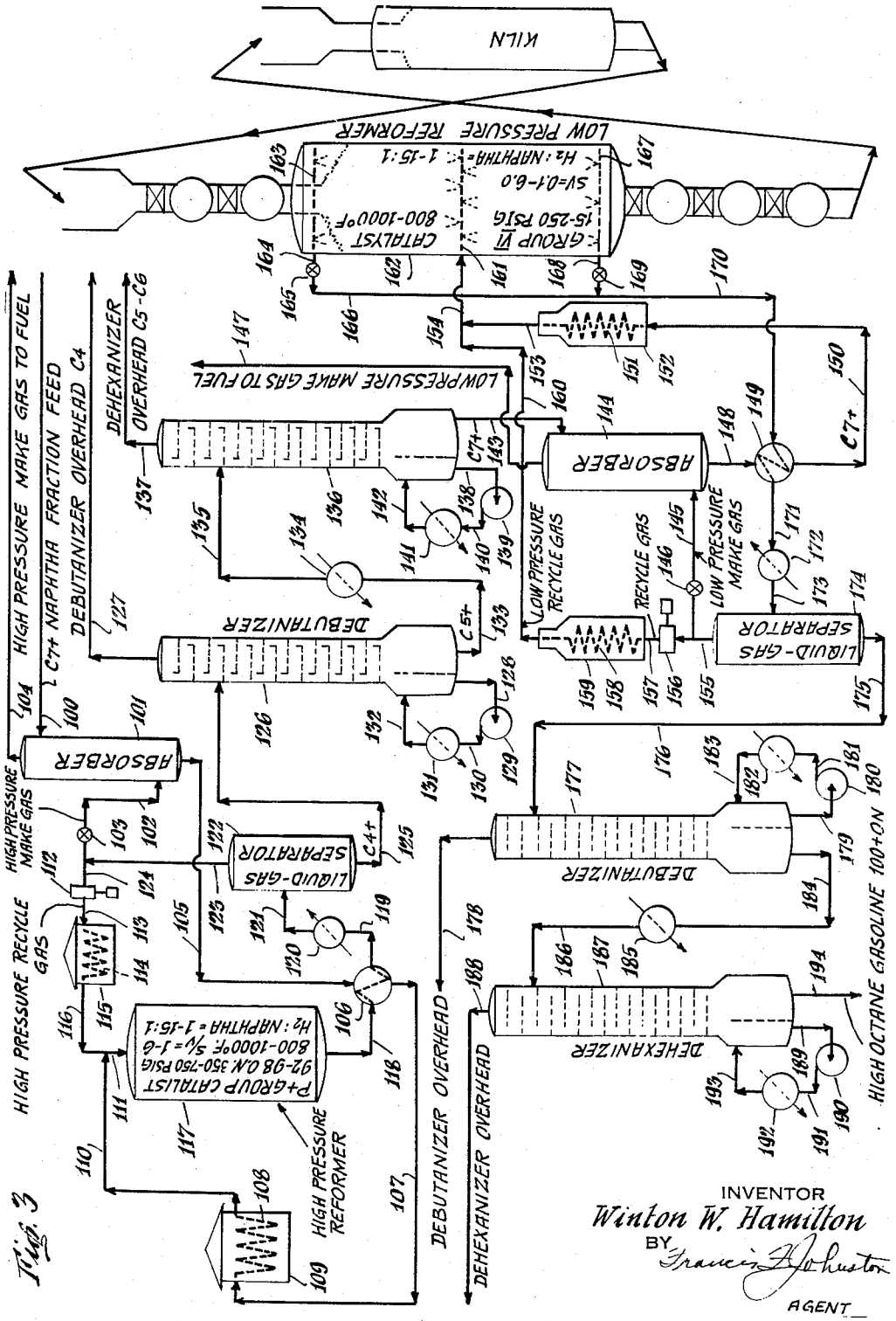


Fig. 3

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TWO-STAGE REFORMING WITH INTERMEDIATE FRACTIONATION

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Filed Sept. 6, 1956, Ser. No. 608,294
3 Claims. (Cl. 208—64)

The present invention relates to the production of high octane rating gasoline with improved yields and, more particularly, to reforming gasoline at high pressures in a first stage and at lower pressures in a second stage.

Low octane rating gasoline is a mixture of hydrocarbons having 4 or more carbon atoms in the molecules, classified as paraffins, olefins, naphthenes and aromatic hydrocarbons. The hydrocarbons having 4 carbon atoms will, in a modern refinery, be the normal butane remaining from alkylation and are of little importance in this invention. Conventional catalytic reforming converts the pentanes and hexanes to hydrocarbons having a higher octane rating than the original C_5 and C_6 hydrocarbons but at a yield which is not as economic as conversion by other methods. In conventional reforming, the reactions of the C_7 and heavier molecules depend on the class and molecular weight of the molecules.

The heptane and heavier fraction of a gasoline from a Mid-Continent crude has the following composition:

Hydrocarbon type:	Volume, percent
Paraffins	46.5
Olefins	3.0
Naphthenes	43.8
Aromatics	6.7
Total	100.0

The olefins will usually be converted to paraffins either in a pretreater or on the first contact with reforming catalyst. Thus the charge to the reformer can be considered to be mainly paraffins, naphthenes and aromatics.

