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PRODUCTION OF MOTOR FUEL

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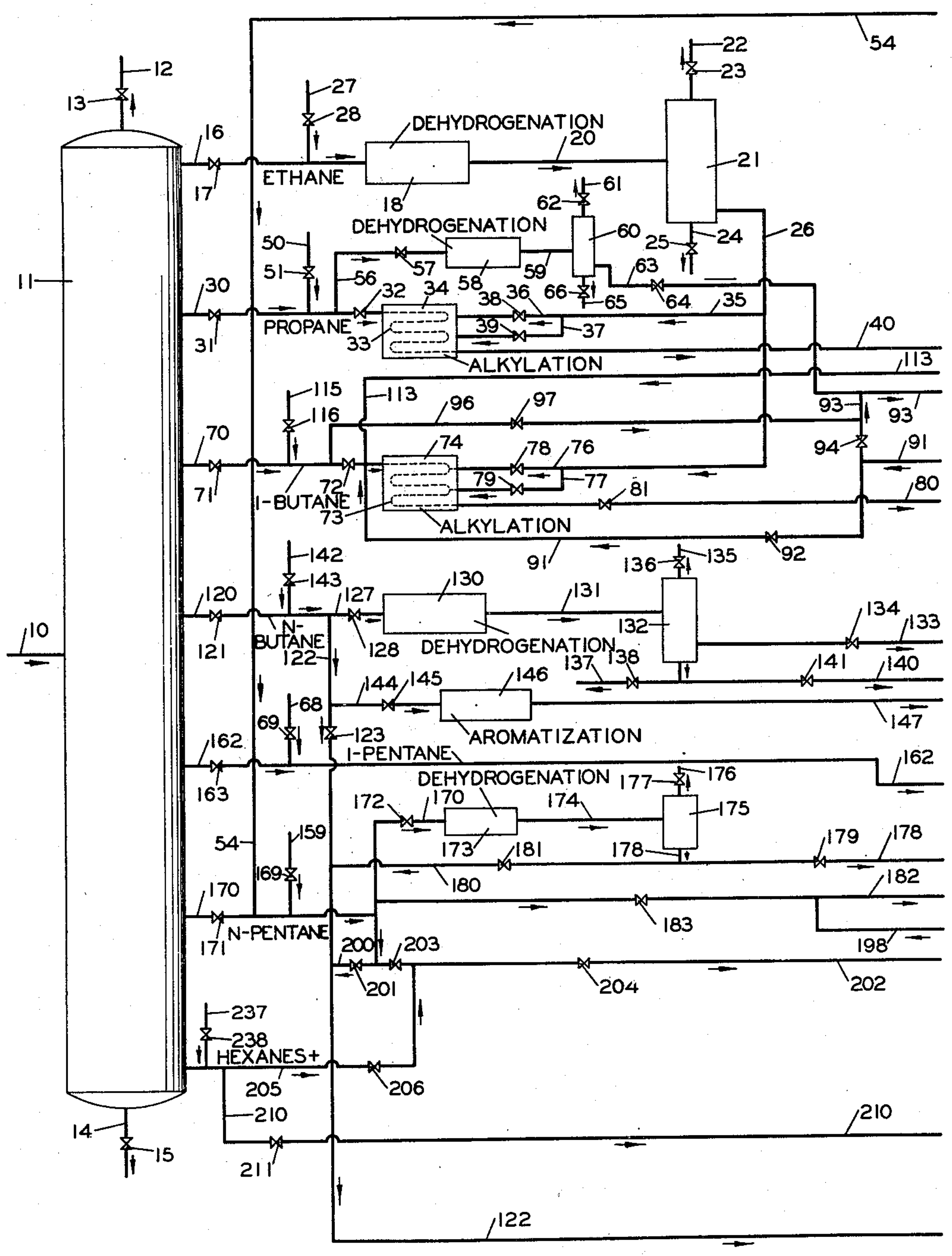

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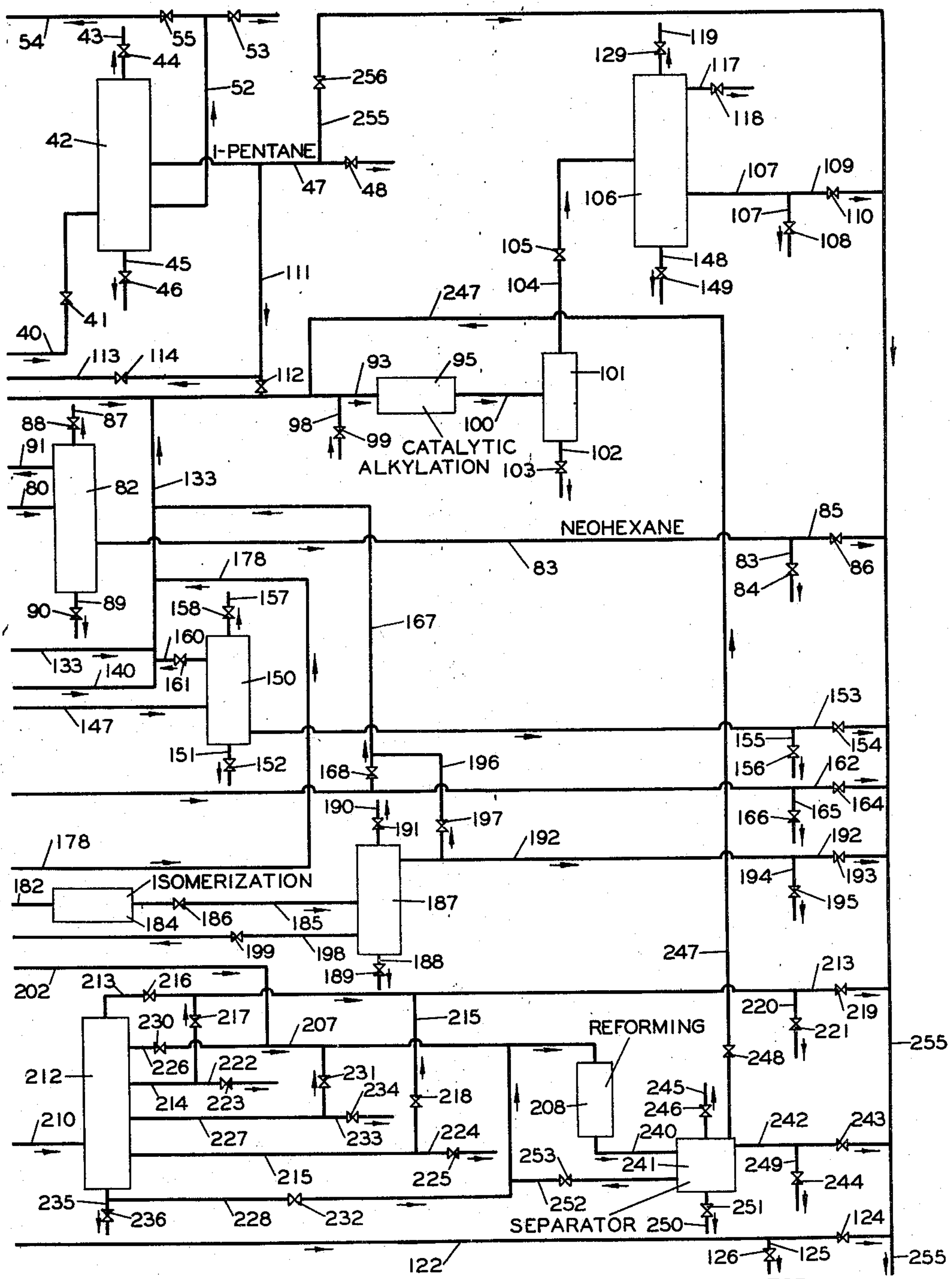

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2,376,077

PRODUCTION OF MOTOR FUEL

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Application March 14, 1941, Serial No. 383,430

9 Claims. (Cl. 260—683.4)

This invention relates to the production of hydrocarbon stocks in the motor fuel boiling range from lower boiling hydrocarbon material. It relates more particularly to the production of motor fuels having gasoline characteristics and premium qualities especially as to antidetonating values from hydrocarbons available in so-called wet natural gases. It relates still more particularly to the production of such motor fuels in high yields by the utilization of the major part of the C_2 and heavier hydrocarbons available in natural gas.

