March 14, 1972 R. G. GRAVEN **3,649,520**

PRODUCTION OF LEAD FREE GASOLINE

Filed March 13, 1970

2 Sheets-Sheet 1

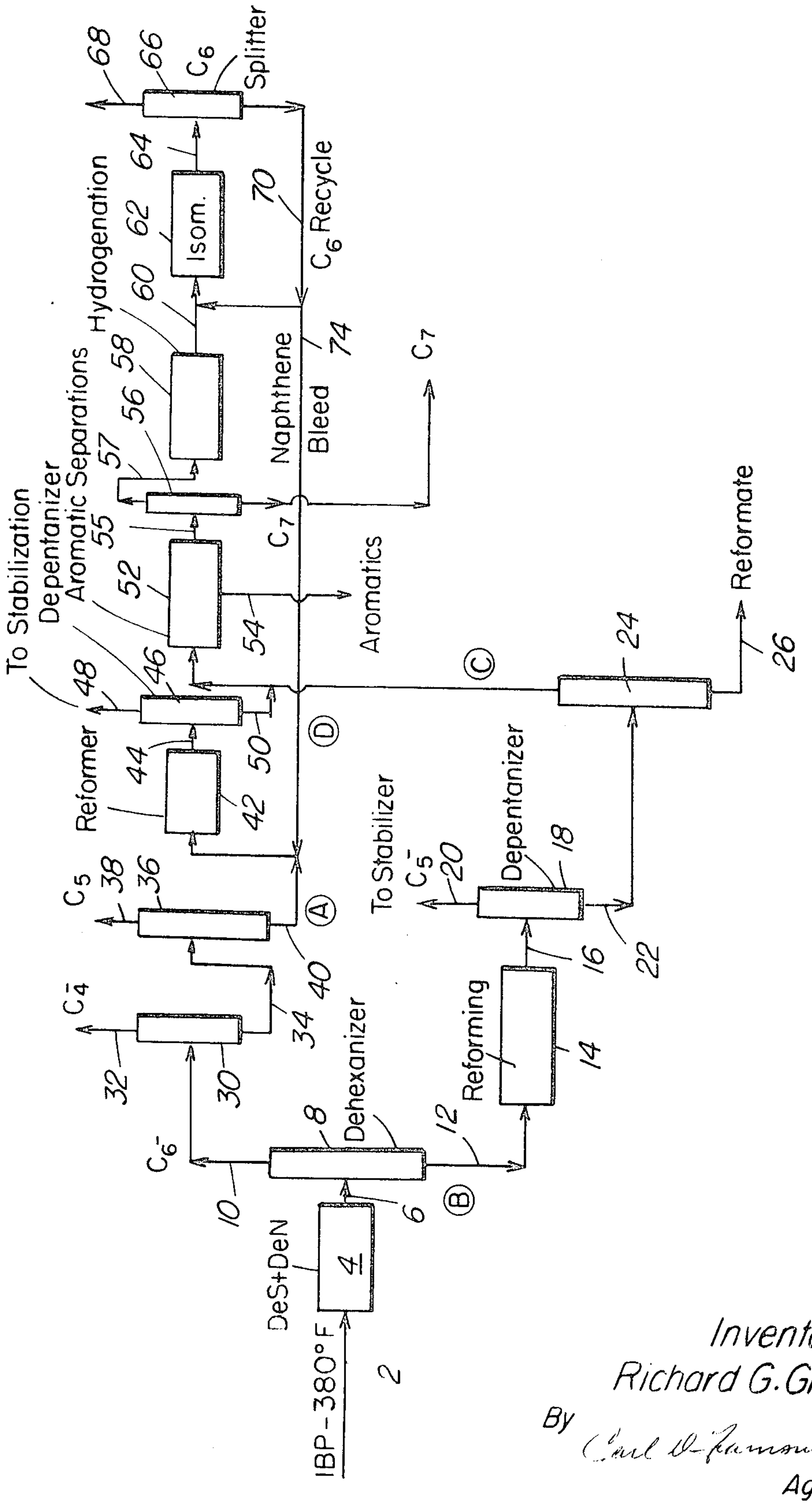

FIG. 1

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Filed March 13, 1970 2 Sheets-Sheet 2