The aromatic hydrocarbons have a high octane number and are changed very little if any during conventional catalytic reforming. The naphthenes are converted almost quantitatively to aromatic hydrocarbons under reforming conditions. The reactions of the paraffin hydrocarbons depend on the reforming conditions, and the molecular weight of the paraffins. The paraffins range from C_7 to about C_{12} usually and in catalytic reforming are either dehydrocyclized to aromatics or hydrocracked to lower molecular weight hydrocarbons. High pressure catalytic reforming favors hydrocracking whereas low pressure reforming favors dehydrocyclization.

For the higher molecular weight paraffins, hydrocracking is preferred over dehydrocyclization. The products of hydrocracking are likely to be in the gasoline boiling range. For example, hydrocracking a C_{10} paraffin into two C_5 molecules will produce a yield about 120 vol. percent and an increase in octane rating of about 100 units. When a paraffin is reformed by dehydrocyclization to the corresponding aromatic hydrocarbon, the aromatic hydrocarbon produced has a boiling point higher than the original paraffin. Consequently, when dehydrocyclizing a high molecular weight paraffin, say a C_{12} paraffin, the produced aromatic often has a boiling point too high to be included in the reformed gasoline.

For the lower molecular weight paraffins, dehydrocyclization is preferred over hydrocracking. The products of hydrocracking are likely to be outside the gasoline boiling range. For an example, if a C_7 paraffin is hydrocracked to produce one C_3 paraffin molecule and one C_4 paraffin molecule, it is not economic to include the C_3 paraffin in gasoline and the C_4 paraffin can be included to only a limited extent. However, if a low molecular weight paraffin is dehydrocyclized to an aromatic, the aromatic has a very high octane number and has a low enough boiling point to be included in the gasoline. For example, if a C_7 paraffin is dehydrocyclized to toluene, the toluene is well within the normal gasoline boiling range.

Therefore, the preferred reactions are: hydrocracking for the higher molecular weight paraffins, and dehydrocyclization for the lower molecular weight paraffins. This would apparently call for reforming the high molecular weight paraffins at high pressure and the low molecular weight paraffins at low pressure. However, it has been found that the high molecular weight paraffins crack more rapidly than the low molecular weight paraffins. Therefore a mixture of high and low molecular weight paraffins can be reformed at high pressure and a moderate severity, thereby hydrocracking most of the high molecular weight paraffins while hydrocracking the low molecular weight paraffins to only a moderate extent. The remaining paraffins can then be subjected to low pressure reforming where the remaining low molecular weight paraffins are dehydrocyclized to aromatics with hydrocracking being minimized.

While hydrocracking of low molecular weight paraffins has been minimized in the high pressure reformer by operating at moderate severity and in the low pressure reformer by the low pressure itself, some hydrocracking of low molecular weight paraffins will occur in both reformers. Therefore, the lowest molecular weight paraffins present in a full boiling range gasoline can be removed and charged to a more economic process rather than being charged to reforming where some hydrocracking will occur. For example, the C_5, C_6, and possibly the C_7 hydrocarbons could be removed by distillation and charged to an isomerization unit rather than being charged to the high pressure reformer. Low molecular weight hydrocarbons will be produced in the high pressure reformer so the C_5, C_6 and possibly the C_7 hydrocarbons can be removed from the reformate from the high pressure reformer before charging the heavier portion to the low pressure reformer. The lighter portion removed by distillation can go to the isomerization unit.

Illustrative of the preferential cracking of high molecular weight paraffins and the slight or moderate cracking of low molecular weight paraffins under high severities are the data presented in Table I.

TABLE I

	Charge	Ex. 1	Ex. 2	Ex. 3
Severity		A	B	C
Pressure, p.s.i.g.		500	500	500
Reactor Temp. of Space Velocity		940	940	940
V./hr./v.		3	2	1
Hydrogen to naphtha Mol Ratio		10	10	10
Res. O.N+3 cc. TEL	76	90	100	103
Hydrocarbon:				
Paraffins, vol. percent	46.5	51.7	40.6	30.8
Aromatics, vol. percent	6.7	32.8	41.6	41.8
Naphthenes, vol. percent	43.8	9.0		
Other, vol. percent	3.0	2.0	0.6	0.4
	100.0	95.5	82.8	73.0
Paraffin Distribution:				
C_5	0.0	3.0	6.5	7.5
C_6	3.6	6.2	8.9	10.0
C_7	10.6	13.2	11.5	8.4
C_8	12.4	13.8	9.1	4.0
C_9	10.0	8.9	3.4	0.9
C_{10}	6.2	4.6	1.2	
C_{11}	3.3	2.0		
C_{12}	0.4			
	46.5	51.7	40.6	30.8

In Table II data are presented showing the yield of aromatic hydrocarbons from paraffins when reforming at various pressures. The severity of the reforming conditions can be sufficient to convert the paraffins charged completely to aromatic hydrocarbons or lower boiling paraffins. The data establishes that the lower the pressure, the greater the fraction of paraffins converted to aromatic hydrocarbons. However, the lower the pressure, the poorer the catalyst life. Consequently the determination of the lowest pressure to be used in the low pressure or second reformer of the present invention is determined by overall economics considering as factors, yields, catalyst cost, investment, and other operating costs.