By far the outstanding trend in motor fuels in recent years has been the tendency toward increase in antidetonating characteristics as measured by increase in octane numbers. Automobile manufacturers have continuously designed their cars to make use of the increased efficiency and performance afforded by high octane gasolines, and refiners have attempted above all to produce motor fuels giving satisfactory performance in the new higher compression motors. In the earlier days of the petroleum industry natural gasoline, which is a product separated from naturally occurring normally gaseous mixtures, was in great demand among refiners because the vapor pressure and volatility afforded by blending natural gasoline with their products allowed them to cut deeper into the kerosine fractions of crude oil and thus produce higher yields of gasoline. Minimum volatility specifications were some of the most important specifications at that time, and the most difficult ones to meet. Moreover, with the recognition of the superior performance characteristics of volatile fuels, volatility became the most desired quality, and gasoline and natural gasoline as a blending stock appeared to be the only means to obtain this volatility.

The use of cracking processes for manufacturing gasoline was originally motivated by the desire for higher yields of gasoline and has more recently been stimulated by the demand for higher octane numbers. Likewise the more recent use of gas conversion processes has resulted in increased yields of motor fuel stocks with high octane numbers and has also resulted in the use of lighter hydrocarbon fractions available from natural sources which formerly were wasted. However, from the view point of the natural gasoline industries perhaps the most important effect of cracking and gas conversion processes was the production of more volatile motor fuel stocks in the refineries. As an example of these trends, in Mid-Continent gasolines, during the past 15 years Table I is presented, which shows clearly that while the volatility of motor fuels has been increasing for many years, this increase has been more than made up by volatile fractions produced at refineries, and there has resulted a decrease rather than an increase in the amount of natural gasoline used per gallon of finished gasoline product.

TABLE I

Estimated composition of motor fuel (per cent by volume)

	Constituent	Years					
		1925	1928	1931	1934	1937	1938
1	Refinery base (50% evaporated at 284° F.) (includes straight run and heavier cracked fractions)	90.5	85.0	77.8	67.2	66.2	66.1
2	Volatile refinery products (volatility characteristics based on 12 lb. natural) (includes vapor recovery and light cracked fractions)	Negligible	2.8	9.4	20.1	20.2	20.5
3	Natural gasoline (12 lb. vapor pressure)	6.2	7.1	7.4	7.0	7.1	6.9
4	Butane (natural and refinery)	3.3	5.1	5.4	5.7	6.5	6.5
		100.0	100.0	100.0	100.0	100.0	100.0

In addition to this, natural gasoline constitutes only a small proportion of the hydrocarbon material available in natural occurring normally gaseous hydrocarbon stocks such as natural gas. In Table II is shown in column 1 the composition of a natural gas which may be assumed to be typical.

TABLE II

Raw natural gasoline, 125° A. P. I.

Component	1 Natural gas, mol per cent	2 Liquid vol. per cent	3 Mol per cent	4 26–70 natural gasoline liquid, vol. per cent	5 Octane No.
Methane	87.0	2.2	3.1	------	------
Ethane	6.0	10.0	12.0	------	------
Propane	4.0	37.0	40.3	------	------
Isobutane	1.7	7.9	7.2	33	91
N-butane		24.0	22.8		
Isopentane	1.3	5.5	4.6	17	90
N-pentane		4.9	4.2	17	61
Isohexanes		3.3	2.5	33	55
N-hexane		2.2	1.6		
Heptanes and heavier.		3.0	1.7		
	100.0	100.0	100.0	100	

A very large proportion of this natural gas is methane which as yet is still practically unavailable for conversion in the motor fuel stocks. Only about 3 mol per cent of this natural gas comprises C_4 and heavier hydrocarbons, which are normally included in natural gasolines, and although there is a large proportion of natural gas which is methane, there is roughly three times as much ethane and propane as material available directly for natural gasoline. Processes are now available which without undue expense can extract substantially all of the C_2 and heavier hydrocarbons from such natural gas. Columns 2 and 3 respectively of Table II show the composition of the product which can be extracted from this natural gas in commercial quantities without undue expense. It will be noted that although this product contains only a small portion of the available ethane, nevertheless on a liquid volume basis not more than about 30% comprises those constituents which make up natural gasoline, since ordinarily only about one-half or less of the butanes are included to form a 26–70 natural gasoline. The approximate composition of a natural gasoline blending stock known to the trade as 26–70 natural gasoline is shown in column 4, together with the octane number of the principle fractions which are shown in column 5.

The lightest third of 26–70 natural gasoline is butane hydrocarbons whose vapor pressure makes it unsuitable for blending directly into motor fuel in any large proportion. Because of the limitations to its use as a blending stock large quantities of butane are now being processed in polymerization operations or are being marketed as such in a variety of fuel applications. Half of the remainder of natural gasoline consists of pentanes which are hydrocarbons of intermediate vapor pressure but which have a high volatility so that these materials can not be used in large percentages in blending with many other motor fuel stocks because of their effect in increase in the volatility of the final gasoline product as indicated by the percentage evaporated at 212° F.

The other half of butane-free natural gasoline is a low vapor pressure hexane and heavier fraction. About ten years ago this fraction had an octane number which compared favorably with the average octane number of motor fuels of that time. However, at present the average octane number of most of the gasolines on the market is around 75 or even higher and as a result the low octane number of this portion of natural gasoline places it in the same class as low end point straight run gasoline.

It is, therefore, readily seen that in order to utilize natural occurring low boiling hydrocarbons to the maximum advantage it is necessary to increase the octane number of fractions of low volatility which are directly available as well as to convert hydrocarbons of 2–5 carbon atoms per molecule into hydrocarbon fractions which have high octane numbers and which are not highly volatile.

We have now invented a process which produces high yields of motor fuel stocks having gasoline characteristics, or suitable for blending stocks to produce such gasolines, which utilizes to a high degree of efficiency substantially all of the C_2 and heavier hydrocarbons which can be obtained from natural gas, or similar hydrocarbon sources, by a combination of process steps which not only cooperate to produce products which may be successfully blended together, but which are also so cooperatively combined that byproduct fractions from one process step are efficiently utilized in other process steps along with hydrocarbon fractions primarily charged to such other process steps.

It is an object of our invention to produce a motor fuel stock of high value from lower boiling hydrocarbons.

Another object of our invention is to utilize the ethane and heavier constituents of natural gas to maximum advantage in the production of motor fuel.

A further object of our invention is to establish a process for treating naturally occurring gaseous and liquid hydrocarbons to produce a composite blended motor fuel with well balanced characteristics.

Another object of our invention is to produce from any mixture or mixtures of normally gaseous hydrocarbons of limited methane content a motor fuel having high antiknock qualities, and to produce such a motor fuel in a particularly high yield with reference to the hydrocarbons treated and/or available.

Still another object is to separate from a natural gas substantially all of the C_2 and heavier hydrocarbon content therein and to produce therefrom a normally liquid motor fuel whose volatility, saturate content, and aromaticity may be varied at will.

Still another object of our invention is to establish a process in which separate constituents of a hydrocarbon mixture extracted from a wet natural gas are subjected to various conversion steps to produce motor fuel stocks which can be blended together to produce a composite motor fuel of gasoline characteristics, the said conversion steps cooperating among themselves to effect the conversions in an optimum manner with high yields.

Other objects and advantages of our invention will become apparent from the accompanying description and disclosure.

In the present specification and claims by motor fuel of gasoline characteristics is meant a hydrocarbon mixture, which may or may not contain small amounts of added chemicals such as antidetonants and gum inhibitors and the like, which will meet any set of the various specifications recognized in the trade for gasoline. As an example of such specifications the following Table III is quoted from the Bureau of Mines Report of Investigations 3492. These, however, are not necessarily to be considered limiting as to any particular characteristic or group of characteristics. In addition to the characteristics shown, it is assumed that all the gasolines are sweet and contain inhibitors to prevent excessive gum formation where necessary, and meet any other qualifications usual to the trade.