METHOD for PRODUCING UNLEADED GASOLINES

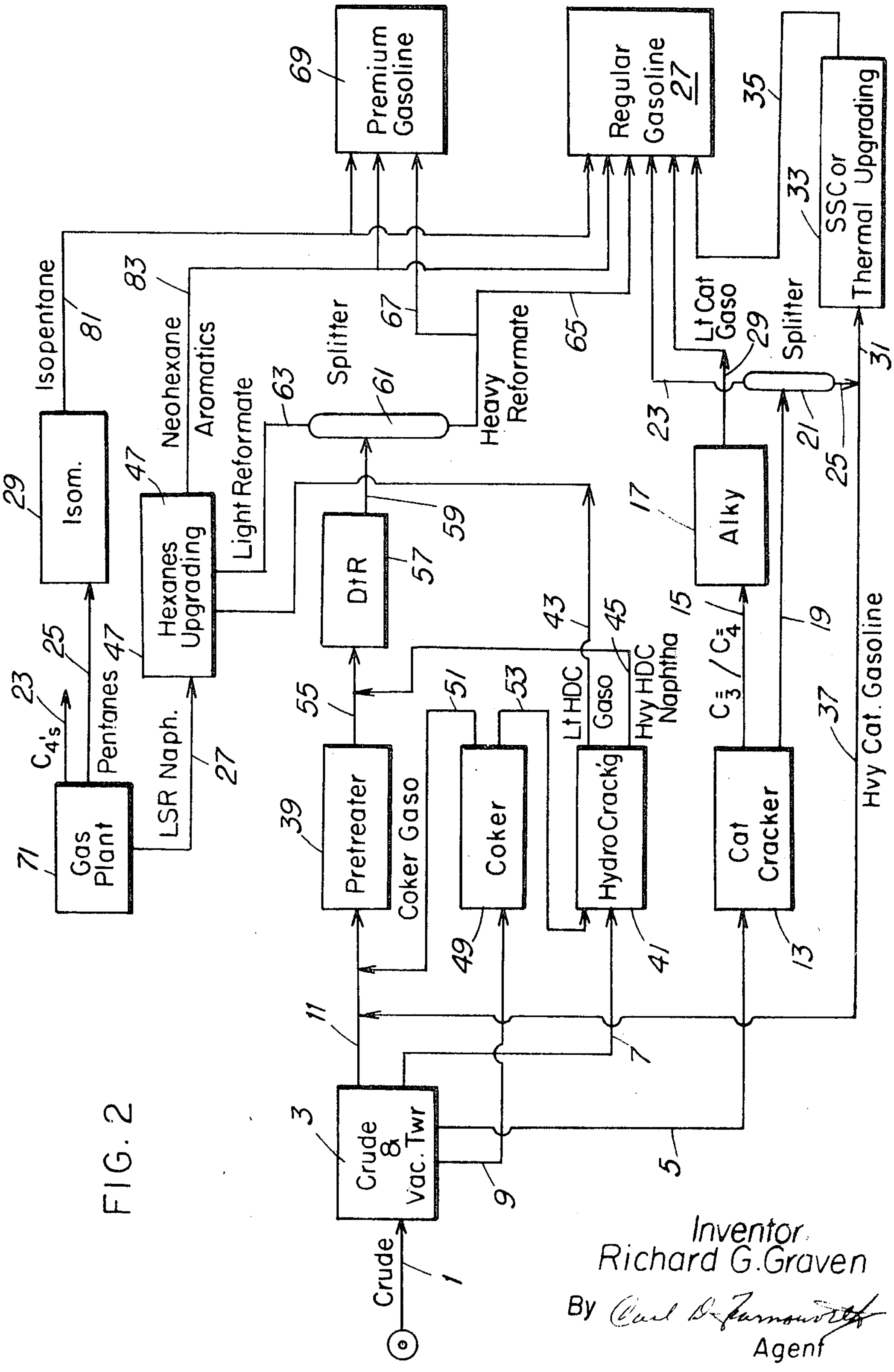

FIG. 2

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United States Patent Office

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PRODUCTION OF LEAD FREE GASOLINE

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U.S. Cl. 208—93 3 Claims

ABSTRACT OF THE DISCLOSURE

Production of lead free gasoline is described by the process combination of reforming, aromatic recovery and isomerization arranged to isolate among other things C_6 hydrocarbons upgraded to a higher octane product by isomerization thereby contributing to the yield of acceptable octane product for blending with reformate product.

BACKGROUND OF THE INVENTION

The present invention is concerned with the production of gasoline. In particular the present invention is concerned with a novel method and arrangement of known processing steps for producing lead-free gasoline. The need for providing a lead free gasoline product has been prompted in recent years by air pollution problems confronting sections of the world employing combustion engines in relatively high density. Therefore the greatest application of lead-free gasoline will be in those areas of high automobile density where the presence of lead additive combustion products are considered harmful and a major contributor to atmospheric pollution. Thus it is predictable that both relatively low and high octane gasoline products free of lead additives or other additives contributing to air pollution will be required in the near and/or immediate future to meet certain government restrictions and demands, on the one hand, while fulfilling the demands of the public and automobile manufacturers on the other hand. Thus the present invention is concerned with identifying a processing scheme compatible with present processing technology and/or refinery installations, one might employ to upgrade relatively low octane gasoline material to an acceptable higher octane product suitable for use in a combustion engine known today and for the immediate future. Some patents of interest in producing unleaded gasoline are U.S. Pats. 2,905,619, 3,165,461 and 2,900,323.

SUMMARY OF THE INVENTION

The present invention is directed to upgrading low octane gasoline boiling range constituents to a higher octane gasoline product. In a particular aspect it is concerned with upgrading C_6 hydrocarbon constituents suitable for blending with higher octane gasoline product of reforming. In yet another aspect the present invention is concerned with increasing the yield of lead free gasoline product when upgrading low octane gasoline boiling material by a combination of processing steps generally known in the prior art. The petroleum refining operations employed to advantage in the present invention include hydrogenation, reforming, aromatic recovery, isomerization and product separation steps arranged in a combination which will be particularly effective for producing gasoline products of desired octane rating. The present invention particularly emphasizes the method for upgrading relatively low octane C_6 hydrocarbon components, as well as the removal of low octane C_7 paraffins.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 identifies an arrangement of processing steps effective for upgrading naphtha or gasoline boiling range materials in a sequence of processing steps which includes reforming C_6 hydrocarbons, aromatics recovery, isomerization and fractionation steps which are particularly effective for isolating and upgrading C_6 hydrocarbon components of low octane rating to higher octane constituents.