TABLE II

Pressure, p.s.i.g.	100	200	350	500
Reactor Temp., percent	950	950	950	950
Space Velocity, v./hr./v.	2	2	2	2
Hydrogen to naphtha mol ratio	10	10	10	10
Yield of Aromatics,[1] Vol. % of charge	42	32	16	8

[1] Balance of paraffins hydrocracked to lighter paraffins.

In Table III are presented data showing the yields obtained when treating a C_5+ gasoline in accordance with the principles of the present invention including isomerization of the C_5 and C_6 hydrocarbons.

TABLE III

Total low octane rating gasoline

Hydrocarbons	Barrels/Day	Treatment
C_5	1,240	Isomerized.
C_6	1,260	Do.
C_7+	8,740	High Pressure Reforming.

Product from high pressure reforming

Hydrocarbon	Barrels/Day	Treatment
C_5	358	Isomerized.
C_6	977	Do.
C_7+	6,622	Low Pressure Reforming.

Product from low pressure reforming

Hydrocarbon	Barrels/Day	Treatment
C_5	462	Isomerized.
C_6	217	Do.
C_7+	4,680	Gasoline (substantially pure aromatics).

Products from isomerization

	Barrels/Day	Refinery Product
Isopentane	2,200	Gasoline.
Isohexane	2,210	Do.
Total	4,410	

Gasoline blend

	Barrels/Day	Res. O.N.+3 cc. TEL
Isopentane	2,200	104
Isohexane	2,210	106
Aromatics	4,680	114
Total	9,090	110

Thus, from 11,240 barrels of C_5+ gasoline having a Research O.N.+3 cc. TEL of 76 there was produced by the process of the present invention 9090 barrels of gasoline having a Research O.N.+3 cc. TEL of 110. In contrast, reforming the same gasoline to 110 Research O.N.+3 cc. TEL in accordance with prior art processes yields only 6080 barrels of gasoline of required octane rating. In other words, the process of the present invention provides a yield of about 80.7 volume percent of the charge while prior art processes provide yields of only about 54 volume percent of the charge. Furthermore, when the C_5 and C_6 hydrocarbons produced in the high pressure reformer are charged to the low pressure reformer, in contrast to the principles of the present invention, about 600 barrels per day of hexane and about 120 barrels per day of pentanes are lost by hydrocracking to gas.

FIGURE 1 is a simplified flow diagram illustrative of an operation producing the result presented in Table III.

The simplified flow diagram FIGURE 1 illustrates the preferred embodiment of the present invention. A low octane number gasoline is first pretreated to remove sulfur compounds, and/or nitrogen compounds and other contaminants which have a deleterious effect upon the catalyst, cause corrosion or for other reasons preferably are removed from the charge stock. The pretreated gasoline is then dehexanized, i.e., C_6 and lighter hydrocarbons are removed as an overhead. The bottoms, i.e., C_7 and heavier hydrocarbons are then reformed at high pressures of the order of about 300 to about 750 p.s.i.g. under conditions favoring hydrocracking of the paraffins in the dehexanized charge and dehydrogenation of the naphthenes.

The effluent of the high pressure reformer is dehexanized and the C_7 and heavier hydrocarbons are reformed at low pressures of the order of about 100 to about 300 p.s.i.g. under conditions favoring aromatization of the low boiling paraffins. The effluent from the low pressure reformer is dehexanized. The C_7 and heavier hydrocarbons of the low pressure reformer effluent are the aromatic component of the gasoline blend. The C_6 and lighter hydrocarbons separated from the charge stock, from the high pressure reformer effluent, and from the low pressure reformer effluent preferably are combined and debutanized. The C_4 and lighter hydrocarbons taken as overhead in the debutanizer are used to pressure the blend gasoline, as liquefied petroleum gas and for various other purposes. The debutanized fraction is then treated as by distillation to separate C_6 and lighter. The dehexanized fraction comprising C_7 and heavier hydrocarbons are either admixed with the charge to the low pressure reformer or passed through an adsorber in conjunction with the effluent from an isomerization reaction to which reference is made hereinafter.

The overhead of the dehexanizer comprising C_6 and C_5 hydrocarbons is then treated to remove pentanes. The pentanes pass to a pentane splitter in which the isopentane is taken overhead and the normal pentane is the bottoms fraction.

The bottoms of the depentanizer flows to a C_6 splitter where the isohexane is taken as overhead and the normal C_6 paraffins and methylpentane form the bottoms fraction.

The bottoms from the C_6 splitter and the bottoms of the C_5 splitter are isomerized. The effluent of the isomerization reaction is fractioned to separate the normal C_5 and C_6 hydrocarbons from the isoparaffins having 5 and 6 carbon atoms.