TABLE III

Motor gasoline survey (ranges of 90% of fuels tested)

	Regular price gasolines		Premium price gasolines	
	Summer 1936	Winter 1938–39	Summer 1936	Winter 1938–39
Gravity...° API..	56.8–62.0	59.1–66.6	56.9–65.6	59.3–66.9
Sulfur...per cent..	0.023–0.20	0.026–0.24	0.019–0.087	0.021–0.087
Reid vapor pressure....pounds..	6.0–9.1	8.4–12.1	5.2–8.8	7.5–11.7
ASTM octane No.	68.0–71.0	69.4–72.5	74.0–81.0	75.9–81.3
Initial B. P........	94–114	83–97	95–118	85–103
10% recovered.....	135–161	114–141	133–164	118–147
20%...............	160–192	133–174	159–188	138–175
30%...............	180–218	154–201	176–214	158–199
50%...............	229–264	209–255	206–257	203–246
70%...............	273–310	264–304	239–306	236–293
90%...............	335–371	336–371	286–365	289–363
End point.........	383–419	386–415	349–417	360–413
Distillation loss....	1.0–2.5	1.3–3.4	0.8–2.3	1.0–3.2

Reference will now be made to the drawing which forms a part of the specification and which diagrammatically illustrates by way of a flow sheet an arrangement of apparatus in which our invention, together with various modifications thereof, may be practiced. In the description of this drawing the various process steps will be described in connection with optimum conditions for their operation, which will serve as examples thereof.

Referring now to the drawing, a suitable hydrocarbon mixture, such as the natural gas whose composition was given in Table II or such as the raw natural gasoline separated therefrom whose composition is also given in this table, is charged to a suitable separating apparatus 11 through pipe 10. The separating or fractionating apparatus 11 is diagrammatically illustrated as a fractionating column. It will be appreciated, however, that in actual practice if fractional distillation means only are used, such a separation as is to be hereinafter described will ordinarily require a series of fractionating columns together with normally occurring attendant auxiliary apparatus, and that in many cases it will be desirable to conduct at least one or more of the separations by means of absorbents such as are well known to the art. Extremely light constituents such as methane and inert gases may be removed through a pipe 12 controlled by a valve 13. It is not primarily an object of this invention to treat hydrocarbons which boil substantially above the end point of gasoline, that is above about 400 to 450° F., and any such heavy hydrocarbons which may be present in the material charged through the pipe 10 may be removed from the process through pipe 14 controlled by valve 15.

The separating means 11 is operated so as to effect a separation from the material charged through pipe 10 or fractions having substantially the following compositions. Each fraction may have associated with it minor amounts of hydrocarbons of adjacent boiling range, but such other hydrocarbons should not be present in quantities so large that the fraction can not be satisfactorily identified as shown. In some instances an individual fraction may comprise the indicated hydrocarbon in a purity of about 95 per cent or more.

A. Ethane
B. Propane
C. Isobutane
D. Normal butane
E. Isopentane
F. Normal pentane
G. Hexanes and heavier (in the gasoline range)

In one modification of our invention this "hexanes and heavier" fraction is further subdivided into two or more fractions varying primarily as to octane numbers. This separation may be effected if desired in separating means 11 but will subsequently be described in more detail in connection with a separate separating means 212.

An ethane fraction is removed from separating means 11 through a pipe 16 and a valve 17 and subjected to dehydrogenation in a suitable dehydrogenation unit 18. Although ethane may be dehydrogenated in the presence of any one of a large number of known dehydrogenation catalysts, it is very satisfactorily dehydrogenated in the absence of catalysts by being heated to a high temperature at a low pressure. Such conditions for such a thermal dehydrogenation are a temperature between about 1200 and 1500° F. and a pressure not substantially in excess of 100 pounds per square inch, preferably about 5–30 pounds per square inch gauge, for a period of time such as to effect a content of about 10 or 15 to 40 or 45 per cent unsaturates in the effluent gases. This dehydrogenation is readily accomplished by passing the ethane fraction through a suitable tube coil in a furnace. The dehydrogenation effluent is passed through pipe 20 to separating means 21 wherein a normally gaseous unsaturated hydrocarbon fraction, which will be predominantly ethylene, is separated from other constituents. Light gases comprising primarily methane and hydrogen are removed from the process through a pipe 22 and controlled by valve 23. Undesirably heavy hydrocarbons are removed from the process through a pipe 24 controlled by valve 25. The separating means 21 will generally be so operated that the ethylene fraction will also generally contain unsaturated C_3 hydrocarbons and may also contain unsaturated C_4 hydrocarbons when their presence is not deleterious in the subsequent reaction steps, as well as corresponding paraffins. Such an ethylene fraction is removed through a pipe 26 for subsequent reaction with heavier hydrocarbon fractions as will be hereinafter discussed. A suitable ethane fraction from an outside source, or separated from other process steps of our invention, may be introduced through pipe 27 and valve 28 to pipe 16.

In many methods of operation it will be found desirable to include a substantial part of the propane present in the material charged through pipe 10 in the ethane fraction for conversion into ethylene and propylene, so that the fraction will be better termed an "ethane-propane" fraction. In most instances, however, it will be desirable to separate at least a substantial portion of the propane fraction for separate treatment. In these cases a propane fraction is removed from the separating means 11 through pipe 30 and valve 31 and is passed through valve 32 to a reaction zone illustrated by reaction coil 33, situated in a suitable furnace or the like 34, wherein the propane is reacted under alkylation conditions with ethylene, produced in the step just described, which is passed from pipe 26 through a pipe 35 and is introduced to the reaction mixture and reaction zone 33, preferably at a plurality of points, such as are represented by pipes 36 and 37 controlled by valves **38** and **39** respectively. This alkylation reaction is preferably noncatalytic and carried out at pressures between about 1,000 and 10,000 pounds per square inch, and at temperatures between about 800 and 1200° F. under conditions whereby joint reaction or union of paraffins and olefins is favored to produce higher molecular weight, predominantly saturated hydrocarbon products, although at times catalysts may be used. A suitable reaction time will generally be found between about 1 and 15 minutes and the temperature, pressure and reaction time should be so controlled that appreciable conversion of propane by itself would ordinarily not take place. The unsaturates are so introduced that their concentration at any one point will not exceed about 10 per cent by weight, and in many instances will not be in excess of about 1 or 2 per cent by weight. The effluent of this alkylation step is passed through a pipe **40** and a valve **41** to a suitable separation means **42**. The products of the reaction will be primarily C_5 to C_8 hydrocarbons, isopentane being the predominant single hydrocarbon. An isopentane fraction is removed from separating means **42** through a pipe **47**, and may be discharged from the system for any desired use through a valve **48** or may be passed from pipe **47** through pipe **111**, for further use within the process as will be described, and/or through pipe **255** for blending with other products. Light hydrocarbons may be removed from the process and from separating means **42** through a pipe **43** controlled by a valve **44**. This fraction will generally comprise the larger part of the unreacted propane and lighter hydrocarbons which may be separated and returned to the system either directly to separating means **11** as through pipe **10**, or may be mixed directly with the corresponding fraction or fractions removed through pipe **30** by being added thereto through pipe **50** and valve **51** for propane, or through pipe **27** for ethane. A normal pentane fraction, which may contain heavier hydrocarbons in the gasoline range, may be removed from separating means **42** through a pipe **52** and may be discharged from the process through valve **53**, or may be passed through pipe **54** and valve **55** for subsequent use in the process as will be hereinafter described. Heavier hydrocarbons may be removed from separator **42** and from the process through pipe **45** controlled by valve **46**.

In many cases at least a portion of the propane fraction may be subjected to more or less nondestructive dehydrogenation to form propylene for subsequent reaction in a catalytic alkylation step to be described. In such a case a suitable portion of the propane fraction may be removed from pipe **30** through a pipe **56** and valve **57** to a dehydrogenation unit **58**. The dehydrogenation in unit **58** may be carried out noncatalytically, but in most cases it will be preferable to conduct a more or less clean-cut dehydrogenation to propylene with a minimum production of ethylene, and this is best accomplished by use of a suitable dehydrogenation catalyst such as chromium oxide, alone or in admixture with other oxides such as are known to the art. The dehydrogenation temperatures should generally be between 900 and 1300° F. preferably about 950 to 1200° F., and pressure should not be in excess of 100 pounds per square inch, and will preferably be between 5 and 30 pounds per square inch gauge. The reaction time should be such that about 15 to 30 or 40 per cent of the effluent is unsaturated hydrocarbon material. The effluent of the dehydrogenation unit **58** is passed through the pipe **59** to the separating means **60**. When desired light materials, which will be primarily hydrogen together with some methane, may be removed from separating means **60** and from the process through pipe **61** controlled by valve **62**. A hydrocarbon fraction containing the desired unsaturated hydrocarbons are removed through pipe **63** and valve **64** for subsequent use as will be hereinafter described. Heavier hydrocarbons present may be removed through a pipe **65** and a valve **66**.