FIG. 2 identifies diagrammatically a block flow refinery process arrangement for upgrading crude oil to premium and regular gasoline product by a combination of refinery operations which includes the specific arrangement of FIG. 1.

DESCRIPTION OF SPECIFIC EMBODIMENTS

In accordance with the present invention and diagrammatically represented in the attached drawing, a gasoline boiling range hydrocarbon fraction boiling in the range of from about C_4 hydrocarbons up to about 380° F. and obtained as straight run naphtha, coker naphtha or gasoline and in some cases catalytically cracked or hydrocracked gasoline is introduced to the process by way of line **2** for passage to catalytic pretreatment such as desulfurization or denitrogenation in zone **4**. In the catalytic pretreatment of zone **4** the gasoline charge is subjected to hydrogenation for the purpose of removing sulfur, nitrogen and any other undesired constituents or contaminants found in the gasoline charge. The pretreated gasoline is thereafter passed by line **6** to a separator vessel **8** referred to herein as a dehexanizer tower **8** maintained under temperature and pressure conditions designed to separate and permit recovery from the upper portion thereof hydrocarbon boiling 180° F. and lower boiling by line **10**. Higher boiling gasoline hydrocarbons and boiling from about 180° F. up to about 380° F. and identified as stream B, in Table 1, are withdrawn from the bottom of dehexanizer **8** by line **12**. It is, of course, recognized that a relatively rough separation may be made in dehaxanizer **8** and thus an amount of C_7 hydrocarbons may be carried overhead and/or a portion of C_6 hydrocarbons may withdraw from the bottom along with the intended higher boiling hydrocarbons.

The hydrocarbons in stream B and withdrawn by line **12** are thereafter passed to a reforming operation **14** wherein they are subjected to contact with a platinum catalyst in a catalytic reforming operation maintained under conditions selected to upgrade the gasoline and naphtha charge boiling above 180° F. to a higher octane product. In this reforming step the operating conditions of temperature, pressure and space velocity will be selected to produce reformate product thereof having a clear octane rating in the range of from about 90 up to about 106 and preferably at least about 97 octane rating clear. In some special circumstances, particularly for the production of high octane unleaded gasoline, the reforming severity conditions may be selected to provide a product having an octane rating of at least 103 and preferably 104 octane rating clear. The reforming operation pursued will normally be a relatively sophisticated reforming operation to take advantage of presently known technology. The use of naphthene rich gasoline charge materials may be successfully employed; however with a paraffin rich feed, the hexane upgrading concept of this invention will be even more advantageous. It is to be understood that reforming step **14** may be a regenerative or semi-regenreative operation. The effluent of reforming step **14** is normally separated to recover a hydrogen rich gas from the remaining effluent in equipment not shown and which can be used in other parts of the process such as in a hydrogenation step or an isomerization step hereinafter discussed. This recovery apparatus for hydrogen rich gas and circulation in the system is not specifically shown in the drawing since use of such hydrogen rich gas streams is generally known in the prior art. The reformate product from which hydrogen rich gas has been recovered is thereafter passed by line **16** to separator tower **18** known as a dependanizer. In dependanizer tower **18** the operating conditions are selected and maintained to effect separation and recovery of C_5 and any remaining lower boiling hydrocarbons from a reformate product effluent stream boiling above about C_5 hydrocarbons. The composition of the reformate product in line **22** is identified in Table 3 and comprises about 65% aromatics. The C_5 and lower boiling hydrocarbons are removed from the top of tower **18** by line **20** for further processing as desired and generally known in the prior art. The reformate product boiling above C_5 hydrocarbons are withdrawn from the bottom of dependanizer **18** by line **22**. Since an important aspect of the processing sequence is to concentrate low octane C_6 hydrocarbons, some C_5 hydrocarbons may be withdrawn from the bottom of tower **18** by line **22**. The higher boiling reformate fraction obtained from dependanizer **18**, such as identified in Table 3, is passed by line **22** to a dehexanizer tower **24** wherein the conditions of operation are selected to provide a cut point in the range of 158° F. up to about 225° F. so as to separate an overhead fraction primarily comprising hydrocarbons boiling in the range of C_6 hydrocarbons to a cut point of from about 150° F. up to about 200 or 225° F. from a higher boiling reformate product fraction boiling above the selected cut point. The influence of the cut point selected for tower **24** upon the product can be clearly seen by reference to Table 4. Reformate product in line **26** having the composition identified in Table 4 is withdrawn from the bottom of tower **24** by line **26**. This reformate product material being a relatively high octane product material thus may be utilized as the premium gasoline in unleaded form. The lower boiling material recovered from tower **24** by line **28** and having the composition of stream C, Table 4, is removed as an overhead fraction for further processing as hereinafter described. This recovered hydrocarbon fraction in line **28** comprises primarily the isolated C_6 hydrocarbons of relatively low octane and C_7 hydrocarbons of varying amount depending upon the cut point selected needs to be converted to higher octane product in order to be used in an unleaded gasoline product. When employing a cut point of about 225° F. in tower **24**, more C_7 hydrocarbons will be carried overhead thereby considerably upgrading the product in line **26** as evidenced by the data of Table 4. The C_7 hydrocarbon thus thrown ovehead may be recovered from the process by tower **56** discussed below. The C_7 hydrocarbons thus separated and recovered may be further processed such as by reforming, shape selective cracking or converted to olefin product as by fluid catalytic cracking or thermal cracking.