The isopentane taken as overhead from the C_5 splitter and the isohexane taken as overhead from the C_6 splitter are blended with the aromatic bottoms of the dehexanized effluent from the low pressure reformer to form the gasoline blend.

Suitable catalysts and operating conditions for high pressure and low pressure reforming are listed in Table IV. Table IV is illustrative and not exclusive.

TABLE IV

High pressure reformer

CONDITIONS FAVORING HYDROCRACKING HEAVY (C_{10}+) PARAFFINS, AND DEHYDROGENATING NAPHTHENES

Catalyst	Reactor Pressure, p.s.i.g.	Average Reactor Temp., °F.	Space Velocity	
			v./hr./v.	H_2-Naphtha, mol ratio
Mo—Al	300–500	750–950	0.1–2	1–5
Cr—Al	300–500	800–1,000	0.1–2	1–5
Pt group Metal on Alumina	350–750	800–1,000	1–6	1–10:1

Low pressure reformer

CONDITIONS FAVORING AROMATIZATION OF LOW BOILING, C_7–C_{10} PARAFFINS AND DEHYDROGENATION OF NAPHTHENES

Catalyst	Hydrogen to oil, mol ratio	Reactor Pressure, p.s.i.g.	Av. Reactor Temp., ° F.	Space Velocity, v./hr./v.
Mo—Al	1–10	50–200	750–1,000	0.1–2
Cr—Al	1–10	50–200	800–1,050	0.1–2
Pt group on Alumina	1–15:1	100–300	800–1,000	0.1–6

In FIGURE 2 is illustrated by a more detailed flow sheet high pressure and low pressure reforming with removal of C_5 and C_6 hydrocarbons from the effluents of both reactors employing a platinum group catalyst in both the high pressure reformer and the low pressure reformer.

A full boiling range naphtha pumped from a source not shown at the pressure existing in high pressure reformer **29** flows through line **10** to absorber **11**. A gas containing C_1 to C_6+ hydorcarbons and hydrogen flows through line **22** under control of valve **23** to absorber **11**. The amount of gas flowing through line **22** is regulated by the pressure in gas separator **34** and is about equivalent to the net make of gas in reformer **29**. The naphtha contacts the gas in absorber **11** and extracts the heavier hydrocarbons from the gas. The gas stripped of these hydrocarbons flows from absorber **11** through line **12** to the refinery fuel system.

The charge naphtha enriched with the hydrocarbons absorbed in absorber **11** flows along lines **13** and **14** to heat exchanger **15** where it is in indirect heat exchange with the effluent from reformer **29**. The heated, enriched naphtha flows from heat exchanger **15** through lines **16** and **17** to coil **18** in heater **19** where it is heated to reaction temperature or to a temperature such that, when mixed with recycle gas heated to a temperature above reaction temperature in the mol ratio of 1–10 mols hydrogen per mol of naphtha to form a charge mixture, the charge mixture has a reaction temperature of about 800° to about 1050° F.

The heated naphtha flows from coil **18** through line **20** to line **21**. Recycle gas produced as hereinafter described is pumped by compressor **24** through line **25** to coil **26** in heater **27**. The hydrogen-containing recycle gas is heated in coil **26** to at least reaction temperature and preferably higher thereby reducing the temperature to which the naphtha is heated and concomitantly reducing thermal conversion. The heated hydrogen-containing recycle gas flows from coil **26** through line **28** to line **21** where it is mixed with the heated charge naphtha in the mol ratio of about 1 to about 10 mols of hydrogen per mol of naphtha to form a charge mixture having a temperature of about 800° to about 1050° F. and approximately that of the reaction temperature in high pressure reformer **29**.

The catalyst employed in high pressure reformer **29** can be any reforming catalyst such as group VI metal oxide on a carrier such as alumina; a mixture of group VI and group VII metal oxides on a carrier; a platinum group metal on a support such as alumina and in general a catalyst combining dehydrogenation capabilities with hydrocracking capabilities. For the purpose of illustration a catalyst comprising about 0.6 weight percent platinum and about 0.6 weight percent chlorine on an alumina support has been selected.

The charge naphtha is reformed under conditions favoring the cracking of the high molecular weight paraffins (C_{10}+) with only mild aromatization of the paraffins while dehydrogenating the naphthenes of the charge. By reforming the charge over the catalyst of the illustration to about 92–90 O.N. the foregoing results can be achieved. Reforming to 92–98 O.N. is achieved at about 350 to 750 p.s.i.g at 800° to 1050° F. employing a liquid space velocity of 1–6 volumes of liquid charge per volume of catalyst per hour.

The effluent of high pressure reformer **29** flows through line **30** to heat exchanger **15** previously described and thence through line **31** to cooler **32** where the effluent is cooled to a temperature such that most of the C_5 and heavier hydrocarbons liquefy at the pressure of reformer **29**. The mixture of the uncondensed portion of the effluent and the condensed portion of the effluent flows through line **33** to liquid gas separator **34**.

In liquid-gas separator **34** the uncondensed portion of the effluent from the high pressure reformer flows through line **35** to line **36**. A portion about equivalent to the net make of gas in reformer **29** flows through line **22** under control of valve **23** as previously described. The balance flows to compressor **24** for use as recycle gas.