An isobutane fraction is removed from separator means **11** through a pipe **70** and valve **71** and may be passed through valve **72** to a suitable alkylation unit such as is represented by reaction coil **73** located in a furnace or other suitable heating means **74**. Unsaturated C_2 and/or C_3 hydrocarbons produced in dehydrogenation unit **18** may be passed to the alkylation unit **73** from pipe **26**, and are preferably introduced to the reaction mixture in the reaction zone **73** at a plurality of points, such as are represented by pipes **76** and **77** controlled by valves **78** and **79** respectively. The reaction in coil **73** is preferably conducted under conditions substantially the same as has been discussed in connection with the alkylation of propane with a similar unsaturated material in reaction coil **33**. When the unsaturated hydrocarbon material passed through pipe **26** is primarily ethylene, the principal product produced by the alkylation in coil **73** under these conditions will be hexanes, heptanes and octanes, of which the predominant constituent will be neohexane. The effluent of the reaction coil **73** is passed through a pipe **80** and valve **81** to separating means **82**. A suitable alkylate fraction, which may under suitable conditions be substantially pure neohexane, is removed from separating means **82** through a pipe **83** and may be discharged from the process through valve **84** or part or all of the fraction may be passed through pipe **85** and valve **86** to pipe **255** for blending with other products, as will be described. Undesirably light material will be removed from separating means **82** through pipe **87** controlled by valve **88** and undesirably heavy material may be removed through **89** controlled by valve **90**. An unreacted C_4 hydrocarbon fraction is removed from separating means **82** through a pipe **91** and may be passed entirely or in part back to pipe **70** through valve **92**. This hydrocarbon fraction will contain an appreciable although small amount of unsaturated hydrocarbons, and since it also has a very high proportion of isobutane it will serve as an excellent charge stock for catalytic alkylation with other low boiling unsaturated hydrocarbons. To accomplish this a part or all of the material passing through pipe **91** may be removed through pipe **93** controlled by a valve **94** and passed to a catalytic alkylation unit **95**. In many instances a substantial portion of the isobutane may be passed directly from pipe **70** through pipe **96** and valve **97** to pipe **93** and this catalytic alkylation step.

The proylene fraction produced by dehydrogenation in unit **58** serves as an excellent source of unsaturated material for this catalytic alkylation and may be introduced into pipe **93** from pipe **63** for this reaction. In alkylation unit **95** the hydrocarbons brought thereinto by pipe **93** are treated in the presence of a suitable alkylation calatlyst to form isoparaffins predominantly of 7 and 8 carbon atoms per molecule, which have high octane numbers and low volatility and are therefore desirable ingredients for the gasoline product of our invention. The alkylation process preferably uses a catalyst such as an aluminum halide catalyst, especially aluminum chloride or bromide or any one of numerous metal halo-aluminates known to the art such as sodium chloro-aluminate, or zinc chloride or bromide, boron fluoride or zirconium tetrachloride or the like, or concentrated sulfuric acid, or concentrated hydrofluoric acid.

If a catalytic alkylation process involving a liquid or a mobile catalyst is used, the catalyst may be fed to the system through pipe **98** controlled by valve **99**. In such a process it is advantageous to use sulfuric acid or hydrofluoric acid as the catalyst, since these catalysts appear to be more selective than some of the other alkylation catalysts for the alkylation of isoparaffins, and cause a minimum of side reactions. To minimize concurrent polymerization reactions the mixture of hydrocarbons in the catalyst should be intimately contacted, and the concentration of unsaturated hydrocarbons in any one portion of the mixture preferably should be kept low relative to the concentration of isoparaffins, as may be effected by multipoint addition of olefins to a reacting stream, recirculation of a portion of the reactants in a closed cycle, and the like. In most instances a suitable reaction temperature will be found between about 0 and 125° F., generally between about 30 and 70° F., although higher or lower temperatures may be used, as may be found most suitable for the catalyst used. The hydrocarbon effluent is passed through a pipe **100** to a separator **101** wherein heavy, hydrocarbon-immiscible material is separated from the hydrocarbons and removed through a pipe **102** controlled by valve **103**. When sulfuric acid or hydrofluoric acid is used as the alkylation catalyst, a substantial portion of this material may often be passed directly from pipe **102** to pipe **98** for re-use in the process. A hydrocarbon effluent of the catalytic alkylation is passed from separator **101** through a pipe **104** controlled by a valve **105** to a separating means **106**. An alkylate product is removed from separating means **106** through a pipe **107**, and may be discharged from the process through valve **108** but in most cases this product will be passed from pipe **107** through pipe **109** controlled by a valve **110** to pipe **255** for blending with other hydrocarbon fractions produced from other steps of the process to give a finished gasoline product.

Any undesirable low boiling material which is present in the effluent of the catalytic alkylation step may be removed from separator **106** and from the process through pipe **119** controlled by valve **129**, and intermediate fraction such as propane and/or butane may be removed from separating means **106** through pipe **117** controlled by valve **118**, and may be returned to the process in the most suitable manner. Heavy hydrocarbons may be removed through pipe **148** controlled by valve **149**.

The isopentane fraction separated from separating means **42** through pipe **47**, having been produced by thermal alkylation, will often contain a small but appreciable amount of unsaturated hydrocarbons especially if this fraction is so separated that it contains a substantial portion of the C_4 hydrocarbons produced in the process. For instance, such a fraction recovered from an alkylation of propane with ethylene had substantially the following composition.

Component	Mol per cent
Butenes	15.2
Butane	9.7
Pentenes	3.4
Isopentane	71.7
	100.0

At least a part of this material may well make a suitable charge stock for the catalytic alkylation process just described, and its use will tend to produce an alkylate product of high octane number and still lower volatility. To this end a suitable portion of this isopentane fraction may be removed from pipe **47** through pipe **111** controlled by a valve **112**, which passes directly to pipe **93**. In some cases it may be desirable to submit a portion of this material to alkylation in the unit **73**, and if such is the case a portion thereof may be passed from pipe **111** through pipe **113** controlled by a valve **114** passing to pipe **70**. Isobutane or isopentane from any desirable outside source, or separated from any of the streams discharged from this process, may be introduced to pipe **70** through pipe **115** controlled by valve **116**.

A normal butane fraction is removed from separating means **11** through pipe **120** controlled by a valve **121**. This normal butane fraction may be treated in any one or more of several manners about to be described, or a portion thereof may be included directly in a final blended gasoline product. When a portion is to be blended with the gasoline directly, it may be passed from pipe **120** through pipe **122** and valves **123** and **124** to pipe **255**, or if desired the portion thereof may be removed from the system through a pipe **125** controlled by a valve **126**. Normal butane may be advantageously dehydrogenated to form normal butenes which can then be reacted by alkylation with low boiling isoparaffins such as isobutane and isopentane. To this end a suitable portion of the normal butane fraction is passed from pipe **120** through pipe **127**, valve **128** to the dehydrogenation unit **130**. Although this normal butane fraction may be dehydrogenated in the absence of a catalyst, this method of dehydrogenation is generally not very satisfactory because of the extensive decomposition into C_2 and C_3 hydrocarbons which takes place under conditions necessary to effect noncatalytic dehydrogenation. Therefore, the dehydrogenation carried out in unit **130** is preferably a catalytic operation, more or less as has been discussed for the catalytic dehydrogenation of the propane fraction in the dehydrogenation unit **58**. The optimum temperature for the dehydrogenation of normal butane is somewhat lower than that for the dehydrogenation of propane and will generally be found within the range of 850 to 1150° F. preferably between about 900 and 1050° F. The dehydrogenation pressure should again not be in excess of about 100 pounds per square inch, and preferably is between about 5 and 30 pounds per square inch gauge, with a reaction time such that the effluent contains between about 10 and 35 or 40 per cent of unsaturates and generally between about 15 and 25 per cent of unsaturates. Any suitable dehydrogenation catalyst known to the art may be used although we prefer to utilize a catalyst comprising chromium oxide. The dehydrogenation effluent is passed from unit **130** through pipe **131** to suitable separating means

132. A C_4 fraction containing butenes produced by the dehydrogenation, and which may also contain other hydrocarbons such as propylene and/or pentenes which have also been formed in small amounts in the dehydrogenation, is removed from separating means 132 through a pipe 133 and valve 134 and is introduced to the catalytic alkylation unit 95 by being passed to pipe 93. Undesired low boiling material produced by the dehydrogenation is removed from separating means 132 through a pipe 135 controlled by a valve 136. Any heavier hydrocarbons produced as by-products of the process may be removed therefrom through pipe 137 controlled by valve 138. In some cases a portion of these high boiling materials may be advantageously included in the charge to the catalytic alkylation step and in such a case may be passed from pipe 137 through pipe 140 controlled by valve 141 to pipe 133, or may be removed as a separate fraction from separating means 132.