The light hydrocarbon fraction recovered as overhead from dehexanizer **8** by line **10** and which may contain a small amount of C_7 hydrocarbons may be combined with the C_5 and lighter hydrocarbons recovered from dependanizer **18** or separately processed. The C_6 and lighter hydrocarbons in line **10** are thereafter debutanized and dependanized in the sequence of separation steps hereinafter briefly discussed. The C_6 hydrocarbons and lighter fraction thus recovered are initially passed to debutanizer **30** wherein C_4 and lighter hydrocarbons are separated from higher boiling hydrocarbons to permit recovery thereof from the upper portion of the tower by line **32** with the remaining higher boiling portion being withdrawn from the bottom of debutanizer **30** and passed by line **34** to a dependanizer tower **36**. In dependanizer tower **36**, C_5 hydrocarbons are separated and removed from the upper portion thereof by line **38** with the remaining C_6 and higher boiling hydrocarbons being withdrawn from the bottom of depentaizer tower **36** by line **40**. The sequence above described, provides a hydrocarbon stream rich in C_6 hydrocarbons for upgrading to higher octane product. The C_6 rich hydrocarbon stream in line **40** and having the composition of stream A, Table 1, thereafter is passed to reforming step **42**. The reforming operation contemplated in step **42** is primarily one of dehydrogenation for the purpose of converting C_6 naphthenes to aromatics. Thus the octane rating of the product therefrom will depend considerably upon the type of C_6 hydrocarbons in the charge thereto. It is clear, therefore, that reforming step **42** is operated under conditions which are particularly selective for effecting dehydrogenation of naphthenes to form aromatics and isomerization of isomerizable hydrocarbons. The reformate product effluent of reforming step **42** is separated in a separation zone not shown to recover a hydrogen rich gas stream from a higher boiling reformate product stream. The hydrogen rich gas stream is recycled to the process such as to the pretreating step, reforming step or isomerization step herein discussed. The reformate product freed of hydroggen rich gas is recovered from reforming step **42** and passed by line **44** to a dependanizer tower **46** wherein C_5 and lower boiling hydrocarbons are separated from higher boiling reformate product or aromatic enriched stream with the C_5 hydrocarbons recovered from the upper portion of the tower by line **48**. These C_5 and lower boiling hydrocarbons may thereafter be stabilized in suitable equipment not shown and processed as by isomerization. The aromatic enriched stream separated in dependanizer tower **46** is removed from the bottom thereof by line **50** and passed to an aromatics removal zone such as an extraction step **52**. The aromatic rich stream in line **50** and identified in Table 2 is combined with the isolated C_6 hydrocarbon stream in line **28**. The combined C_6 hydrocarbon stream is passed to the aromatic removal step **52**. Step **52** is primarily for the removal of aromatics such as benzene, toluene and perhaps xylene from the combined C_6 hydrocarbon stream. The aromatic separated in zone **52** as by extraction, molecular sieve adsorption or any other convenient method is withdrawn by line **54**. The aromatic removal step may be substantially any aromatic removal step suitable for effecting an economic recovery of aromatics from the remaining C_6 hydrocarbon components introduced thereto. The aromatic free hydrocarbons recovered from step **52** which may comprise some C_7 hydrocarbons and a small amount of unremoved aromatics is thereafter fractionated when required to separate C_7 hydrocarbons from the lower boiling C_6 hydrocarbons. The C_6 hydrocarbons are then passed by line **56** to hydrogenation step **58**. Any separated C_7 hydrocarbon may be recycled to the reforming steps herein discussed or processed in any desired manner. In hydrogenation step **58** aromatics remaining in the C_6 hydrocarbons are hydrogenated and converted to naphthenes since it has been found that even a small amount of aromatics in the charge to the isomerization step is not particularly desirable. It is of course understood that hydrogen suitable for this hydrogenation step may be recovered from the hydrogen rich reformate product of reforming steps **14** and/or **42**. The hydrogenated C_6 fraction freed of aromatics and C_7 hydrocarbons is thereafter passed by line **60** to isomerization step **62**. The isomerization of hexane hydrocarbons to higher octane product is one requiring relatively strict operating conditions to avoid undesired cracking and low temperatures in the range of 200 to 500° F. are known to favor the isomerization to the higher octane C_6 hydrocarbon components. The production of 2,2-dimethylbutane having an octane rating clear of about 91.8 and which blends as if it had an octane rating of about 100 is enhanced by low temperature isomerization. It is desirable to recover any formed 2,3-dimethylbutane having a clear octane rating of about 103.5. As a word of caution, it is important to the isomerization of C_6 hydrocarbon constituents to minimize not only aromatics in the charge but also naphthenes and C_7 hydrocarbons since such materials have an undesirable influence or effect upon the activity and selectivity of typical solid type isomerization catalyst. In the operation above discussed naphthenes may build up in the isomerization product stream and care should be taken to prevent this from happening. Therefore, the product is isomerization obtained in step **62** is passed by line **64** to a C_6 splitter tower **66**. Splitter tower **66** is operated under conditions to permit the recovery of 2,2-dimethylbutane or neohexane overhead therefrom by line **68**. C_6 hyrdrocarbons not isomerized in step **62** are withdrawn from a lower portion of the tower by line **70** essentially as a recycle stream for recycle to step **62** or step **42**. The C_6 hydrocarbons may be recycled to the isomerization step all or in part, it being important, however, to limit the build up of naphthenes in this C_6 recycle stream because of their undesirable influence on the isomerization step. To prevent this undesired build-up of naphthenes, a naphthene bleed stream **74** is used to pass a portion of this recycle stream to reformer **42** or **14** or separator tower **56**. The processing scheme thus described eliminates low octane C_7 hydrocarbon which may be converted to other products such as by shape selective cracking, fluid cracking and in some cases these hydrocarbons may be cyclized in a very selective low pressure reforming operation.