The condensed portion of the high pressure reformer effluent flows from separator **34** through line **37** to debutanizer **38**. In debutanizer **38** an overhead comprising C_4 and lighter hydrocarbons is taken overhead through line **39** leaving as bottoms C_5 and heavier hydrocarbons.

A portion of the bottoms is circulated through a reboiler comprising line **40**, pump **41**, heat exchanger **42** and line **43** to maintain distillation temperatures in debutanizer **38**. The balance of the bottoms flows from debutanizer **38** through line **44** to heat exchanger **45** where it is heated to a temperature at which C_6 hydrocarbons are vaporized.

The heated debutanizer bottoms flows through line **46** to dehexanizer **47**. In dehexanizer **47** a C_5–C_6 overhead is taken through line **48** preferably to an isomerization unit not shown. The bottoms comprising C_7 and heavier hydrocarbons in part is circulated through a reboiler comprising line **49**, pump **50**, heat exchanger **51** and line **52** to maintain the volatilization temperature required in dehexanizer **47**. The balance flows from dehexanizer **47** through line **53** to low pressure absorber **54**.

In low pressure absorber **54** the C_7 and heavier bottoms from dehexanizer **47** contact gas from low pressure reformer **70** in amount about equivalent to the net make of gas in low pressure reformer **70**. The net make of gas from low pressure reformer **70** flows through line **55** under control of valve **56** to absorber **54**. In absorber **54** the heavier, C_5+ hydrocarbons are absorbed from the net make of gas. The gas stripped of the C_5+ hydrocarbons is vented through line **57** to the refinery fuel system.

The C_7+ dehexanizer bottoms enriched with hydrocarbons stripped from the net make gas flows from absorber **54** through line **58** to heat exchanger **59** where the enriched dehexanizer bottoms are in heat exchange relation with the effluent from low pressure reformer **70**. From heat exchanger **59** the heated enriched dehexanizer bottoms flows through line **60** to coil **61** in heater **62**.

In coil **61** the enriched dehexanizer bottoms are heated to reaction temperature or to a temperature such that, when mixed with heated recycle gas in the ratio of about 1 to 15 mols hydrogen per mol of dehexanizer bottoms to form a charge mixture, the charge mixture has a temperature approximating the reaction temperature the low pressure reformer **70** and about 800° to 1050° F.

Recycle gas obtained as hereinafter described and comprising hydrogen and C_1+ hydrocarbons is pumped by compressor 65 through line 66 to coil 67 in heater 68. In coil 67 the recycle gas is heated to at least the temperature existing in reformer 70. The heated recycle gas flows from coil 68 through line 69 to line 64 where it is mixed with heated enriched dehexanizer bottoms in the ratio of about 1 to 15 mols of hydrogen per mol of bottoms to form a charge mixture.

The charge mixture flows through line 64 to low pressure reformer 70. In low pressure reformer 70 the dehexanizer bottoms contact a reforming catalyst comprising a dehydrogenating catalyst and a support under conditions such that any naphthenes present are dehydrogenated and all paraffins are dehydrocyclicized with cracking being minimized. For a catalyst comprising about 0.6 weight percent platinum and about 0.6 weight percent chlorine on an alumina support the low pressure reformer is operated at a pressure of about 100 to 300 p.s.i.g., a temperature of about 800° to 1050° F., a liquid space velocity of about 0.1–6 v./hr./v. and with a hydrogen to dehexanizer bottoms mol ratio of about 1–15:1.

The effluent from low pressure reformer 70 flows through line 71 to heat exchanger 59 previously described and thence through line 72 to cooler 73 where the low pressure reformer effluent is cooled to a temperature at which most of the C_5 and heavier hydrocarbons liquefy.

From cooler 73 the liquefied and gaseous components of the low pressure reformer effluent flow through line 74 to liquid-gas separator 75. In separator 75 the liquefied effluent separates from the gaseous low pressure reformer effluent. The gaseous low pressure reformer effluent leaves separator 75 through line 76 through which it flows in part to compressor 65 while the net make of gas flows through line 55 to absorber 54 as previously described.

The liquefied portion of the low pressure reformer effluent flows through line 77 to debutanizer 78 from which an overhead comprising C_4 and lighter hydrocarbons is taken overhead through lines 79 and 80 to line 39.

A portion of the debutanizer bottoms comprising C_5 and heavier hydrocarbons flows through a reboiler comprising line 81, pump 82, heat exchanger 83 and line 84 to maintain a temperature in debutanizer 78 high enough to vaporize C_4 and lighter hydrocarbons. The balance of the debutanizer bottoms flows through line 85 to heat exchanger 86 where the temperature is raised to that at which C_6 and lighter hydrocarbons are volatilized. The heated debutanizer bottoms flow from exchanger 86 through line 87 to dehexanizer 88.