Normal butane can be converted inexpensively and with quite satisfactory yields into aromatic hydrocarbons by being subjected to high temperatures and low pressures, and the aromatic hydrocarbons so produced will form valuable constituents of premium motor fuels. If it is desired to produce such aromatics, a portion of the normal butane fraction may be passed from pipe 120 through pipe 122 and pipe 144 controlled by a valve 145 to an aromatization unit 146. In this unit the normal butane fraction is converted at a relatively high temperature of the order of 1300–2000° F., more preferably 1400–1750° F., at a low pressure, not substantially in excess of about 200 pounds per square inch, for a reaction time of about 0.01–0.5 second in the absence of catalysts to produce a satisfactory yield of aromatic hydrocarbons. Catalysts such as are known to the art may be used, but satisfactory operation may be obtained in the absence of catalysts. The reaction effluents are passed through pipe 147 to separating means 150. Undesirably heavy hydrocarbon material and tar may be removed through a pipe 151 controlled by a valve 152 and discharged from the system. A desirable aromatic fraction in the gasoline boiling range may be removed through a pipe 153 and passed through a valve 154 to pipe 255 for blending into a final motor fuel product as will be described. If it is desired to separate any portion of this aromatic stream, for the preparation of aromatic products, such a portion may be separated from pipe 153 through pipe 155 controlled by a valve 156. Any undesirable light material may be removed from separating means 150 through a pipe 157 controlled by valve 158. If it is desired to recycle a normal butane fraction from the effluent of the aromatization unit it may be included in material separated through pipe 157, and after subsequent purification may be reintroduced into the system as through pipe 142, controlled by valve 143, or more directly to the aromatization unit by means not shown. Inasmuch as the C_4 fraction will contain an appreciable portion of unsaturated hydrocarbons suitable for use in the catalytic alkylation step such a fraction may be removed from separating means 150 through pipe 160 controlled by a valve 161 and passed to pipe 133 for reaction as has been described.

In most instances the isopentane separated from the material charged through pipe 10 to the process is suitable, without further conversion, as a blending stock. It is also an excellent reactant for the catalytic alkylation unit 95 and any desired portion may be treated in this manner. An isopentane fraction may be removed from separating means 11 through pipe 162 controlled by a valve 163 and may be passed through valve 164 directly to pipe 255 for blending with the finished product of the process. If desired a portion may be discarded from the process through pipe 165 controlled by a valve 166. Any portion desired for the catalytic alkylation may be passed from pipe 162 through pipe 167 controlled by a valve 168 to pipe 133. In some instances it may be desirable that the catalytic alkylation be conducted with isopentane as the low boiling isoparaffinic reactant, in which case, the material passing through pipe 167 will constitute the principal isoparaffinic charge to this step. Isopentane from an outside source may be added to the system, if desired through pipe 68 controlled by valve 69 to pipe 162.

Normal pentane, although it does not have as high an octane number as isopentane, may also at times be included directly in the finished gasoline without subsequent treatment. However, on account of its low octane number we generally prefer to subject it to an operation which will make it more desirable for use as a gasoline blending stock. Such treatment may be either dehydrogenation, producing pentenes which may be blended directly into the gasoline or which may serve as reactants for the catalytic alkylation, or the normal pentane may be subjected to an isomerization or reforming, either by itself or in combination with other higher boiling hydrocarbons of low octane number as will be subsequently described. A normal pentane fraction is removed from separating means 11 through pipe 170 controlled by valve 171. A portion thereof may be passed through a valve 172 to a dehydrogenation unit 173, which should be operated under substantially the same operating conditions just described for the dehydrogenation unit 130 in which normal butane is dehydrogenated. The effluent of dehydrogenation unit 173 is passed through a pipe 174 to suitable separating means 175. Undesirable low boiling material which will be primarily hydrogen and methane may be discharged through a pipe 176 controlled by a valve 177. A pentene fraction produced by the dehydrogenation may be removed through pipe 178 and passed directly to the catalytic alkylation unit 95 through valve 179 into pipe 133. If it is desired to blend any portion of this normal pentene fraction directly with the gasoline it may be passed from pipe 178 through pipe 180 controlled by a valve 181 to pipe 122 and on to pipe 255.

In some instances it may be desirable to isomerize the normal pentane fraction to produce isoparaffins such as isopentane and/or isobutane, which may be recovered as such for blending with the final gasoline product, or which may be passed to the catalytic alkylation unit 95. To this end any desirable portion of the normal pentane fraction may be passed from pipe 170 through a pipe 182 controlled by a valve 183 to isomerization unit 184. The isomerization may be conducted by any suitable conditions known to the art and is preferably conducted at a temperature between about 0 and 400° F. and a pressure sufficient to maintain the hydrocarbon material in liquid phase and in the presence of an isomerization catalyst such as aluminum chloride or aluminum bromide. The isomerization effluent is passed through a pipe 185 controlled by a valve 186 to suitable separation means 187. Heavy material, which may include a sludge which contains an isomerization catalyst if the isomerization unit in 184 is operated under conditions such as to produce such a material, may be removed through pipe 188 controlled by valve 189. Any undesirable low boiling material may be removed through a pipe 190 controlled by a valve 191. A suitable isoparaffin fraction produced by the isomerization is removed through a pipe 192 and may be passed through valve 193 to pipe 255 for blending in the finished gasoline product, or any desired portion thereof may be discharged from the system through pipe 194 controlled by valve 195. This isoparaffin fraction will contain material which is highly desirable, as discussed, for charge to the catalytic alkylation unit 95 and any portion desired for such reaction may be passed from pipe 192 through pipe 196 controlled by a valve 197. A normal paraffin fraction may be separated from means 187 and returned to isomerization unit 184 through pipe 198 controlled by valve 199. Normal pentane from a separate source for treatment within the process may be introduced to pipe 170 through pipe 159 and valve 169. Material so introduced may include recycled material from one or more of the conversion steps.

In some instances it may be desired to blend a portion of the normal pentane fraction directly in the finished gasoline product, in which case it may be passed from pipe 170 through pipe 200 controlled by a valve 201 to pipe 122. In case it is desired to subject a portion of the normal pentane fraction to isomerization or reforming in conjunction with other fractions of low octane number, a portion suitable for this may be passed from pipe 200 through pipe 202 controlled by valves 203 and 204 to pipe 207 passing to the reforming unit 208, to be described.

In many instances it will be found desirable to subject the hexanes and heavier fraction to a reforming operation to improve its octane number. When this fraction is shown by analysis, as by careful fractional separation and testing of individual fractions, to be comprised predominantly of hydrocarbons of low octane numbers, the entire fraction may be subjected to reforming by being passed from separating means 11 through a pipe 205 controlled by valve 206 to pipe 202 and through valve 204 to pipe 207 and reforming unit 208. In those cases where it is not necessary to reform this hexanes and heavier fraction, or at least not to treat all of it in this manner, it may be passed from pipe 205 to pipe 202 and through valve 203 to pipe 200, and through valve 201 to pipes 122, and 255 for blending directly in the final product. However, in many instances it will be found by suitable analysis that the hexanes and the heavier fraction will contain substantial portions of hydrocarbons of low octane number and substantial portions of hydrocarbons of high octane number, and that such portions may be advantageously separated from each other and only the fractions of low octane number subjected to a reforming operation. In such a case the hexanes and heavier fraction may be passed from pipe 205 through a pipe 210 controlled by a valve 211 to a suitable separating means illustrated by a fractionating column 212. From the separating means 212 there may be separated one or more fractions of low octane number and one or more fractions of high octane number. While the separating means 212 is shown as a fractionating column, it is to be understood that any suitable known method of carrying out the separation desired for any particular hexanes and heavier fraction may be practiced, and in fact, many of the fractions may be more preferably separated by means of selective solvents which will separate aromatic or naphthenic hydrocarbons from paraffinic hydrocarbons. Such selective solvent extraction methods may, of course, be operated in combination with suitable fractional distillation units to effect the desired separations, as will be readily understood, and applied, by one skilled in the art. Material in the hexanes and heavier range from an outside source may be added, as desired, to the process through pipe 237 controlled by valve 238 to pipe 205.