It is immediately clear from the above that the processing scheme specifically discussed above is a most effective processing arrangement for upgrading gasoline material and particularly relatively low octane C_6 hydrocarbons found in the gasoline boiling range. Furthermore, the processing arrangement above discussed results in the production of relatively high octane components from the reforming and isomerization steps which can be blended to suit the refiner in his desired to provide gasoline products which will meet the octane rating standards suitable to provide regular and premium gasoline products having an octane rating of at least 90 clear up to 104 or 106 octane rating clear.

The reforming steps employed in the processing sequence of this invention preferably employ catalyst components comprising platinum and/or platinum-type compound dispersed on alumina. Bimetallic reforming catalysts may also be employed to considerable advantage and the amount of platinum required in the catalyst will be less than that required when platinum is used alone. It is to be understood that the catalyst may be halogen promoted and every suitable operating variable such as moisture control and cracking inhibitors known in the prior art may be called upon to enhance the reforming operation in the direction of optimizing the production of desired octane product. The reforming operation may be effected at temperatures selected from within the range of from about 800° F. up to about 1050° F. under conditions of pressure in the range of from about 100 p.s.i.g. up to about 1000 p.s.i.g. and preferably not more than about 500 p.s.i.g. Generally the pressure will be selected from within the range of from about 200 p.s.i.g. up to about 500 p.s.i.g. The space velocity on a liquid hourly basis may be in the range of from about 0.5 up to about 10 in the presence of hydrogen at mol ratios known in the art. As stated hereinbefore the reforming operation may be semi-regenerative or a regenerative operation wherein regeneration of the catalyst occurs quite frequently and requires the use of an extra reactor in the reforming sequence known as a swing reactor. In any event the upgrading of C_6 hydrocarbons and hydrocarbons boiling above C_6 hydrocarbons such as C_7+ hydrocarbons are particularly effected in a combination of separate reforming operations and the combination of reforming steps are employed in combination with an isomerization operation designed to particularly upgrade low octane C_6 hydrocarbon constituents. Isomerization step **62** may be substantially any of the known isomerization processes of the prior art which will be effective for upgrading C_6 hydrocarbon constituents. The isomerization catalysts employed may be either solid isomerization catalysts or ones which require a liquid phase operation. The extraction step for recovery of aromatics may also be substantially any known method for effecting such separation in an economic manner. For example, extraction may be by adsorption and in particular a selective adsorption with a crystalline zeolite of proper pore dimensions. The aromatic freed product may in one type of operation be recovered from the zeolite such as by stripping and thereafter passed to the isomerization step. An effective material for the stripping operation could be hydrogen rich gas recovered from the reforming step of the process since the presence of such hydrogen gas is desirable in the isomerization step.

It is to be understood that methods for preparing the naphtha charge to the process and boiling up to about 380° F. and provide for recovering a C_6 hydrocarbon rich stream from a higher boiling hydrocarbon fraction may rely upon other fractioning processing arrangements for effecting stabilization of the naphtha charge and the recovery of C_4 and C_5 hydrocarbons. Furthermore, desulfurization and denitrogenation of the naphtha charge or fractions thereof may be accomplished as specifically shown in FIG. 1 or separate fractions such as the specific hydrocarbon charge to the separate reforming steps may be separately subjected to desulfurization treatment. For example, the product stream in line **6** of FIG. 1 recovered from pretreater **4** may pass through a separate stabilizer tower not shown for removal of C_4 and lower boiling constituents before passage of the remaining pretreated charge to dehexanizer tower such as tower **8**. In yet another arrangement the crude tower of the refining process may be relied upon to separate a hydrocarbon fraction boiling from about 160° F. up to about 380° F. from a lower boiling C_6 to 160° F. hydrocarbon fraction. The thus obtained fraction boiling above 160° F. may be passed to desulfurization before being reformed in a platinum reforming operation. A fraction boiling below about 160° F. may be recoverd from the crude tower and after stabilization thereof to recover C_4 and C_5 hydrocarbons therefrom, this hexane rich fraction may be separately desulfurized before effecting reforming thereof. In any of these arrangements the important consideration within the concept of the present invention is to effect a separation of low octane C_6 hydrocarbons from higher boiling gasoline constitutents so that each can be efficiently processed to a higher octane component thereby effecting a significant increse in overall product yield of desired higher octane product.