In dehexanizer 88 a C_5–C_6 overhead is taken through line 89, preferably to an isomerization unit. The bottoms comprising C_7 and heavier hydrocarbons in part is circulated through a reboiler comprising line 90, pump 91, heat exchanger 92 and line 93 to maintain a temperature at which C_6 hydrocarbons are volatile. The balance of the dehexanizer bottom flows therefrom through line 94 to provide a highly aromatic component of the gasoline blend. This component can be substantially pure aromatics.

The flow sheet FIGURE 2 illustrates the use of static catalyst beds in both the high pressure and the low pressure reformers. However, the present invention is not so limited and moving bed or fluidized beds of catalyst can be used in both or either reformer. The flow sheet of FIGURE 3 illustrates the use of a static bed of catalyst in the high pressure reformer and a moving bed of catalyst in the low pressure reformer. Thus, the catalyst in the high pressure reformer can be the platinum group metal catalyst previously described while the catalyst employed in the low pressure moving bed reformer can be a chromium oxide-aluminum oxide reforming catalyst comprising at least 70 mol percent aluminum oxide (alumina) and 18 to 30 mol percent chromium oxide (chromia).

As illustrated in FIGURE 3 the preferred C_7 and heavier fraction of naphtha is pumped from a source at the pressure existing in high pressure reformer 117 through line 100 to absorber 101. In absorber 101 the C_7+ naphtha charge is contacted with gas from liquid-gas separator 122 flowing through line 102 and regulated by valve 103 to the amount of the net make of gas in high pressure reformer 117. The C_7+ feed strips C_4+ hydrocarbons from the gas and is thus enriched. The stripped gas leaves the absorber 101 through line 104 and flows to the refinery fuel system.

The enriched C_7+ fraction flows from absorber 101 through line 105 to heat exchanger 106 where it is in heat exchange relation with the effluent of high pressure reformer 117. From heat exchanger 106 the heated, enriched C_7+ fraction flows through line 107 to coil 108 in heater 109.

In coil 108 the enriched C_7+ fraction is heated to a temperature such that, when mixed with heated recycle gas in the mol ratio of 1 to 15 mols of hydrogen per mol of C_7+ fraction to form a charge mixture, the temperature of the charge mixture is that of the high pressure reformer and about 800° to 1050° F.

Recycle gas comprising hydrogen and C_1+ hydrocarbons flows from liquid-gas separator 122 through lines 123 and 124 to compressor 112 thence through line 113 to coil 114 in heater 115. In coil 114 the recycle gas is heated to at least the temperature existing in high pressure reformer 117. The heated recycle gas flows from coil 114 through line 116 to line 111 where it is mixed with the heated enriched C_7+ fraction to form a heated charge mixture.

The heated charge mixture flows through line 111 into high pressure reformer 117. The high pressure reformer effluent flows from high pressure reformer 117 through line 118 to heat exchanger 106 previously described and thence through line 119 to cooler 120.

In cooler 120 the high pressure reformer effluent is cooled to a temperature at which most of the C_5 and heavier hydrocarbons are liquefied. The mixture of liquefied hydrocarbons and gas flows through line 121 to liquid-gas separator 122. From liquid-gas separator 122 the gaseous portion of the high pressure reformer effluent flows through line 123 to line 124. Here a portion about equivalent to the net gas make in the high pressure reformer flows through line 102 while the balance as recycle gas flows to compressor 112.

The liquid portion of the high pressure reformer effluent flows from separator 122 through line 125 to debutanizer 126 where C_4 and lighter hydrocarbons are taken as overhead through line 127 and the C_5 and heavier hydrocarbons form a bottoms.

A portion of the bottoms is circulated through a reboiler comprising line 128, pump 129, line 130, heat exchanger 131 and line 132 to maintain a temperature in debutanizer 126 at which C_4 and lighter hydrocarbon volatilize. The balance of the debutanizer bottoms flows through line 133 to heat exchanger 134 where the temperature of the debutanizer bottoms is raised to volatilize C_6 and lighter hydrocarbons. The heated debutanizer bottoms flow from exchanger 134 through line 135 to dehexanizer 136.

In dehexanizer 136 the C_6 and lighter hydrocarbons are removed as overhead through line 137 preferably to an isomerizing reaction. The C_7 and heavier hydrocarbons form a bottoms product. A portion of the bottoms is circulated through a reboiler comprising line 138, pump 139, line 140, heat exchanger 141 and line 142 to maintain a temperature in dehexanizer 136 at which C_6 and lighter hydrocarbons are volatile. The balance of the C_7+ bottoms of the dehexanizer flows through line 143 to absorber 144.

In absorber 144 the C_7+ bottoms contact gas from liquid-gas separator 174 in amount about equivalent to the net make of gas in low pressure reformer 162. This net gas make flows from liquid-gas separator 174 through lines 155 and 145 under control of valve 146. In absorber 144 the net make gas is stripped of C_5+ hydrocarbons. The stripped gas leaves absorber 144 through line 147 to flow to the refinery fuel system.

The C_7+ bottoms enriched with the hydrocarbons stripped from the net make gas flows at the pressure of low pressure reformer 162 from absorber 144 through line 148. The enriched C_7+ bottoms flow through line 148 to heat exchanger 149 where the relatively cold C_7+ bottoms are in heat exchange relation with the hot effluent of the low pressure reformer. From heat exchanger 149 the heated C_7+ bottoms flow through line 150 to coil 151 in heater 152.