In the present process fractions of high octane number are shown as being separated, from the material charged through pipe 210, by means of pipes 213, 214 and 215 controlled by valves 216, 217 and 218 respectively. Such fractions will comprise highly branched paraffin hydrocarbons, aromatic hydrocarbons, some of the lower boiling naphthenes, and/or the like. The fractions from pipes 214 and 215 may be blended with the fraction in pipe 213 and passed through valve 219 to pipe 255 for subsequent blending in a finished gasoline product, or may be discharged from the system through pipe 220 controlled by a valve 221. Selected fractions may be removed from the process as from pipe 214 through pipe 222 controlled by a valve 223, and from pipe 215 through pipe 224 controlled by a valve 225. Fractions of low octane number, primarily more or less straight-chain paraffins, may be removed from the material passing through pipe 210 through pipes 226, 227 and 228 controlled by valves 230, 231 and 232 respectively. These fractions of low octane number may be blended together by being passed to pipe 207 and are subjected to a reforming in unit 208. Selected fractions for any suitable use may be removed from one or more of these streams as by being passed from pipe 227 through pipe 233 controlled by a valve 234, or from pipe 228 through pipe 235 controlled by a valve 236.

The material of low octane number passed through pipe 207 to reforming unit 208 may be treated in any suitable manner to improve its octane number. This treatment may be carried out as an isomerization treatment under conditions similar to those described for the isomerization unit 184 or may be carried out by any suitable thermal reforming treatment at elevated temperatures and pressures.

However, we prefer to improve the octane number of this material by treating it in the presence of a catalyst under conditions such that there is a minimum of production of normally gaseous material or a minimum change in the boiling range characteristics of the material treated. Such a catalytic reforming may be carried out by passing the hydrocarbon stock over a suitable solid granular catalyst such as bauxite or other mineral materials, either alone or impregnated with suitable materials such as chromium oxide. For these operations the temperatures should be in the range of about 750 to 1100° F. preferably in the range of about 900–1050° F. under a pressure not substantially in excess of about 150 pounds per square inch, preferably within the range of 5–30 pounds per gauge, and at a flow rate of about 0.5 to 5 liquid volumes of hydrocarbons charged per volume of space occupied by the granular catalyst per hour. Under these conditions dehydrogenation and isomerization reactions take place with a minimum formation of light gases other than hydrogen. Free hydrogen may or may not be added to the charge to such a treatment as by being introduced to pipe 207 by means not shown, as may be found desirable. Of the hydrocarbon gases produced the major portion is C_3 and C_4 unsaturated hydrocarbon material which can be subsequently used in other steps of the process as will be described. For example, in such a treatment there was produced, for every barrel of hydrocarbon stock charged, about 247 cubic feet of C_4 and lighter gases, which were predominantly free hydrogen and of which about 82 cubic feet comprised C_3 and C_4 hydrocarbons, of which over 70 mol per cent were olefins.

The effluent of the reforming unit 208 is passed through pipe 240 to a separation unit 241 which may include fractional distillation units and/or selective solvent absorption units as will be found most desirable. A reformed gasoline stock of high octane number is removed from separation unit 241 through a pipe 242 and is passed through a valve 243 to pipe 255 for blending with other stocks which are passed to pipe 255 to produce a finished motor fuel of gasoline characteristics and of high octane number. Any portion of the material passing through pipe 242 may be removed from the system through pipe 249 controlled by a valve 244. Light gases comprising primarily free hydrogen and methane and C_2 hydrocarbons may be removed through the system through pipe 245 controlled by a valve 246. C_3 and C_4 hydrocarbons, which will be predominantly unsaturated and highly suitable as a portion of the charge stock to the catalytic alkylation unit 95, may be removed from separation unit 241 through pipe 247 controlled by a valve 248 and passed directly to pipe 93. Any heavy undesired material may be removed through pipe 250 controlled by a valve 251. A hydrocarbon stock in the gasoline range of low octane number, or a portion of the stock passed through pipe 242, may be passed from separation unit 241 through pipe 252 controlled by a valve 253 to pipe 228 for subsequent retreatment in the reforming unit 208. When this recycle stock comprises a portion of the material removed through pipe 242 the result will be, after a steady state of operation has been reached, a higher octane number for the material passing through pipe 242. When selective solvent extraction is employed in the separation unit 241, a separation may be readily accomplished between products of high octane number and unreacted material of low octane number, which latter can then be recycled through pipe 252 for retreatment.

A portion of the isopentane fraction produced in the thermal alkylation reaction zone 33 and removed from separation unit 42 through pipe 47 may be passed therefrom through pipe 255 controlled by a valve 256 and blended with the reformed hexanes and heavier fraction passing through pipe 242. Other hydrocarbon fractions produced in the process and passed through pipes 109, 85, 153, 162, 192, 213, 242, and/or 122, controlled by valves 110, 86, 154, 164, 193, 219 243, and 124, respectively, may be blended in pipe 255, to produce a motor fuel of gasoline characteristics as a final product of the process.

The reformed hexanes and heavier fraction and the catalytic alkylate will be the principal stocks of low volatility, and to these materials it is necessary to add one or more additional hydrocarbon fractions of higher volatility to produce a finished motor fuel of gasoline characteristics. In most cases it will be necessary to add two or more of the other fractions described herein. Isopentane may be added directly from the separating means 11 or may be added as a product of a process of the alkylation unit 33. The aromatic hydrocarbons produced in the aromatization of normal butane will be intermediate in volatility between the stocks of low volatility and stocks of high volatility. The neohexane fraction will be relatively high as to volatility and octane number, but will be low as to vapor pressure. Appreciable amounts of normal butane may be used directly as a result of the production of considerable quantities of a stock of extremely low volatility by the catalytic alkylation unit. When treating an initial stock charged through pipe 10 which contains appreciable amounts of sulfur compounds, they should be removed so as not to exceed the limits required by specifications for the final product. Most sulfur compounds present in the lighter fractions may be removed by simple alkali washes, carried out where necessary by apparatus not shown. The treatment described as preferred for the reforming unit 208 also converts the majority of the sulfur compounds which may be present in the hexanes and heavier fraction treated therein, and resulting hydrogen sulfide, or the like, is readily removed by suitable treatment such as an alkali wash, or distillation, forming a part of separation unit 241. Other known desulfurization operations may be carried out where suitable or necessary, as can be readily determined and applied by one skilled in the art.

It will be readily appreciated that our invention comprises combinations of process steps, each of which is separately known to the art, and that the accompanying flow sheet is diagrammatic only. Some of the process steps are operated under quite high superatmospheric pressures, while others are operated under relatively low pressures, which may at times even be subatmospheric. For all of the process steps desirable operating conditions and ranges have been disclosed and discussed, and in all cases flows of materials treated and produced have been shown. The adaptation of our invention, or any particular modification thereof, to operation on a commercial scale with commercial epuipment such as pumps, compressors, heat exchangers, heating units and furnaces, cooling units, catalyst chambers and reactors, separating equipment such as fractional distillation columns, absorbers, and solvent extractors, etc., may be readily made by one skilled in the art in view of the teachings of the present disclosure. Various modifications of our invention may be carried out without departing from the spirit of the disclosure or from the scope of the claims.

We claim:

1. A process for converting normally gaseous hydrocarbons having two to four carbon atoms per molecule into hydrocarbons boiling in the gasoline range, which comprises reacting propane with ethylene under noncatalytic alkylation conditions to form pentanes and recovering from effluents of said alkylation an isopentane fraction so produced and containing a minor amount of olefins, separately reacting isobutane with ethylene under noncatalytic alkylation conditions to form hexanes and recovering from effluents of the last said alkylation a hexane fraction so produced and an unreacted isobutane fraction con-

taining a minor amount of olefins, passing to a catalytic alkylation step said isopentane fraction and said unreacted isobutane fraction to react olefins contained therein with said isoparaffins to form a normally liquid paraffinic fraction boiling in the gasoline range, separating from effluents of said catalytic alkylation a gasoline range fraction so produced and blending same with the aforesaid hexane fraction to produce a gasoline of high octane number.