FIG. 2 identifies a block flow refinery arrangement for upgrading crude oil to premium and regular grade gasoline product. The specific processing arrangement of FIG. 1 discussed hereinbefore may be employed in the overall refining operation of FIG. 2. In the refining arrangement of FIG. 2, a crude oil is introduced to the process by line **1** for passage to an atmospheric crude tower and vacuum tower arrangement diagrammatically represented by block **2**. The operation of an atmospheric crude tower as well as a vacuum tower is well known in petroleum processing and suitable combinations thereof which will provide the refinery feeds hereinafter discussed will be suitable for use in the processing scheme of the invention herein described. In this refinery arrangement a catalytic cracking feed stock is withdrawn by line **5** from the crude tower. A charge stock suitable for hydrocracking is withdrawn by line **7**. The charge stocks for a coking operation is withdrawn by line **9** and a naphtha charge suitable for platinum reforming is withdrawn by line **11**. The gas oil charge in line **5** and selected to be processed in a catalytic cracking unit such as a fluid catalytic cracking unit is passed to a catalytic cracker **13**. Products of catalytic cracking such as obtained by fluid catalytic cracking are separated in suitable fractioning equipment not shown to permit the recovery of olefin products suitable for passage by line **15** to an alkylation unit represented by block **17**. Higher boiling catalytic product material is passed by line **19** to a splitter tower **21** wherein a separation is made between light catalytic gasoline withdrawn overhead by line **23** from heavy catalytic gasoline withdrawn from the bottom thereof by line **25**. In the arrangement of FIG. 2, the light catalytic gasoline obtained from the catalytic cracking operation is passed by line **23** to a regular gasoline pool represented by block **27**. In addition the product of alkylation is passed by line **29** to regular gasoline pool **27**. The heavy catalytic gasoline withdrawn by line **25** may be passed by line **31** to block **33** for effecting a shape selective cracking thereof or thermal upgrading to gasoline product. The material thus treated is passed by line **35** to regular gasoline pool **27**. In addition heavy catalytic gasoline instead of going through the steps of block **33** may be passed by line **37** to a pretreating step such as pretreater **39** for upgrading as discussed herein. The hydrocarbon charge in line **7** and suitable for processing by hydrocracking is passed to hydrocracker **41** wherein the charge is converted to products including light hydrocracking gasoline withdrawn by line **43** and heavy hydrocracked naphtha withdrawn by line **45**. The light hydrocracked gasoline product in line **43** is passed to hexane upgrading represented by block **47**. The hydrocarbon charge in line **9** and suitable for conversion by coking such as a delayed coker is passed to coker **49**. In the coking operation represented by block **49** the hydrocarbon charge is converted and a light coker gasoline is recoverd therefrom by line **51** with a high boiling product by line **53** which is suitable for further processing in a hydrocracker represented by **41**. The coker gasoline in line **51** is passed to pretreating step **39**. In the pretreting step **39** straight-run gasoline, coker gasoline, and heavy catalytic cracked gasoline, in combination with one another or separately, are treated under hydrogenation conditions to effect desulfurization and denitrogenation of the charge where required. The gasoline charge is thus pretreated by hydrogenation and may be combined with heavy naphtha product of hydrocracking obtained from **41** and thereafter the combined charge is passed by line **55** to a platinum reforming operation represented by block **57**. It is to be understood that the processing scheme of FIG. 1 may replace the processing arrangement represented by pretreater **39** and platinum reforming **57**. In any event the product of platinum reforming obtained in **57** is thereafter passed by line **59** to a separator **61** wherein separation is made between a light reformate product and a heavy reformate product. The light reformate product is withdrawn by line **63** and passed to hexane upgrading **47**. This, of course, is very much in the same manner but less detailed than that described in FIG. 1. The heavy reformate product depending upon the cut point of splitter **61** may be passed to either premium gasoline pool, regular gasoline pool or both in some cases. In one arrangement the heavy reformate product is passed by line **65** to regular gasoline pool **27** or by line **67** to premium gasoline pool **69**. In the arrangement of FIG. 2, block **71** and identified as a gas plant is concerned with the refinery operation which effects the recovery C_4 hydrocarbons from pentanes and light straight-run naphtha. The C_4's are withdrawn by line **73**, the pentanes by line **75** and the straight-run naphtha by line **77**. The arrangement of FIG. 2 shows isomerization of pentanes in block **79**, from which is recovered an isopentane material in line **81** for passage to premium and regular gasoline pools **69** and **27** respectively. The light straight-run naphtha in line **77** is passed to hexane upgrading **47** from which is recovered neohexane and aromatics by line **83** which may then be passed to either premium gasoline pool **69** or regular gasoline pool **27**. It is thus seen from the above brief description that the production of premium and regular gasoline in significant quantities whether on a clear or leaded basis requires considerable processing knowhow and refinery equipment for effecting catalytic upgrading steps, all of which are designed to upgrade particular constituents of the crude charged to the operation. It is also immediately clear from the discussion herein before presented that any improvement one might make in yield of desired product is of considerable benefit to the refiner, as well as the product user. However, this takes on an added importance when one is concerned with the preparation of regular and premium gasoline products free of lead. Therefore the processing concept of this invention is concerned with maximizing the yields of hydrocarbon constituents having an acceptable octane rating and the specific arrangements described and discussed represent one method for achieving this desired improvement.