In heater 152 the C_7+ bottoms are heated to a temperature such that when mixed with heated recycle gas in the ratio of about 1 to 15 mols of hydrogen per mol of C_7+ bottoms to form a charge mixture the charge mixture has a temperature approximating that of the low pressure reformer and about 800° to about 1050° F. The heated C_7+ bottoms flow from heater 152 through line 153 to line 154.

Recycle gas containing at least 25 percent hydrogen and the balance C_1+ hydrocarbons flows from liquid-gas separator 174 through line 155 to recycle gas compressor 156. A portion of the recycle gas approximating the net make of gas in the low pressure reformer is bled-off through line 145 under control of valve 146 as described hereinbefore.

Recycle gas compressor 156 pumps the recycle gas through line 157 at the pressure of the low pressure reformer to coil 158 in heater 159. In heater 159 the recycle gas is heated to at least the temperature of the low pressure reformer and preferably to a higher temperature such that the charge mixture of recycle gas and enriched C_7+ bottoms is at the temperature of the low pressure reformer as described hereinbefore. The heated recycle gas at low pressure reformer pressure flows from heater 159 through line 160 to line 154 where it mixes with the heated enriched C_7+ bottoms to form the charge mixture described hereinbefore. The heated charge mixture flows through line 154 to distributor 161 in low pressure reformer 162.

A portion of the heated charge mixture flows upwardly from distributor 161 countercurrent to the downwardly flowing particle-form reforming catalyst to flow from low pressure reformer 162 through collector 163 and line 164 under control of valve 165 to line 166. The balance of the charge mixture flows downwardly from distributor 161 concurrently with the downwardly flowing particle-form solid reforming catalyst and leaves low pressure reformer 162 through collector 167 and line 168 under control of valve 169 to line 166.

The effluent from the upper reaction zone of low pressure reformer 162 flowing through line 164 to line 166 and the effluent from the lower reaction zone of low pressure reformer 162 flowing through line 168 are mixed in line 166 to form a total low pressure reformer effluent which flows from line 166 through line 170 to heat exchanger 149 where the total low pressure reformer effluent is in heat exchange relation with the enriched C_7+ bottoms as described hereinbefore.

The total low pressure effluent flows from exchanger 149 through line 171 to cooler 172 where the total effluent is cooled to a temperature at which most of the C_4+ hydrocarbons condense. The cooled total effluent flows through line 173 to liquid-gas separator 174 where the uncondensed portion of the total effluent comprising hydrogen and C_1+ hydrocarbons and equal in amount to the recycle gas in the charge mixture to low pressure reformer 162 plus the net make of gas in low pressure reformer 162 separates from the condensed portion of the total effluent from low pressure reformer 162.

The uncondensed portion of the total effluent flows from liquid-gas separator 174 through line 155 to compressor 156 and absorber 144 as described hereinbefore. The condensed portion of the total effluent flows from separator 174 through lines 175 and 176 to debutanizer 177.

In debutanizer 177 an overhead of C_4 and lighter hydrocarbons is taken through line 178. The balance of the condensed portion of the total effluent forms a bottoms product.

A portion of the bottoms is circulated through a reboiler comprising line 179, pump 180, line 181, heat exchanger 182 and line 183 to maintain the bottoms product at a temperature at which C_4 and lighter hydrocarbons are volatile. The balance of the bottoms flows through line 184 to heat exchanger 185 where the temperature of the debutanizer bottoms is raised to that at which C_6 and lighter hydrocarbons are volatile. The heated debutanizer bottoms flow from exchanger 185 through line 186 to dehexanizer 187.

An overhead of C_6 and lighter hydrocarbons is taken from dehexanizer 187 through line 188 preferably to an isomerization reaction. The balance of the debutanizer bottoms forms a dehexanizer bottoms.

A portion of the dehexanizer bottoms is circulated through a reboiler comprising line 189, pump 190, line 191, heat exchanger 192 and line 193 to maintain the dehexanizer bottoms at a temperature at which C_6 and lighter hydrocarbons are volatile. The balance of the dehexanizer bottoms is a high octane number highly aromatic product which is suitable after cooling for use as a spark ignited internal combustion engine fuel or suitable for blending as described hereinbefore.

It will be observed that in the flow diagrams FIGURES 2 and 3 provision has been made to heat the debutanizer bottoms prior to introduction into the dehexanizers. These heaters can be eliminated when the dehexanizers are operated at lower pressures than the debutanizers. The lower pressures in the dehexanizers will provide the required vaporization.