2. A multistage process for the conversion of substantially all of the natural gas hydrocarbons heavier than methane and boiling in and below the gasoline range contained in a hydrocarbon mixture recovered from a wet natural gas to a hydrocarbon material having gasoline characteristics, which comprises separating from a wet natural gas a fraction comprising ethane, a fraction comprising propane, a fraction comprising isobutane, a fraction comprising normal butane, a fraction comprising a pentane, and a fraction in the gasoline boiling range of relatively low antiknock value and comprising heavier hydrocarbons, said fractions together comprising essentially all of the hydrocarbon material heavier than methane and boiling in and below the gasoline range originally in said wet natural gas, dehydrogenating said ethane fraction to form ethylene, reacting ethylene so produced with a portion of said propane to form predominantly saturated hydrocarbons comprising isopentane, separating from the effluent an isopentane fraction, dehydrogenating a further portion of said propane to form propylene, reacting said propylene, said isobutane, and said isopentane fraction from said alkylation in a catalytic alkylation step to form predominantly saturated hydrocarbons in the gasoline boiling range of relatively high antiknock value, reforming said heavier fraction to increase the antiknock value thereof without materially changing the boiling characteristics, and blending said normal butane, said natural pentane fraction, said reformed heavier fraction, and said catalytic alkylate in the gasoline range to produce a composite hydrocarbon liquid having gasoline characteristics of boiling range, vapor pressure and volatility and having a high antiknock value.

3. A process for the production of a normally liquid hydrocarbon material of gasoline characteristics and relatively high antiknock value, which comprises separating from a natural gas a hydrocarbon material comprising substantially all of the hydrocarbons having two and more carbon atoms per molecule including normally liquid hydrocarbons in the gasoline boiling range and of relatively low antiknock value, separating from said hydrocarbon material an ethane fraction, a propane fraction, an isobutane fraction, a normal butane fraction, a pentane fraction, and a natural gasoline fraction in the gasoline boiling range of relatively low antiknock value, dehydrogenating said ethane fraction to form ethylene and recovering ethylene so produced, dehydrogenating said propane fraction to form propylene and recovering a propylene fraction so produced, reacting said ethylene with said isobutane fraction under noncatalytic alkylating conditions to form isomeric hexanes and recovering a resultant alkylate fraction in the gasoline boiling range and an unreacted isobutane fraction, dehydrogenating at least a part of said normal butane fraction to produce butenes and recovering a butene fraction so produced, reacting said unreacted isobutane fraction, said propylene fraction and said butene fraction under catalytic alkylation conditions to form a catalytic alkylate and recovering a catalytic alkylate in the gasoline boiling range so produced, subjecting said natural gasoline fraction of low antiknock value to a catalytic treatment at elevated temperature to increase the antiknock value without essentially changing the boiling characteristics, recovering a reformed natural gasoline so produced, and blending said reformed natural gasoline, said catalytic alkylate fraction, said noncatalytic alkylate fraction, said pentane fraction and a portion of said normal butane fraction to produce a liquid hydrocarbon material having gasoline characteristics of boiling range, vapor pressure and volatility and of relatively high antiknock value.

4. A process for producing a balanced gasoline of premium characteristics from the ethane and heavier constituents of a wet natural gas, which comprises separating from a wet natural gas an ethane-propane fraction, an isobutane fraction, a normal butane fraction, an isopentane fraction, and a natural gasoline fraction in the gasoline boiling range, said fractions together comprising substantially all of the hydrocarbon material heavier than methane and boiling in and below the gasoline range originally in said wet natural gas, dehydrogenating said ethane-propane fraction to produce ethylene and recovering from the effluents an ethylene fraction, reacting said ethylene fraction and said isobutane fraction under noncatalytic alkylation conditions to produce a noncatalytic alkylate comprising isohexanes and separating from the effluent a noncatalytic alkylate fraction in the gasoline boiling range, reacting a portion of said normal butane fraction under aromatizing conditions to produce low boiling aromatics and separating from the effluent an aromatic fraction in the gasoline boiling range, separating by fractional distillation said natural gasoline fraction into a fraction comprising predominantly constituents of poor antiknock values and a fraction comprising predominantly constituents of good antiknock values, catalytically reforming said poor antiknock fraction to improve the antiknock value without materially altering the boiling characteristics and recovering from the effluent a reformed natural gasoline fraction, and blending together said reformed fraction, said high antiknock natural gasoline fraction, said aromatic fraction, said noncatalytic alkylate fraction, said isopentane fraction, and a portion of said normal butane fraction to form a balanced gasoline of high antiknock value and containing all the hydrocarbon material obtained from the aforesaid fractions.

5. A process for producing a high yield of a liquid hydrocarbon material having gasoline characteristics of boiling range and vapor pressure, and of relatively high antiknock value from a wet natural gas, which comprises separating from said wet natural gas to an ethane-propane fraction, an isobutane fraction, a normal butane fraction, a pentane fraction, and a hexane and heavier fraction in the gasoline boiling range, said fractions together comprising substantially all of the hydrocarbon material heavier than methane and boiling in and below the gasoline range originally in said wet natural gas, dehydrogenating said ethane-propane fraction to form ethylene and propylene and separating from the effluents an ethylene-propylene fraction so produced, reacting said ethylene-propylene fraction with said isobutane fraction under noncatalytic alkylating conditions to form low boiling normally liquid,

predominantly paraffinic hydrocarbons and separating from the effluents a noncatalytic alkylate fraction in the gasoline boiling range, so produced, subjecting at least a portion of said normal butane fraction to an elevated temperature and relatively low pressure to form low boiling, normally liquid, predominantly aromatic hydrocarbons and separating from the effluents an aromatic fraction in the gasoline boiling range, separating said hexanes and heavier fraction into a fraction of high antiknock value and a fraction of low antiknock value, subjecting said low antiknock fraction to a catalytic reforming at elevated temperature to improve the antiknock value without substantial change in boiling characteristics, and recovering the resultant hydrocarbons in the gasoline boiling range, and blending said reformed fraction, said high antiknock hexanes and heavier fraction, said aromatic fraction, and said alkylate fraction together with said pentane fraction and a portion of said normal butane fraction to form a liquid hydrocarbon material containing all the hydrocarbon material obtained from the aforesaid fractions and having gasoline characteristics of boiling range and vapor pressure and of relatively high antiknock value.

6. A process for producing a high yield of a liquid hydrocarbon material having gasoline characteristics of boiling range and vapor pressure and of relatively high antiknock value from a wet natural gas, which comprises separating from said wet natural gas an ethane fraction, a propane fraction, an isobutane fraction, a normal butane fraction, a normal pentane fraction, and a hexane and heavier fraction in the gasoline boiling range, said fractions together comprising substantially all of the hydrocarbon material heavier than methane and boiling in and below the gasoline range originally in said wet natural gas, dehydrogenating said ethane fraction to form ethylene and recovering an ethylene fraction so produced, dehydrogenating a portion of said propane fraction to produce propylene and recovering a propylene fraction so produced, reacting a portion of said ethylene fraction and a further portion of said propane fraction under noncatalytic alkylating conditions to produce highly volatile normally liquid predominantly paraffinic hydrocarbons and recovering from the effluents a pentane fraction so produced, reacting said isobutane fraction and a further portion of said ethylene fraction under noncatalytic alkylating conditions to form low boiling normally liquid predominantly paraffinic hydrocarbons and separating from the effluents a noncatalytic alkylate fraction in the gasoline boiling range so produced, separating also an unreacted isoparaffin fraction, subjecting said hexanes and heavier fraction to catalytic reforming at an elevated temperature to increase the antiknock value thereof without substantial change in boiling characteristics, separating a reformed fraction from the effluents, separating also a C_3–C_4 fraction, subjecting in admixture said C_3–C_4 fraction, said unreacted isoparaffin fraction, said noncatalytic alkylate pentane fraction and said propylene fraction to catalytic alkylation to form a catalytic alkylate and separating from the effluents a catalytic alkylate fraction in the gasoline boiling range, and blending said catalytic alkylate fraction, said noncatalytic alkylate fraction, said reformed fraction, and said normal butane and said normal pentane fraction to produce a normally liquid hydrocarbon material containing all the hydrocarbon material obtained from the aforesaid fractions and with gasoline characteristics of boiling range and vapor pressure and of relatively high antiknock value.

7. A process for the production of a motor fuel having gasoline characteristics of boiling range and vapor pressure and a relatively high antiknock value from a wet natural gas containing normally gaseous hydrocarbons heavier than methane and normally liquid hydrocarbons in the gasoline boiling range, which comprises separating from said hydrocarbon mixture an ethane-propane fraction, a propane fraction, an isobutane fraction, a normal butane fraction, an isopentane fraction, a normal pentane fraction, a natural gasoline fraction boiling in the gasoline range of high antiknock value, and a natural gasoline fraction boiling in the gasoline range of low antiknock value, said fractions together representing substantially all the hydrocarbons originally in said wet natural gas heavier than methane and boiling in and below the gasoline boiling range, dehydrogenating said ethane-propane fraction to produce ethylene and recovering from effluents of said dehydrogenation an ethylene fraction, dehydrogenating a portion of said propane fraction to produce propylene and recovering from effluents of said dehydrogenation a propylene fraction, reacting a portion of said ethylene fraction and a further portion of said propane fraction under alkylation conditions to produce highly volatile normally liquid predominantly paraffinic hydrocarbons and recovering from effluents of said alkylation a pentane fraction so produced, reacting a further portion of said ethylene fraction and a portion of said isobutane fraction under alkylation conditions to produce low-boiling normally liquid predominantly paraffinic hydrocarbons and separating from effluents of said alkylation an alkylate fraction so produced and boiling in the gasoline range, separating also from effluents of said alkylation an unreacted isoparaffin fraction, subjecting a portion of said normal butane fraction to aromatizing conditions to produce low-boiling aromatic hydrocarbons and also normally gaseous olefins by concomitant dehydrogenation reactions, separating from effluents of said aromatizing an aromatic hydrocarbon fraction boiling in the gasoline range, separating also from said aromatizing a normally gaseous olefin fraction, subjecting said normal pentane fraction to catalytic isomerization to form low-boiling isoparaffins and recovering from effluents of said isomerization a low-boiling isoparaffin fraction, subjecting said natural gasoline fraction of low antiknock value to reforming conditions to produce a stock of a higher antiknock value and substantially the same boiling characteristics and minor amounts of olefinic C_3 and C_4 hydrocarbons by minor concomitant cracking reactions, separating from effluents of said reforming a reformed fraction boiling in the gasoline range, separating also from effluents of said reforming a C_3–C_4 fraction, subjecting in admixture said C_3–C_4 fraction, the aforesaid pentane fraction from said propane alkylation, said propylene fraction, the aforesaid unreacted isoparaffin fraction, a further portion of said isobutane fraction, the aforesaid low-boiling isoparaffin fraction, and the aforesaid normally gaseous olefin fraction from said aromatizing to catalytic alkylation to form a catalytic alkylate, separating from effluents of said catalytic alkylation a catalytic alkylate fraction boiling in the gasoline range, and blending said catalytic alkylate, said alkylate fraction from isobutane al-

kylation, said aromatic fraction, a further portion of said normal butane fraction, said isopentane fraction, said natural gasoline fraction of high antiknock value, and said reformed fraction to produce a normally liquid hydrocarbon material containing all the hydrocarbon material obtained from the aforesaid fractions and with gasoline characteristics of boiling range and vapor pressure and of relatively high antiknock value.

8. A process for the production of a motor fuel having gasoline characteristics of boiling range and vapor pressure and a relatively high antiknock value from a saturated hydrocarbon mixture containing normally gaseous hydrocarbons heavier than methane and normally liquid hydrocarbons in the gasoline boiling range, which comprises separating from said hydrocarbon mixture an ethane-propane fraction, a propane fraction, an isobutane fraction, a normal butane fraction, a pentane fraction, a natural gasoline fraction boiling in the gasoline range of high antiknock value, and a natural gasoline fraction boiling in the gasoline range of low antiknock value, said fractions together comprising substantially all of the hydrocarbon material heavier than methane and boiling in and below the gasoline range originally in said wet natural gas, dehydrogenating said ethane-propane fraction to produce ethylene and recovering from effluents of said dehydrogenation an ethylene fraction, dehydrogenating a portion of said propane fraction to produce propylene and recovering from effluents of said dehydrogenation a propylene fraction, reacting a portion of said ethylene fraction and a further portion of said propane fraction under alkylation conditions to produce highly volatile normally liquid predominantly paraffinic hydrocarbons and recovering from effluents of said alkylation a pentane fraction so produced, reacting a further portion of said ethylene fraction and a portion of said isobutane fraction under alkylation conditions to produce low-boiling normally liquid predominantly paraffinic hydrocarbons and separating from effluents of said alkylation an alkylate fraction so produced and boiling in the gasoline range, separating also from effluents of said alkylation an unreacted isoparaffin fraction, subjecting a portion of said normal butane fraction to aromatizing conditions to produce low-boiling aromatic hydrocarbons and also normally gaseous olefins by concomitant dehydrogenation reactions, separating from effluents of said aromatizing an aromatic hydrocarbon fraction boiling in the gasoline range, separating also from said aromatizing a normally gaseous olefin fraction, subjecting said natural gasoline fraction of low antiknock value to reforming conditions to produce a stock of a higher antiknock value and substantially the same boiling characteristics and minor amounts of olefinic C_3 and C_4 hydrocarbons by minor concomitant cracking reactions, separating from effluents of said reforming a reformed fraction boiling in the gasoline range, separating also from effluents of said reforming a C_3–C_4 fraction, subjecting in admixture said C_3–C_4 fraction, the aforesaid pentane fraction from said propane alkylation, said propylene fraction, the aforesaid unreacted isoparaffin fraction, a further portion of said isobutane fraction, and the aforesaid normally gaseous olefin fraction from said aromatizing to catalytic alkylation to form a catalytic alkylate, separating from effluents of said catalytic alkylation a catalytic alkylate fraction boiling in the gasoline range, and blending said catalytic alkylate, said alkylate fraction from isobutane alkylation, said aromatic fraction, a further portion of said normal butane fraction, said pentane fraction, said natural gasoline fraction of high antiknock value, and said reformed fraction to produce a normally liquid hydrocarbon material containing all the hydrocarbon material obtained from the aforesaid fractions and with gasoline characteristics of boiling range and vapor pressure and of relatively high antiknock value.

9. A process for producing a high yield of a liquid hydrocarbon material having gasoline characteristics of boiling range and vapor pressure and a relatively high antiknock value from a wet natural gas, which comprises separating from said wet natural gas an ethane-propane fraction, a propane fraction, an isobutane fraction, a normal butane fraction, a pentane fraction, a natural gasoline fraction boiling in the gasoline range and having a high antiknock value, and a natural gasoline fraction boiling in the gasoline range and having a low antiknock value, said fractions together representing essentially all of the hydrocarbon material originally present in said wet natural gas heavier than methane and boiling in and below the gasoline boiling range, dehydrogenating said ethane-propane fraction to form ethylene and separating from effluents of said dehydrogenation ethylene so produced, reacting said propane fraction with a portion of said ethylene under noncatalytic alkylation conditions to form pentane and recovering from effluents of said alkylation an isopentane fraction so produced containing a minor amount of olefins, separately reacting said isobutane fraction with the remainder of said ethylene under noncatalytic alkylation conditions to form hexanes and recovering from effluents of the last said alkylation a hexane fraction so produced and an unreacted isobutane fraction containing a minor amount of olefins, passing to a catalytic alkylation step said isopentane fraction and said unreacted isobutane fraction to react olefins containing therein with said isoparaffins to form a normally liquid paraffinic fraction boiling in the gasoline range, separating from effluents of said catalytic alkylation a gasoline range fraction so produced, subjecting a portion of said normal butane fraction to an elevated temperature and relatively low pressure to form low-boiling normally liquid aromatic hydrocarbons and separating from effluents thereof an aromatic hydrocarbon fraction in the gasoline boiling range so produced, subjecting said natural gasoline fraction having a low antiknock value to reforming conditions to produce hydrocarbons having relatively high antiknock value and separating from effluents of said reforming a reformed fraction boiling in the gasoline range and of relatively high antiknock value so produced, blending said fraction from catalytic alkylation, said hexanes and heavier fraction from said noncatalytic isobutane alkylation, said aromatic fraction, a further portion of said normal butane fraction, said pentane fraction, said natural gasoline fraction having a high antiknock value, and said reformed fraction to produce a normally liquid hydrocarbon material containing all the hydrocarbon material obtained from the aforesaid fractions and boiling in the gasoline range, and having gasoline characteristics of boiling range and vapor pressure and having a relatively high antiknock value.

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