TABLE 1.—PROPERTIES AND COMPOSITION OF NAPHTHA STREAMS

Fraction	Stream A, C_6–180° F., TBP mid-continent	Stream B, 180–380° F., TBP MCS
Yield, volume percent of crude	4.1	29.8
Gravity, ° API	72.5	56.4
Specific gravity	0.6936	0.7531
ASTM distillation, ° F.:		
IBP	142	205
Volume:		
5%	146	
10%	150	240
20%	152	
30%	154	260
40%	156	
50%	158	281
60%	160	
70%	162	308
80%	164	
90%	168	335
EP	192	364

C_6 plus PONA analysis	Percent at—			
	Volume	Weight	Volume	Weight
Paraffins	71.8	68.4	58.0	54.6
Naphthenes	25.8	28.6	32.3	33.9
Aromatics	2.4	3.0	9.7	11.5
Paraffins:				
C_5	2.7			
C_6	62.1			
C_7	6.9			
C_8	0.1			
Naphthenes:				
C_5	2.7			
C_6	18.7			
C_7	4.3			
C_8	0.1			
Aromatics:				
Benzene	2.3			
Toluene	0.1			

TABLE 2

[Yields and composition of C_6+ reformate from 150 p.s.i.g. Reforming of C_6–180° F. TBP Mid-continent naphtha at 98 C_5 plus R+3 ON severity]

	Percent at—	
	Volume	Weight
C_6+ yields (based on C_6–180° F. TBP S.R.)	65.8	71.0
Paraffins	36.3	34.9
Olefins	1.0	1.0
Naphthenes	0	0
Aromatics	28.5	35.1
C_6 paraffins	25.4	24.2
2–2 dimethylbutane		1.2
2–3 dimethylbutane		1.5
2 methylpentane		10.6
3 methylpentane		6.3
N-hexane		7.6
C_7 paraffins	10.9	10.7
2–2 dimethylpentane		0.4
2–3 dimethylpentane		0.5
3–3 dimethylpentane		1.2
2–3 dimethylpentane		0.4
2 methylhexane		2.4
3 methylhexane		3.3
3 ethylpentane		0.3
N-heptane		2.2
Total aromatics	28.5	35.1
Benzene	8.2	10.2
Toluene	20.3	24.9

TABLE 3

[Yields and composition of C_6 + reformate from 350 p.s.i.g. Reforming of 180–380° F. MCS naphtha at 102 C_5 + R+3 ON severity]

	Percent at—	
	Volume	Weight
C_6 + yields (based on 180–380° F. TBP MCS)	74.1	80.1
P	23.9	21.6
O	1.2	1.1
N	0.8	0.8
A	48.2	56.6
Paraffins C_6P	8.3	7.2
2-2 dimethylbutane		0.4
2-3 dimethylbutane		0.4
2 methylpentane		2.2
3 methylpentane		1.9
N-hexane		2.3
C_7P	7.8	7.1
2-2 dimethylpentane		0.2
2-4 dimethylpentane		0.3
3-3 dimethylpentane		0.8
2-3 dimethylpentane		0.3
2 methylhexane		1.6
3 methylhexane		2.2
3 ethylpentane		0.2
N-heptane		1.5
C_8P	5.1	4.7
2-2-4 trimethylpentane		0.05
2-2-3 trimethylpentane		0.05
2 methyl 3-ethylpentane		0.3
3 methyl 3-ethylpentane		0.05
2-2 dimethylhexane		0.05
2-3 dimethylhexane		0.2
2-4 dimethylhexane		0.4
2-5 dimethylhexane		0.2
3-4 dimethylhexane		0.2
2 methylheptane		0.8
3 methylheptane		0.9
4 methylheptane		0.4
3 ethylhexane		0.3
N-octane		0.8
C_9 + P	2.7	2.6
Benzene	1.5	1.8
Toluene	8.9	10.3
C_8A	16.3	18.8
Ethylbenzene		2.1
O-xylene		4.1
M-xylene		8.7
P-xy ene		3.9
C_9 + A	21.5	25.7

TABLE 4

Composition of C_6+reformate fractions split at 158° F. and 200° F. (C_6+reformate from 350 p.s.i.g. reforming of 180–380° F. TBP MCS naphtha at 102 C_5+ R+3 ON severity)]

	Split A		Split B	
Fraction	Stream C, C_6– 158° F.	Stream 26, 158° F.+	Stream C, C_6– 200° F.	Stream 26, 200° F.+
Yields, percent volume of C_6+ reformate	11.7	83.3	21.7	78.3
Compositions; component, percent volume:				
C_6 Paraffins	91.7		51.6	
2, 2 dimethylbutane	4.9		2.6	
2, 3 dimethylbutane	5.7		3.1	
2 methylpentane	30.4		16.2	
3 methylpentane	25.0		13.4	
N-hexane	25.7		16.3	
C_7 paraffins	0.0			
2, 2 dimethylpentane	0.0		1.8	
2, 3 dimethylpentane	0.0		5.4	
2, 4 dimethylpentane	0.0		2.2	
3, 3 dimethylpentane	0.0		1.7	
2 methylhexane	0.0		10.7	
3 methylhexane	0.0		9.8	
N-heptane	0.0		0.0	
Monoolefins	4.7		4.0	
Methylcyclopentane	1.9		1.0	
Naphthenes	0.0		2.4	
Benzene	1.7		9.3	
Total	100.0		100.0	
Paraffins		24.5		18.1
C_6		0.6		
C_7		11.9		4.7
C_8		7.8		8.8
C_9		4.1		4.7
Monoolefins		1.2		1.0
Naphthenes		1.0		0.4
Aromatics		73.4		80.5
Benzene		2.1		
Toluene		13.6		15.4
C_8		24.9		28.1
C_9+		32.7		37.0
Total		100.0		100.0
Properties:				
Specific gravity	0.6693	0.8371	0.6955	0.8514
RVP, lbs	6.1	1.1	5.1	0.8
Octane ratings:				
R+O	67.6	98.8	70.8	101.3
R+3 cc. TEL/USG	87.6	103.0	90.0	104.0

Having thus provided a general description of the method and process of this invention and defined a specific embodiment for practising the concept of the invention, it is understood that no undue restrictions are to be imposed by reason thereof except as defined in the appended claims.

I claim:

1. A method for upgrading gasoline product of coking, hydrocracking, catalytic cracking and straight run gasoline which comprises

(a) desulfurizing gasoline product obtained as by coking and straight run gasoline,

(b) separating a first C_6 rich hydrocarbon fraction from a higher boiling gasoline fraction following said desulfurizing step,

(c) reforming said higher boiling gasoline fraction to provide a reformate product of improved octane rating,

(d) separating and recovering from said reformate product a product fraction having an initial boiling point in the range of 150° to about 225° F. from a second C_6 rich hydrocarbon fraction,

(e) reforming said first C_6 rich hydrocarbon fraction and separating aromatics therefrom after combining with said second C_6 rich hydrocarbon fraction,

(f) hydrogenating the C_6 hydrocarbons fraction after separation of aromatics and C_7 hydrocarbons therefrom but before effecting isomerization thereof and

(g) combining product of said isomerization step having an octane rating in excess of 90 with said reformate product having an initial boiling point in the range of 150° F. up to about 225° F.

2. A method for upgrading straight run gasoline hydrocracked gasoline, coker and heavy gasoline product of catalytic cracking which comprises,

(a) separating and recovering from gasoline product of coking, catalytic and hydrocracked gasoline as well as straight run gasoline, a first C_6 rich hydrocarbon stream from a higher boiling gasoline fraction comprising C_7 hydrocarbons,

(b) desulfurizing said gasoline boiling range hydrocarbons before or after the above separation step,

(c) reforming said higher boiling hydrocarbon fraction,

(d) separating product of reforming to recover a second C_6 rich hydrocarbon stream from a higher boiling reformate having an initial boiling point in the range of 150 to about 225° F.,

(e) reforming said first C_6 rich hydrocarbon stream and stabilizing the product thereof,

(f) combining stabilized C_6 reformate product with the second C_6 rich hydrocarbon stream and removing aromatic and entrained C_7 hydrocarbon therefrom to provide a stream rich in normal hexane,

(g) isomerizing said normal hexane rich stream under conditions to produce isomers thereof having an octane rating above 90 on a clear basis and

(h) passing aromatic products of said reforming steps and products of said isomerizing steps to regular and premium gasoline products for blending with gasoline product of catalytic cracking, alkylation, and pentane isomerization.

3. A method for upgrading gasoline fractions boiling in the range of C_4 hydrocarbons up to about 380° F. which comprises

(a) stabilizing and desulfurizing said gasoline fraction so as to recover a first hydrocarbon stream rich in C_6 hydrocarbons from a second higher boiling hydrocarbon stream comprising C_7 hydrocarbons,

(b) separately reforming said first and second hydrocarbon streams with a platinum-type reforming catalyst, under conditions, to produce aromatic rich reformate streams,

(c) recovering reformate product having an initial boiling point in the range of 150 to 225° F. as one product of the process suitable for use in regular or premium grade gasoline,

(d) recovering C_6 rich hydrocarbon materials from said reforming operations and separating aromatics and C_7 hydrocarbons therefrom to provide a hexane rich stream,

(e) hydrogenating any aromatics remaining in said hexane rich stream,

(f) isomerizing the hydrogenated hexane rich stream and

(g) combining product of said isomerization step in said regular and premium gasoline pool.

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