Thus, the present invention provides, generally, for reforming a charge stock in the presence of a reforming catalyst having dehydrogenating and cracking capabilities and in the presence of hydrogen at high reactor pressures under conditions of temperature and space velocity to crack $C_{10}+$ hydrocarbons whilst dehydrogenating naphthenes to obtain a high pressure effluent comprising hydrogen and C_1+ hydrocarbons, separating hydrogen and C_4 and lighter hydrocarbons from C_5 and heavier hydrocarbons, separating C_5 and C_6 hydrocarbons from C_7 and heavier hydrocarbons, reforming said C_7 and heavier hydrocarbons in the presence of a reforming catalyst having dehydrocyclizing capabilities and in the presence of hydrogen at a pressure lower than the aforesaid high reactor pressure and under conditions of temperature, pressure and space velocity to dehydrocyclicize said C_7 and heavier paraffin hydrocarbons, to dehydrogenate C_7 and heavier naphthenes and to avoid substantial cracking of said hydrocarbons to produce a low pressure effluent comprising hydrogen and C_1 and heavier hydrocarbons, separating hydrogen and C_1 to C_4 and lighter hydrocarbons from a fraction comprising C_5 and heavier hydrocarbons and separating C_6 and lighter hydrocarbons from C_7 and heavier hydrocarbons to obtain a product boiling in the gasoline boiling range containing C_7 and heavier hydrocarbons which can be substantially devoid of non-aromatic hydrocarbons. In the preferred form the C_5 and C_6 hydrocarbons separated from the C_7 and heavier hydrocarbons are isomerized to provide a high octane number component in the gasoline boiling range.

I claim:

1. A method of producing high octane gasoline which

comprises reforming low octane gasoline containing principally C_7 and heavier hydrocarbons in the presence of hydrogen and a reforming catalyst at relatively high pressures of at least 300 p.s.i.g. but below 750 p.s.i.g. and at a temperature in the range 750° to 1050° F. and a space velocity in the range 0.1 to 6 v./hr./v. to crack C_{10} and heavier hydrocarbons whilst dehydrogenating naphthenes to obtain a high pressure reaction zone effluent comprising hydrogen and C_1+ hydrocarbons, separating hydrogen and C_1–C_6 hydrocarbons from said high pressure zone effluent to obtain a low pressure zone charge stock comprising principally C_7 and heavier hydrocarbons, reforming said low pressure zone charge stock in the presence of a reforming catalyst and hydrogen at a reaction pressure lower than the aforesaid high pressure and not exceeding 300 p.s.i.g. and reforming conditions of temperature in the range 750° to 1050° F. and space velocity in the range 0.1 to 6 v./hr./v. to dehydrogenate naphthenes and dehydrocyclicize C_7 and heavier paraffins without substantial cracking of said paraffins to obtain a low pressure zone effluent comprising hydrogen and C_1 and heavier hydrocarbons, separating hydrogen and C_1–C_6 hydrocarbons from said low pressure zone effluent to obtain a product containing C_7 and heavier hydrocarbons, said product being highly aromatic and boiling in the gasoline range.

2. The method set forth and described in claim 1 wherein C_5 and C_6 hydrocarbons are separated from the high pressure zone and low pressure zone effluents and the separated C_5 and C_6 hydrocarbons are isomerized to more highly branched C_5 and C_6 hydrocarbons of higher octane values.

3. A method of producing high octane gasoline which comprises fractionating a low octane charge stock boiling in the gasoline range to separate an overhead fraction containing principally C_5 and C_6 hydrocarbons and a bottoms fraction containing principally C_7 and heavier hydrocarbons, reforming said bottoms fraction in the presence of hydrogen and a reforming catalyst at relatively high pressures of at least 300 p.s.i.g. but below 750 p.s.i.g. and at a temperature in the range 750° to 1050° F. and a space velocity in the range 0.1 to 6 v./hr./v. to crack C_{10} and heavier hydrocarbons whilst dehydrogenating naphthenes to obtain a high pressure reaction zone effluent comprising hydrogen and C_1+ hydrocarbons, separating hydrogen and C_1–C_6 hydrocarbons from said high pressure zone effluent to obtain a low pressure zone charge stock comprising principally C_7 and heavier hydrocarbons, reforming said low pressure zone charge stock in the presence of a reforming catalyst and hydrogen at a reaction pressure lower than the aforesaid high pressure and not exceeding 300 p.s.i.g. and reforming conditions of temperature in the range 750° to 1050° F. and space velocity in the range 0.1 to 6 v./hr./v. to dehydrogenate naphthenes and dehydrocyclicize C_7 and heavier paraffins without substantial cracking of said paraffins to obtain a low pressure zone effluent comprising hydrogen and C_1 and heavier hydrocarbons, separating hydrogen and C_1–C_6 hydrocarbons from C_7 and heavier hydrocarbons to obtain a highly aromatic product boiling in the gasoline range, combining the C_5 and C_6 hydrocarbons separated from said low octane gasoline with C_5 and C_6 hydrocarbons produced during reforming and isomerizing the combined C_5 and C_6 hydrocarbons to more highly branched C_5 and C_6 hydrocarbons of higher octane values.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,002,916 October 3, 1961

Winton W. Hamilton

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, "TABLE III", under the heading "Total low octane rating gasoline" for "Hydrocarbons" read -- Hydrocarbon --; column 6, line 11, for "92-90" read -- 92-98 --.

Signed and sealed this 15th day of May 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents