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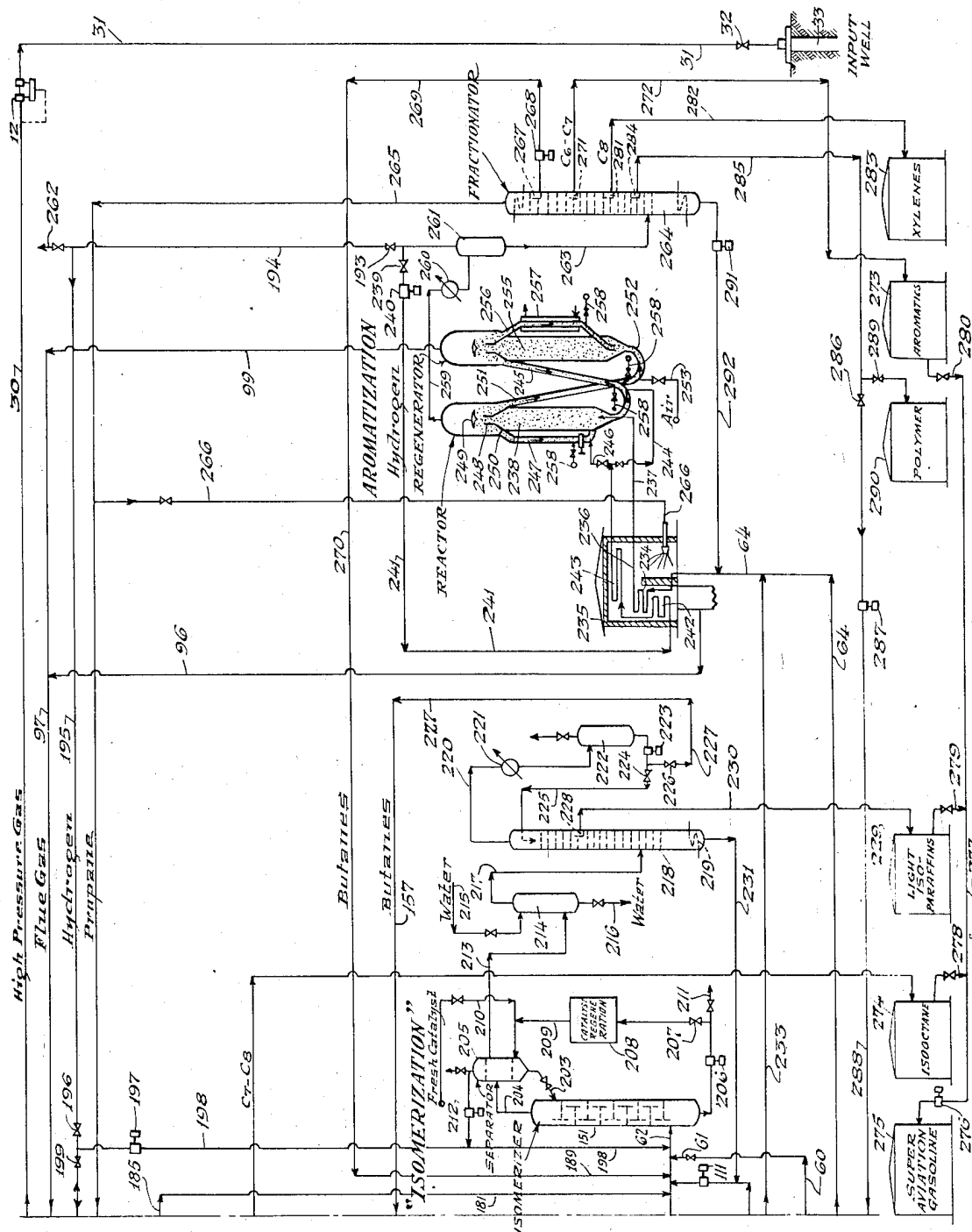
M. H. ARVESON

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HYDROCARBON CONVERSION

Filed April 24, 1941

2 Sheets-Sheet 1



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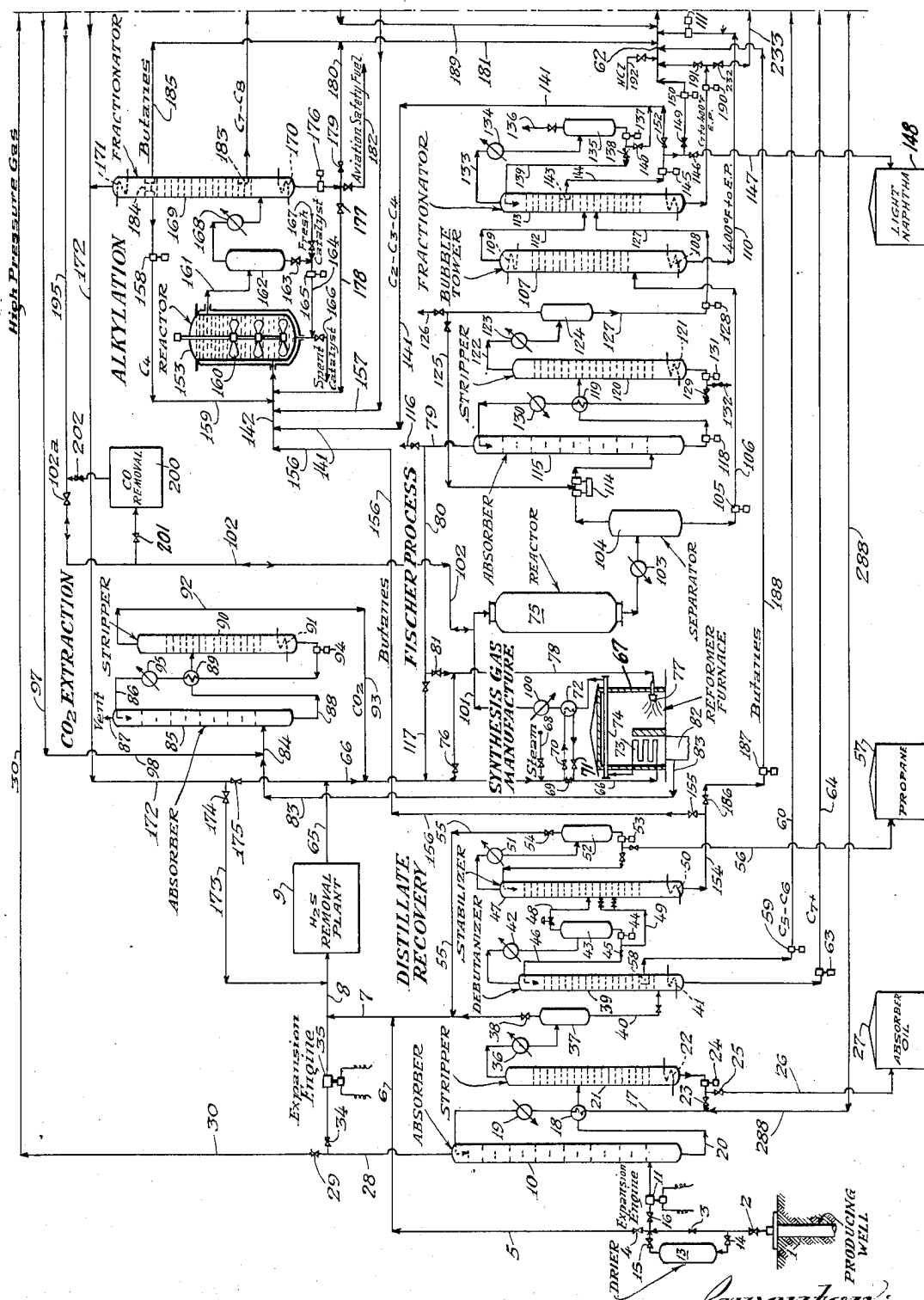
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2 Sheets-Sheet 2



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## UNITED STATES PATENT OFFICE

2,360,463

## HYDROCARBON CONVERSION

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This invention relates to the conversion of hydrocarbons into useful products and particularly into high quality gasolines and still more particularly aviation gasolines. The invention relates especially to the conversion of methane into heavier high quality hydrocarbon products.

One of the outstanding problems in the oil and gas industry is the efficient and economic utilization of methane. In the past methane has been utilized only for fuel value and in fact has often been completely wasted. Processes have heretofore been known for the conversion of methane into heavier hydrocarbons and the conversion of methane to carbon monoxide and hydrogen followed by the Fischer synthesis is an outstanding instance of this. In the Fischer process carbon monoxide and hydrogen are converted into liquid, gaseous and solid hydrocarbons. However, this Fischer synthesis is subject to very serious disadvantages since the products produced by it constitute very inferior motor fuels and the process produces large quantities of wax and other fractions which are very difficult to utilize.

I have provided a combination process in which methane taken from a gas well or from a high pressure well of the so-called distillate or condensate type can be processed by steps including the Fischer synthesis and other operations to produce a highly superior product in very high yields. Moreover, I have combined the various steps of this process in certain new and advantageous manners as will subsequently become apparent, so that each of them contributes to the improved utility and efficiency of the other. Furthermore, I have combined the processing of hydrocarbons resulting from methane with the processing of hydrocarbons heavier than methane and particularly three and four carbon atom hydrocarbons and hydrocarbons of the gasoline boiling point range resulting from distillate recovery operations, as will be described.

One of the objects of my invention is to provide a more efficient method for the utilization of methane and in particular for the conversion of methane into high yields of motor fuels of unusually good quality. It is a more particular object of my invention to provide for the conversion of methane into so-called aviation super fuels. Another object of my invention is to provide for the cooperative processing of methane and heavier hydrocarbons in such manner that the processing of each facilitates the processing of the other.

It is also an object of my invention to convert hydrocarbons produced in the Fischer process

into products rich in branched chain and/or aromatic hydrocarbons.

A still further object of my invention is to utilize my various processing steps in a way which makes possible the utilization of low grade by-products from one step for the production of high quality motor fuels or motor fuel components in another step.

Other and more detailed objects, advantages and uses of my invention will become apparent as the description thereof proceeds.

My invention will now be described in detail with particular reference to the accompanying flow diagram which illustrates various embodiments of my process. It will be understood that this flow diagram is in highly simplified form and that modifications of it can and will be made by those skilled in the art. In particular I have omitted various features such as flow and temperature control. Furthermore, while this flow diagram illustrates a number of alternatives it will be understood that these alternatives will not all be used in connection with a single installation but that they have been combined into a single flow diagram in order to avoid needless multiplication of the drawings.

Turning now to the drawings in more detail, the hydrocarbons used in my process can suitably come from a well 1 which can be a gas well or, preferably, a well of the so-called distillate or condensate type. Since my invention in certain of its forms relates primarily to the processing of the products resulting from the Fischer synthesis, it will be apparent that the hydrocarbons used to supply the synthesis gas can come from still other sources such as refinery gas or gas produced along with crude oil. In fact, while I prefer to make the Fischer synthesis gas, consisting of carbon monoxide and hydrogen, from hydrocarbon sources and particularly from methane produced from oil or gas wells, this synthesis gas can be made from coal and water or in other manners known to the art.

Returning to well 1, it will be understood that while a single well is shown, a number of wells will usually be employed and in fact my process can be applied most economically to a large gas or distillate field including a considerable number of wells. If well 1 is a gas well, the gas is passed through valves 2, 3 and 4, and lines 5, 6, 7 and 8 to a hydrogen sulfide removal plant 9 which is shown merely as a rectangle since this sulfur removal part of the process can be carried out in various ways and is conventional. It should be mentioned, however, that one suitable

method of removing the hydrogen sulfide is to wash it with an alkaline purification medium and the ethanolamines including the mono-, di- and tri-ethanolamine are suitable for this purpose.

While my process can thus be applied to methane, usually containing small amounts of heavier hydrocarbons, produced from a gas well or to similar off gases from a natural gasoline plant, it is particularly advantageous as applied to wells or fields of the so-called distillate or condensate type.

These distillate fields have become increasingly common in recent years and are typified by high reservoir pressures within the retrograde condensation range with the result that the hydrocarbons present in such a reservoir are wholly or largely in a single phase which can be referred to as a vapor phase or supercritical phase. When the pressure and temperature of such fluids are reduced in the course of their passage upward in a well, a portion of the heavier hydrocarbons is usually precipitated as a result of the cooling and particularly as a result of the retrograde condensation resulting from the pressure drop. Further quantities of valuable hydrocarbons including propanes and butanes and particularly gasoline range hydrocarbons are then recovered together usually with some slight amount of heavier hydrocarbons by a distillate recovery process.

This distillate recovery process can be of the retrograde condensation type in which the recovery is effectuated by further cooling the well fluids and reducing their pressure to a point within the retrograde condensation range, for instance to a pressure of 700 to 1500 pounds per square inch. The pressure chosen will depend on the composition of the well fluids and the economics of the particular situation.

It is generally preferred, however, to recover these so-called distillate or condensate hydrocarbons by a high pressure absorption process in which the well fluids are contacted concurrently or countercurrently with an absorption medium at a high pressure such as 1000 to 3000 pounds per square inch, for instance 1500 pounds per square inch. The absorption medium chosen can be a portion of the heavy ends of the distillate itself but superior results can be obtained by the utilization of other types of absorption media and the relatively heavy, predominantly aromatic hydrocarbons resulting from processes such as catalytic aromatization have been found to be particularly suitable.

Assuming that well 1 is of the distillate type, the well fluids therefrom, after separation, if so desired, of the readily separated liquids are passed to an absorber 10. Since pressure reduction is usually required, particularly when the well operates at a very high pressure such as 4000 or 5000 pounds per square inch, these well fluids can advantageously be passed through an expansion engine 11 with a resultant increase of the degree of cooling and with recovery of power which can be utilized to supply part of the energy necessary to operate compressors 12 in connection with the plant itself or can be utilized in other ways.

In case the well fluids contain an undesirable quantity of moisture, these fluids can be passed through one or more driers 13 by closing valve 3 and opening valves 14 and 15, thus avoiding the formation of natural gas hydrates which would otherwise interfere in some instances with the operation of expansion engine 11 and/or absorber 10.

These driers can be of various types but simple calcium chloride driers are suitable. Provision can, of course, be made for regenerating the calcium chloride but in the interests of simplicity this has not been shown. A separator between well 1 and absorber 10 is also often desirable to remove water and liquid hydrocarbons.

In any event all or most of the well fluids pass through valve 16 into absorber 10, valve 4 being closed. In absorber 10 the well fluids contact an absorption medium which is introduced from line 17 through heat exchanger 18 and cooler 19 into the top of absorber tower 10 in which the absorption medium passes downward countercurrent to the rising well fluids and serves to absorb from the well fluids the desired normally liquid hydrocarbons together with substantial quantities of propane and butanes and also some lighter hydrocarbons. Absorption plants of this type are sometimes complicated and provision is often made for mist recovery and the like but again in the interests of simplicity the process has been shown in its elemental form.

From the base of absorber tower 10 the rich oil is passed by means of line 20 through heat exchanger 18 wherein its temperature is raised and then into stripper tower 21. This stripper is heated at the base by means of coil 22, and the lean oil is removed from the base of the stripper and passed through valve 23, line 17, heat exchanger 18 and cooler 19 into absorber tower 10 by pump 24. Any excess absorption medium is withdrawn through valve 25 and line 26 to tank 27.

Returning to absorber tower 10, part of the off gases, predominantly methane, pass through line 28, valve 29 and line 30 to compressor 12 and are reinjected into a subsurface formation through line 31, valve 32 and well 33. A plurality of input wells can and usually will be used. This reinjection of gas serves an important purpose in increasing the ultimate recovery of valuable hydrocarbons from the reservoir and in preventing retrograde condensation within the reservoir. The remainder of the predominantly methaneaceous gas from absorber 10 passes through valve 34 to hydrogen sulfide removal plant 9 previously described. Since the hydrogen sulfide removal operation normally operates at moderate pressures, these gases can suitably be passed through expansion engine 35 to recover power which can be utilized as described in the case of expansion engine 11.

An additional source of gases for the hydrogen sulfide removal plant is obtained by passing the overhead from stripper 21 through condenser 36 to a separating drum 37. This condenser is operated at such temperature as to condense substantially all of the butane and heavier hydrocarbons together with at least a substantial part of the propane coming overhead from the stripper. The uncondensed gases pass through valve 38 and lines 7 and 8 to hydrogen sulfide removal plant 9.

The liquid fraction from separating drum 37 passes to debutanizer tower 39 through valved pipe 40. The debutanizer tower is heated at the base by coil 41 and provided with reflux by means of condenser 42, separating drum 43 and pump 44 which takes a portion of the liquid phase from separating drum 43 and reintroduces it into the top of debutanizer tower 39 through valve 45 and line 46. The remainder of the liquid phase from separating drum 43 together with the vapor phase

from this same drum pass to a stabilization tower 47 through valved lines 48 and 49. Tower 47 is heated at the base by coil 50 and provided with reflux by means of condenser 51, separating drum 52 and pump 53. The fixed gas from the last mentioned separating drum passes through valve 54 and lines 55, 7 and 8 to the hydrogen sulfide removal plant 9. The liquid phase from this separating drum is largely propane and passes through valved line 56 to storage tank 57.

Reverting to debutanizer 39, a sidestream composed predominantly of five and six carbon atom hydrocarbons can suitably be removed by means of trapout plate 58 and passed by means of pump 59 through line 60, valved line 61 and line 62 to a so-called paraffin isomerization process which will later be described. The bottom from the debutanizer tower consisting largely of the heptane and heavier fraction of the distillate is preferably passed by means of pump 63 through valved line 64 to a catalytic aromatization operation which will likewise be described subsequently.

I have referred to various sources of hydrocarbon gas, consisting predominantly of methane, passing to hydrogen sulfide removal plant 9. It will, of course, be understood that it is not necessary to use hydrocarbons from all these sources and it will likewise be understood that hydrocarbons from still other sources can be introduced at this point. Furthermore, any available sources of methanaceous gases which are free of sulfur may be introduced directly into the Fischer process synthesis gas manufacturing operation rather than passing through the hydrogen sulfide removal plant but it is necessary to make a very thorough clean-up of sulfur since it tends to poison the catalysts normally used in the manufacture of synthesis gas for the Fischer process.

From the hydrogen sulfide removal plant the purified gases pass through lines 65 and 66 to a reformer furnace 67. In line 66 they are joined with other hydrocarbon streams and also with steam introduced through valved line 68. The hydrocarbons and steam in line 66 are preferably preheated by closing valve 69 and opening valves 70 and 71, thus passing them through a preheater 72 wherein they pick up heat from the synthesis gas passing out of the furnace 67.

In furnace 67 the feed gases pass through coils 73 wherein they are heated to a temperature in the neighborhood of 1500° F. and substantially atmospheric pressure and then pass to catalyst tubes contained in reactor 74 at substantially this same temperature and pressure.

Reformer furnace 67 can be heated in various ways but the suitable sources of fuel include a portion of the hydrocarbon stream which would otherwise pass to coil 73. Thus valve 76 can be opened and fuel supplied to burner 77 through line 78. Alternatively, or in addition, fuel can be supplied from line 79 through line 80 and valved line 81.

The reaction between methane and steam theoretically produces one mol of carbon monoxide to three mols of hydrogen and in practice the production is very similar. The presence of heavier hydrocarbons increases somewhat the mol ratio of carbon monoxide to hydrogen but in any event this mol ratio is lower than that required in the conversion of this gas mixture into heavier hydrocarbons. This situation can be remedied in various ways but I prefer to rectify the matter by removing carbon dioxide from flue gas, preferably made from sulfur-free fuel and

introducing this into reformer furnace 67 where it is reduced to carbon monoxide.

Thus flue gas from flue 82 of reformer furnace 67 can be passed through lines 83 and 84 into absorber tower 85 in which carbon dioxide from these flue gases is absorbed by passing an absorption medium such as a dilute alkaline solution, for instance sodium carbonate or mono-ethanolamine solution, downward through the absorber tower from line 86. The remaining flue gases are vented through vent line 87. The liquid from the base of absorber tower 85 is passed through line 88 and heater 89 into stripper tower 90, heated at the base by coil 91, and carbon dioxide removed in the stripping operation is passed through lines 92 and 93 and 66 back to coil 73 of reformer furnace 67. The stripped absorption medium is, of course, removed from the base of stripper 90 and introduced by means of pump 94 through heat exchanger 89, cooler 95 and line 86 into absorber tower 85. Additional flue gas from the catalytic aromatization process, which will subsequently be described, can likewise be passed through lines 96, 97, 98 and 84 to this carbon dioxide recovery system. Flue gas resulting from revivification of aromatization catalyst can be used similarly if desired being introduced into absorber 85 through lines 99, 97, 98 and 84. The recovered carbon dioxide plays a part in the reactions within the reformer furnace 67 and results in an increase in the ratio of carbon monoxide to hydrogen.

Synthesis gas from reformer furnace 67 passes out through preheater 72, heat exchanger 100 and line 101 into the Fischer reactor 75. In line 101 the synthesis gas is preferably supplemented by hydrogen resulting from the catalytic aromatization process and introduced through line 102 although, as will subsequently be described, instead of introducing hydrogen through this line 102, it may sometimes be advantageous to utilize a portion of the synthesis gas passing through this line 101 from reformer furnace 67 in another phase of my process; namely, the so-called paraffin isomerization step. In the latter case the flow in line 102 is, of course, the reverse of that used when hydrogen is introduced from line 102 into line 101.

In any event the composition of the synthesis gas passing to reactor 75 is adjusted by controlling the amount of carbon dioxide introduced into coil 73 or by controlling the amount of hydrogen, if any, introduced through line 102 or by still other means in order to bring the mol ratio of carbon monoxide to hydrogen to the optimum figure desired in connection with the synthesis of heavier hydrocarbons in the Fischer synthesis. This optimum mol ratio is approximately 0.5 or slightly higher.

In the manufacture of Fischer liquid from carbon monoxide and hydrogen the synthesis gas is contacted with a catalyst which can suitably be made of cobalt, thorium oxide and magnesium oxide mounted on kieselguhr although other catalysts known to the art can, of course, be used. The reaction conditions for this conversion step include a temperature of about 350° F. to about 450° F., for instance about 400° F. The temperature must be controlled within very narrow limits. The reaction is carried on at a moderate pressure which may be atmospheric pressure or considerably higher. Thus the pressure can be from about minus 2 to about 25 pounds per square inch gauge, for instance about 2 pounds per square inch gauge. Various types of reactors

can be employed in contacting the synthesis gas made up of carbon monoxide and hydrogen with the Fischer catalyst, the main necessity being provision for removal of the exothermic heat of reaction for precise temperature control of the process.

In the type of reactor shown the catalyst is granular in form and is disposed in a large number of small tubes to facilitate removal of the heat of reaction. These tubes can suitably be immersed in water maintained under pressure such that the boiling point is at the desired reaction temperature. Steam thus generated can be used in the synthesis gas manufacture step, being introduced through valved line 68.

The Fischer products pass out through cooler 103 to separator 104. Cooler 103 is operated to condense the bulk of the gasoline range hydrocarbons and these are removed from the base of separator 104 by pump 105 and pass through line 106 to bubble tower 107. This bubble tower is heated at the base by coil 108 and reflux is provided at the top by coil 109. The bubble tower is so operated as to take off as a bottom product material heavier than gasoline which is preferably passed through line 110, pump 111 and line 62, into the so-called paraffin isomerization process which will be described later. The overhead from bubble tower 107 passes through line 112 into fractionating tower 113.

Reverting to separator 104, the vapor phase from this separator is drawn off through compressors 114 into absorber 115 where it meets a descending stream of absorption medium which can be a conventional absorber oil. Unabsorbed gas from absorber 115 is preferably used as fuel in reformer furnace 67 via line 80 and lines 81 and 78. Alternatively, all or part of it can be vented through valved line 116 or cycled to coil 73 in furnace 67 by means of line 80, valved line 117 and line 66.

The rich oil from the base of absorber tower 115 is passed by means of pump 118 through heat exchanger 119 into stripper tower 120 which is heated at the base by coil 121 and from which the previously absorbed hydrocarbons pass overhead through line 122 and condenser 123 to separator 124. The vapors from this separator can be recycled to the absorber through valved line 125 and one of compressors 114 or vented through valved line 126. Liquids from this separator are passed through line 127 by pump 128 to the previously mentioned fractionating tower 113. Lean oil from the base of stripper 120 is, of course, cycled through valve 129, heat exchanger 119 and cooler 130 by means of pump 131 to the top of absorber 115. Excess absorber oil can be removed or make-up absorber oil added by means of valved line 132.

In fractionating column 113 the gasoline range and lighter hydrocarbons produced in the Fischer synthesis are preferably fractionated into three cuts of which the lightest is made up of two, three and four carbon atom hydrocarbons, the intermediate is made up of light naphtha and the heaviest is made up of heavy naphtha, for instance a fraction containing seven carbon atom hydrocarbons and heavier and having an end point in the general vicinity of 400° F. The first fraction is withdrawn from the top of the column through line 133 and condenser 134 to separator 135 from which fixed gases are vented through valved line 136 and the liquid is cycled in part back to the column as reflux by means of pump 137, valve 138 and line 139 while

the residue passes, as will subsequently be described, through valve 140 and lines 141 and 142 to the alkylation step which forms a part of the preferred embodiment of my process.

The intermediate or light naphtha fraction from column 113 is withdrawn by means of trap-out plate 143 and can be passed by means of line 144, pump 145, valve 146 and line 147 into storage tank 148, or, alternatively, can be passed in whole or in part through valve 149, pump 150 and line 62 to isomerizer 151. However, this is not the preferred procedure since the light naphtha from the Fischer process contains a fairly high degree of unsaturation which makes it somewhat inferior as a paraffin isomerization process feed. The preferred procedure is to remove this unsaturation prior to isomerization by cycling all or part of this light naphtha fraction of the Fischer synthesis products through line 144, pump 145, valve 152, and lines 141 and 142 to the alkylation reactor 153. When all of the light naphtha and the two, three and four carbon atom fractions are both to be sent to alkylation reactor 153, trapout plate 143 is, of course, unnecessary and all of these components can be taken overhead as a single fraction.

The feed to the alkylation step of my process can come from various sources. In general this feed comprises one or more sources of light olefins ranging from two to six carbon atoms per molecule and one or more sources of branched chain paraffin hydrocarbons, particularly isobutane. As previously mentioned, one source of olefin hydrocarbons is the light naphtha from the Fischer process removed from fractionating column 113. This feed contains substantial quantities of pentenes and hexenes. The other preferred source of olefinic hydrocarbons is likewise from the Fischer process; namely, the normally gaseous olefins removed from the top of fractionating column 113 and passed into the alkylation system through lines 141 and 142. These light hydrocarbons normally predominate in three and four carbon atom hydrocarbons but may contain large quantities of two carbon atom hydrocarbons rich in ethylene. In general the lighter products from the Fischer synthesis are rich in olefins while the heavier fractions such as seven carbon atom hydrocarbons and heavier are made up very largely of straight chain paraffinic hydrocarbons.

The olefins from the Fischer process together, if desired, with olefins produced by dehydrogenation or otherwise, are introduced into an alkylation reactor 153 along with hydrocarbons rich in isobutane. The latter can suitably come from the distillate recovery operation since many distillates and natural gasolines are rich in isobutane. Such materials can be fractionated to secure a high concentration of isobutane but preferably a butane cut containing normal as well as isobutane is utilized. This cut can, for instance, come from the base of the stabilizer column 47 through line 154, valve 155 and lines 156 and 142 into alkylation reactor 153. Another and highly preferable source of isobutane which can, if desired, constitute the only source used in the alkylation reaction, is the so-called paraffin isomerization process, which will later be described. Isobutane from this source passes into alkylation reactor 153 through lines 157 and 142.

In the alkylation process the ratio of isobutane to olefins must be maintained high, for instance from 2:1 to 6:1 and preferably 3:1 or 4:1 with the result that the off gases from the alkyla-

tion reaction normally contain substantial amounts of isobutane and part of this material can be recycled to the alkylation reactor by means of pump 158 and line 159. The alkylation process can be carried on by the use of various alkylation catalysts, for instance sulfuric acid or sulfuric acid containing a promoter. I prefer, however, particularly when the olefinic gases contain substantial amounts of ethylene or five and six carbon atom olefins from the Fischer synthesis, to use aluminum chloride or an aluminum chloride complex as the catalyst in the alkylation reaction. The complexes formed by the reaction of aluminum chloride with hydrocarbons are decidedly preferable to the use of aluminum chloride alone and these complexes differ radically in their efficiencies as alkylation catalysts. I prefer in particular to use a complex formed by the reaction of aluminum chloride with paraffin hydrocarbons although olefin hydrocarbon complexes can likewise be used. Complexes formed with aromatic hydrocarbons are much less desirable. One particularly satisfactory type of complex is that formed between isooctane and aluminum chloride.

The alkylation reactor 153 is shown in highly simplified form as a vessel containing a set of agitators 160 to promote intimate contact between the liquid complex, aluminum chloride or other catalyst on the one hand and the reacting gas on the other hand. Products from this alkylation reactor pass off through line 161 to separator 162 and the liquid is pumped back to the reactor through valve 163 and line 164 by pump 165. Spent catalyst can be removed through valved line 166 and fresh catalyst introduced from time to time through valved line 167 as required. The products from separator 162 pass through heat exchanger 168 into fractionating column 169 which is heated at its base by coil 170 and cooled at the top by reflux coil 171.

Overhead gas from fractionator 169, largely two and three carbon atom hydrocarbons, can be used in synthesis gas manufacture, passing to this step via lines 172 and 66. If this gas contains a deleterious amount of sulfur it can be routed through hydrogen sulfide removal plant 9 via line 173 by opening valve 174 and closing valve 175.

An important feature of my invention is that of cycling to alkylation reactor 153 or isomerization reactor 151 heavy alkylate, particularly alkylate heavier than octanes, resulting from the reaction of pentenes and hexenes from the Fischer synthesis with isobutane under the influence of an aluminum halide or aluminum halide complex. One or both of two procedures can be followed: first, this heavy alkylate can be recycled to the alkylation reactor from the base of fractionator 169 via pump 176, valve 177, line 178 and line 142 for conversion to lower boiling, highly branched hydrocarbons; and/or, second, especially when sulfuric acid is used as the catalyst in reactor 153 rather than an aluminum halide or aluminum halide complex type catalyst, the heavier-than-octane alkylate can be cycled to isomerization reactor 151 via pump 176, valve 179 and lines 180, 181 and 62 and then recycled to completion in this so-called paraffin isomerization process which results in the conversion of this heavy alkylate to high knock rating gasoline range hydrocarbons.

If desired, a portion, or even all, of this heavy alkylate can be withdrawn through valved line 182 as a high boiling aviation safety fuel or safety fuel component. Alternatively a part of this heavy alkylate can be included in the heptane-octane

cut withdrawn from trapout plate 183 of fractionating column 169 by selection of appropriate operating conditions for this column.

As shown, two product fractions are withdrawn from column 169, one from trapout plate 183 and the other from trapout plate 184. The operation of the column can be readily controlled, as will be apparent to those skilled in the art, in order to control the character and nature of the two fractions thus withdrawn. However, the fraction withdrawn from the upper trapout plate 184 includes the butanes and that withdrawn from the lower trapout plate 183 includes the seven and eight carbon atom hydrocarbons which are very rich in branched chain products, notably the so-called isoheptanes and isooctanes. The six and seven carbon atom hydrocarbons formed in the alkylation process or passing through the alkylation process can be included in either fraction or can be separately withdrawn. However, if light Fischer naphtha from column 113 is sent to the alkylation reaction through lines 141 and 142, I prefer to include all or a large part of these six and seven carbon atom hydrocarbons in the stream withdrawn from the upper trapout plate 184 through line 185 and passed through this line and lines 181 and 62 to the so-called paraffin isomerization step of my process. The reason for this preference is that the paraffin hydrocarbons contained in the light Fischer naphtha are almost wholly normal and therefore pass through the alkylation step unchanged. Since these normal paraffin hydrocarbons are not desirable motor fuel components, they can be greatly improved by the paraffin isomerization operation. On the other hand, if the feed to the alkylation process does not include any large quantity of normal  $C_6$  and  $C_7$  paraffin hydrocarbons, the  $C_6$  and  $C_7$  components of the alkylation off gases can better be included along with the  $C_7$  and  $C_8$  products in the stream withdrawn from trapout plate 183 and passed to product storage since in this instance these materials are rich in high anti-knock branched chain components.

The next step in my combination process can be referred to as paraffin isomerization although the strict accuracy of this term may be open to question since the process produces molecular weight changes as well as structural rearrangements with certain particular feed stocks. In any event under appropriate conditions normal paraffinic hydrocarbons heavier than propane are converted in large measure into branched chain paraffin hydrocarbons under the influence of metal halide catalysts such as aluminum chloride, aluminum bromide and their hydrocarbon complexes in the presence of hydrochloric acid or other hydrohalogen acid or material which will decompose to form hydrohalogen acid. Thus normal butane charged to a process of this type gives high yields of isobutane while heavier normal hydrocarbons charged to the process result in the production of the same or lower molecular weight branched chain paraffin hydrocarbons. A still more interesting phenomenon results when a heavy normal paraffinic charging stock is subjected to such catalysts in the presence of a light paraffinic material such as butane or isobutane. These two charging stocks react together in the presence of so-called paraffin isomerization catalysts under reaction conditions to be described and produce materials of molecular weight intermediate to the molecular weight of the two parts of the charge or, in other words, within the gasoline boiling point range. Moreover, these prod-



ucts are highly branched and therefore constitute extremely valuable motor fuel components particularly where a very high grade aviation motor fuel is required.

I prefer that the charge to isomerization reactor 151 include as its main components the Fischer synthesis products heavier than gasoline or a selected fraction of those products and butanes from the alkylation process or from the distillate recovery operation or both. Thus the Fischer products boiling above 400° F. removed from the base of bubble tower 107 can be introduced into isomerization reactor 151 by means of line 110, pump 111 and line 62 together with the butane-containing fraction withdrawn from column 169 of the alkylation process through lines 185 and 181. Similarly all or part of the butane from the distillate recovery operation can, if desired, be introduced into isomerization reactor 151 through line 154, valve 186, pump 187, and lines 188 and 62. Another source of butane for the paraffin isomerization process is from the aromatization process which will later be described. The butane from this source can be introduced into isomerization reactor 151 through lines 189 and 62.

While the main preferred charges to the so-called paraffin isomerization process are the heavier-than-gasoline Fischer process products and butanes, five and six carbon atom hydrocarbons from the distillate recovery operation can likewise be charged to this reaction in order to isomerize them and improve their quality as motor fuel components and this can be accomplished by means of pump 59, line 60, valve 61 and line 62. Another feed which can be used to advantage in the isomerization reaction is the heavy alkylate from lines 180, 181 and 62, as previously described. The light naphtha from the Fischer process can likewise go to isomerizer 151 through valve 149, pump 150 and line 62 but, as previously mentioned, it is preferable to send it to alkylation reactor 153. Similarly the heavy Fischer naphtha can be isomerized by introducing it into isomerizer 151 via pump 190, valve 191 and line 62 but I prefer to aromatize this heavy naphtha as will hereinafter appear. Hydrogen chloride or other promoter is likewise introduced into isomerizer 151 by means of valved line 192.

The optimum conditions existing in isomerization reactor 151 are influenced to some extent by the nature of the charge to the isomerization reaction and by the nature of the desired products as well as by the precise catalyst chosen. However, in general these conditions include a temperature of from about 100° F. to about 450° F., for instance 280° F. and a pressure sufficient to maintain at least a substantial portion of the charge in the liquid phase. While aluminum chloride is the preferred catalyst, aluminum bromide and other polyvalent metallic halides can be used and the aluminum chloride or other metal halide forms a complex in the course of the reaction, which complex in all probability acts as the actual catalyst.

It is desirable to introduce hydrogen into isomerization reactor 151 in order to improve catalyst life, and the partial pressure of the hydrogen in the reactor can suitably be from about 50 to about 1500 or more pounds per square inch, for instance about 1000 pounds per square inch. The lower the temperature, the lower should be the hydrogen partial pressure. In connection with my process, the hydrogen fed to the isomerization reactor preferably comes from the aromatization operation via valve 193, lines 194 and 195, valve 196, compressor 197 (if required), and lines 198 and 62. Alternatively it can come from the Fischer synthesis gas (particularly if the aromatization step is omitted) via line 102, valve 102a, line 195, valve 199, compressor 197 and lines 198 and 62. This synthesis gas contains, of course, carbon monoxide as well as hydrogen but it can nevertheless be used effectively in the isomerization reactor. Alternatively, however, synthesis gas from line 102 can be passed through a carbon monoxide removal step shown diagrammatically as purifier 200 by closing valve 102a and opening valves 201 and 202. This carbon monoxide purification can, for example, be carried out by oxidation of the carbon monoxide to carbon dioxide with steam followed by the removal of the carbon dioxide by some such means as absorber 85 and related elements.

Various types of isomerization reactors can be used, for instance a tubular reactor or a vessel equipped with an agitator as in the case of alkylation reactor 153. However, as shown, the charge is fed to a tower 151 which can be a bubble tower, packed tower, or baffle tower and is therein agitated with the aluminum chloride complex or other liquid catalyst entering through conduit 203. The products pass overhead through line 204 to separator 205 in which any entrained catalyst together with some of the heavier product liquid settles out and returns to the isomerizer through valved conduit 203. The catalyst reaching the bottom of the isomerizer tower is removed by means of pump 206 and passed through valve 207 to regenerator 208 and thence back to isomerizer 151 through line 209, separator 205 and conduit 203. Regeneration can be accomplished by hydrogenation or by decomposition and rechlorination or by electrolytic or other means. However, this regeneration does not constitute a part of the present invention and is merely indicated diagrammatically. From time to time fresh catalyst must be added and this is accomplished by means of valved line 210. Similarly spent catalyst can be removed through valved line 211.

The reaction liquid from isomerizer 151 passes into separator 205 and, as previously mentioned, the liquid catalyst separates out as a lower liquid phase and is returned under the control of the valve in conduit 203. The hydrogen and other fixed gases likewise separate at the top of separator 205 and are recycled by means of compressor 212 and lines 198 and 62. The liquid isomerization product passes through line 213 to a wash tower 214 where residual hydrogen chloride is removed by an alkaline and/or water wash, the wash liquid being introduced by valved line 215 and withdrawn through valved line 216. The washed product then passes through line 217 to fractionating tower 218 where it is preferably divided into three fractions. This tower is heated at its base by reboiler coil 219.

A light fraction is removed from tower 218 via line 220 and passed through condenser 221 to separator 222 from which a portion of it is returned to the top of the tower as reflux by means of pump 223, valve 224 and line 225, and the remainder, consisting largely of four carbon atom hydrocarbons and rich in isobutane, is preferably cycled through valve 226 and lines 227, 157 and 142 to alkylation reactor 153 and normally constitutes the main part of the iso-paraffin fed to the alkylation reaction.

The intermediate cut from fractionating tower



218 is withdrawn from trapout plate 228 and is used as a component of high grade motor fuel. This fraction is composed wholly or largely of hydrocarbons having from five to seven carbon atoms per molecule and is rich in branched chain hydrocarbons of high antiknock value. This fraction passes to storage tank 229 through line 230 and can be blended therein or otherwise with the isoheptane or isooctane fraction from the alkylation step and preferably also with the aromatic hydrocarbons produced in the aromatization reaction, as will hereinafter appear.

Reverting to fractionating column 218, the heaviest fraction is preferably recycled to isomerizer 151 by means of line 231, pump 111 and line 62. This heavy fraction tends to break down into lighter compounds in the presence of the butane which is likewise introduced into isomerizer 151 and the process converts the heavy hydrocarbons charged to it in large measure into valuable motor fuel components and isobutane for use in the alkylation reaction.

The process as thus far described converts into valuable motor fuel components practically all of the original well fluids with the exception of hydrocarbons boiling between the boiling point of the seven carbon atom hydrocarbons and the gasoline end point which is typically in the neighborhood of 400° F. These hydrocarbons can be utilized most effectively and efficiently by raising their antiknock value without any radical change in their volatility, thereby producing a final motor fuel of balanced distillation range and of uniformly high antiknock quality throughout its distillation range. These heavy naphtha hydrocarbons from the Fischer synthesis and also from the distillate recovery operation, if such operation is utilized, constitute an extraordinarily effective charge for a catalytic aromatization process.

Processes of this latter type are sometimes referred to as catalytic reforming in the presence of hydrogen or as dehydroaromatization processes. They are also sometimes popularly described as hydroforming processes. These processes are conducted in the presence of added hydrogen but nevertheless produce hydrogen since they operate by transforming naphthenic, olefinic and paraffinic hydrocarbons into aromatic hydrocarbons with resultant dehydrogenation. In the present instance the charge is almost exclusively paraffinic and thus very substantial amounts of hydrogen are produced. Nevertheless the addition of hydrogen is essential in order to direct the reaction and particularly in order to prolong catalyst life.

Catalytic aromatization as contemplated in connection with the present invention is carried on in the presence of metal oxide catalysts and more particularly catalysts made up of oxides of one or more metals selected from the left hand columns of groups IV, V and VI of the periodic table. These oxides, preferably vanadium oxide, chromium oxide or still better molybdenum oxide, are most effective when supported on alumina. Thus, for instance, one particularly suitable catalyst is made up of about 8% molybdenum oxide precipitated on the surface of activated alumina. Reaction conditions are critical and include a pressure of from about 50 to about 450 pounds per square inch, for instance about 250 pounds per square inch, a temperature of from about 850 to about 1025° F., for instance about 975° F., a space velocity of from about 0.04 to about 10 volumes of charge measured as liquid per gross

volume of catalyst per hour, for instance about 0.7 volume per volume per hour. The volume of catalyst referred to above is the volume which the catalyst would occupy at rest or in a pelleted or compacted condition. The amount of hydrogen used should range from about 1 to about 10 mols per mol of charge, for instance about 2 mols of hydrogen per mol of charge.

This catalytic aromatization reaction can be carried out with the catalyst in a fixed bed or a moving bed but, as shown, it is carried out by the use of an upflow reactor in which the flow velocity is adjusted to obtain a phenomenon sometimes known as hindered settling in which the catalyst is maintained in a state of agitation resembling in appearance a boiling liquid. Typically this flow velocity is from 0.2 to about 3.0 feet per second, for instance 1.0 foot per second. These velocities are for finely powdered catalyst and the velocity used will vary with the particle size of the catalyst. The velocity should be high enough to avoid "bridging" of the catalyst, but low enough to maintain a dense catalyst suspension phase in the reactor.

Turning more particularly to the flow diagram, the heavy naphtha from the Fischer process passes through pump 190, valve 232 and lines 233 and 64 into coil 234 of aromatization furnace 235. Heavy naphtha from the distillate recovery operation, if any, passes through pump 63 and joins the Fischer heavy naphtha in line 64 and passes with it through coils 234 and 236 in furnace 235 and thence through transfer line 237 into upflow reactor 238. In this reactor the naphtha meets a stream of hydrogen which is preferably part of the hydrogen produced in the process recycled by means of valve 239, compressor 240, line 241 and coils 242 and 243 of furnace 235. Alternatively, the hydrogen and charge can be heated together but better control can be obtained by heating them in separate coils.

As shown, the hot hydrogen is sent through valved line 244 and picks up regenerated catalyst from standpipe 245 and then enters the base of the reactor. A portion of the hydrogen can likewise be passed through valved line 246 and serves to introduce further catalyst into the reactor from standpipe 247. This latter catalyst is recycled without regeneration since in general in this process catalyst can effectively be passed through the reactor more than once before regeneration is required. Furthermore, in order to maintain the desired "fluid" conditions within reactor 238 a high ratio of catalyst to oil fed to the reactor is required and this can effectively be maintained by recycling a portion of the catalyst without regeneration, thereby reducing the load on the regeneration system.

The upflowing catalyst for reaction gases passes through throat 248 to deflector 249 which causes the bulk of the catalyst to precipitate on top of baffle 250. Further means can be utilized to recover residual catalyst including cyclone separators located in the separation zone of the reactor and Cottrell precipitators but these have been omitted in the interests of simplicity. A portion of the catalyst passes through standpipe 251 to conduit 252 where it is picked up in a stream of air introduced through valved line 253 and passed to a regenerator 255 which is preferably of the upflow hindered settling type as described previously. The amount of air introduced is such as to oxidize the carbonaceous deposits on the catalyst and thus restore the catalyst activity but is insufficient to cause overheat-

ing with consequent deleterious effect on the catalyst. Since the upflow type of reactor gives good heat distribution with practically no temperature gradients, the problems of local hot spots usually encountered in other oxidation and revivification systems is avoided.

As in the case of reactor 238, a portion of the catalyst reaching the top of regenerator 255 is cycled via standpipe 256 back to the regenerator while another portion passes through standpipe 245 and is picked up by the stream of hydrogen and introduced into reactor 238 as previously described. The catalyst passing through standpipe 256 can advantageously be cooled by cooler 257. The catalyst in standpipes 245, 247, 251 and 256 is maintained in aerated condition by introducing small amounts of gas through valved lines 258. As previously described, the flue gas from regenerator 255 can suitably be passed through lines 99, 97, 98 and 84 and stripped of its carbon dioxide in absorber 85, thereby augmenting the supply of carbon dioxide for use in connection with the manufacture of synthesis gas for the Fischer process.

Returning to reactor 238, the products after catalyst removal pass through line 259 and condenser 260 to separator 261 and the hydrogen remaining uncondensed along with some contaminants passes in part back to the aromatization process and in part to the so-called paraffin isomerization process via valve 193, lines 194 and 195, valve 196, compressor 197 and lines 198 and 62. Also, as previously mentioned, a portion of this hydrogen can be used as part of the synthesis gas for the Fischer reaction, being sent to Fischer reactor 75 as hereinabove described. Excess hydrogen, if any, can be vented through valved line 262.

The liquid from separator 261 passes through line 263 into fractionating tower 264 which serves to separate the aromatization products into the desired fractions. This aromatization product contains a very small amount of the C<sub>2</sub> and C<sub>3</sub> hydrocarbons and the former can suitably be used in the manufacture of synthesis gas for the Fischer process being sent to the reformer coils 73 and 74 from the top of fractionator 264 through lines 265, 172 and 66. This gas can also be used as fuel for furnace 67 and/or 235 using valved line 76 in the first instance and valved line 266 in the second.

The four carbon atom hydrocarbons are taken off from tower 264 through trapout plate 267 and can suitably constitute part of the feed to the so-called paraffin isomerization process passing to that process through pump 268 and lines 269, 270, 189 and 62. Any five carbon atom hydrocarbons present in the products from the aromatization reaction can, if desired, also be sent to this isomerization process and this is desirable since five carbon atom hydrocarbons cannot be aromatized but do form branched chain hydrocarbons of high antiknock value in the isomerization reaction. Care should be taken, however, that no aromatics are cycled to the isomerization process since they poison the catalyst.

Aromatization products heavier than C<sub>5</sub> and within the motor fuel distillation range, say up to 400° F., can be utilized in the manufacture of automotive and aviation motor fuels in various ways. Thus a cut rich in hydrocarbons having six and seven carbon atoms per molecule is particularly desirable for use in aviation gasoline of extremely high knock rating. A fraction of this type can be withdrawn from trapout plate 271 75

and passed through line 272 to storage tank 273 for blending with an isooheptane and/or isooctane fraction from the alkylation operation, contained in tank 274, and/or with a branched chain fraction from the so-called paraffin isomerization operation, contained in tank 229. This blending can be accomplished using super aviation gasoline tank 275, pump 276, line 277 and valved lines 278, 279 and 280.

The fraction from the aromatization operation which contains the xylenes and heavier components within the gasoline range can suitably be withdrawn from trapout plate 281 through line 282 and introduced into storage tank 283 for subsequent blending in the manufacture of high grade gasoline engine motor fuels since these heavier aromatics are somewhat inferior to the highly branched paraffins of like boiling point when used in high temperature engines such as are increasingly typical of aviation practice.

The aromatization reaction produces a small quantity of hydrocarbons heavier than gasoline and these are often referred to as "polymer." Also when hydrocarbons heavier than gasoline from the distillate recovery process are charged to the aromatization step, they are aromatized and form a part of the heavy product. This heavier-than-gasoline aromatized fraction constitutes an extremely effective absorption medium for use in connection with distillate recovery by high pressure absorption and all or a portion of this fraction can thus suitably be withdrawn from tower 264 by means of trapout plate 284 and directed through line 285, valve 286, pump 287, lines 288 and 17, heat exchanger 18 and cooler 19 into absorber 10. The remainder can be passed through valved line 289 to polymer storage tank 290 and can subsequently be used in various ways suitable for highly aromatic materials of this boiling range.

Any small amount of catalyst passing overhead from reactor 238 finds its way to the base of fractionating tower 264 and can be recycled along with any extremely heavy hydrocarbons back into the aromatization reactor by means of pump 291, lines 292, coils 234 and 236 and transfer line 237.

While I have described my invention in connection with certain preferred embodiments thereof, it is to be understood that these are by way of illustration and not by way of limitation and I do not mean to be restricted thereto but only to the scope of the appended claims.

I claim:

1. A method for manufacturing high quality motor fuel comprising passing well fluids produced by a well of the distillate type into an absorption zone at high pressure, contacting said well fluids in said absorption zone with a heavy absorber oil comprising aromatic hydrocarbons produced by an aromatization operation, recovering from the rich absorber oil a fraction rich in butanes and a heavy naphtha fraction, compressing a portion of the unabsorbed gases from said absorption zone and injecting same into a subsurface hydrocarbon reservoir, passing a further portion of the unabsorbed gases from said absorption zone to a hydrogen sulfide removal zone and removing hydrogen sulfide from said gases in said last mentioned zone, reacting said purified gases with steam in the presence of a catalyst to produce carbon monoxide and hydrogen therefrom, reacting said carbon monoxide and hydrogen in the presence of a catalyst of the Fischer synthesis type to produce a synthetic crude oil therefrom, fractionating said synthetic

crude oil to produce fractions including a predominantly paraffinic heavy naphtha fraction, passing at least a substantial part of said heavy naphtha fraction from said synthetic crude oil and at least a substantial part of said heavy naphtha fraction recovered from said rich absorber oil to a catalytic aromatization zone and contacting it in said zone with an aromatization catalyst of the metal oxide type in the presence of hydrogen to produce aromatic hydrocarbons and hydrogen, fractionating said aromatic hydrocarbons into at least one gasoline range fraction and at least one heavier-than-gasoline fraction, and cycling at least a substantial part of said last mentioned fraction to said contacting step as said heavy absorber oil.

2. A method for manufacturing high quality motor fuel comprising passing well fluids produced by a well of the distillate type into an absorption zone at high pressure, contacting said well fluids in said absorption zone with a heavy absorber oil comprising aromatic hydrocarbons produced by an aromatization operation, recovering from the rich absorber oil a fraction rich in butanes and a heavy naphtha fraction, compressing a portion of the unabsorbed gases from said absorption zone and passing said compressed gases to a subsurface hydrocarbon reservoir, reacting at least a substantial part of said gases with steam in the presence of a catalyst to produce carbon monoxide and hydrogen therefrom, reacting said carbon monoxide and hydrogen in the presence of a catalyst of the Fischer synthesis type to produce a synthetic crude oil therefrom, fractionating said synthetic crude oil to produce a light fraction rich in olefinic hydrocarbons, a heavy naphtha fraction and a predominantly paraffinic fraction boiling predominantly above the gasoline boiling point range, passing at least a substantial part of said last mentioned fraction and at least a substantial part of said heavy naphtha fraction recovered from said rich absorber oil into a paraffin isomerization zone and contacting it therein with butane to react said predominantly paraffinic fraction with said butane in the presence of a catalyst of the aluminum chloride type to produce isobutane and predominantly branched chain hydrocarbons intermediate in boiling point between said butane and said predominantly paraffinic fraction, passing at least a substantial part of said isobutane together with at least a substantial part of said light fraction from said synthetic crude oil to an alkylation zone and contacting said isobutane and said last mentioned fraction with each other and with a catalyst of the aluminum chloride type to produce a highly branched chain alkylation product together with a normal butane fraction passing through said alkylation zone, passing at least a substantial part of said normal butane fraction and at least a substantial part of said fraction rich in butanes recovered from said rich absorber oil to said isomerization zone as at least a part of the butane contacted in said isomerization zone as aforementioned, passing at least a substantial part of said heavy naphtha fraction from said synthetic crude oil to a catalytic aromatization zone and contacting it in said zone with an aromatization catalyst of the metal oxide type in the presence of hydrogen to produce aromatic hydrocarbons and hydrogen, cycling at least a substantial portion of said produced hydrogen to said paraffin isomerization zone to increase the life of said catalyst of the aluminum chloride

type present in said isomerization zone, fractionating said aromatic hydrocarbons into at least one gasoline range fraction and at least one heavier-than-gasoline fraction, cycling at least a substantial part of said last mentioned fraction to the first mentioned contacting step as said heavy absorber oil, and blending selected gasoline range fractions of the products produced in said alkylation, isomerization and aromatization steps to produce a superior motor fuel of high antiknock value.

3. A method for manufacturing high quality motor fuel comprising passing well fluids produced by a well of the distillate type into an absorption zone at high pressure, contacting said well fluids in said absorption zone with a heavy absorber oil comprising aromatic hydrocarbons produced by an aromatization operation, recovering from the rich absorber oil a fraction rich in butanes and a heavy naphtha fraction, compressing a portion of the unabsorbed gases from said absorption zone and passing said compressed gases to a subsurface hydrocarbon reservoir, passing a further portion of the unabsorbed gases from said absorption zone to a hydrogen sulfide removal zone and removing hydrogen sulfide from said gases in said last mentioned zone, reacting said purified gases with steam in the presence of a catalyst to produce carbon monoxide and hydrogen therefrom, reacting said carbon monoxide and hydrogen in the presence of a catalyst of the Fischer synthesis type to produce a synthetic crude oil therefrom, fractionating said synthetic crude oil to produce a light fraction rich in olefinic hydrocarbons, a heavy naphtha fraction and a predominantly paraffinic fraction boiling predominantly above the gasoline boiling point range, passing at least a substantial part of said last mentioned fraction and at least a substantial part of said heavy naphtha fraction recovered from said rich absorber oil into a paraffin isomerization zone and contacting it therein with butane to react said predominantly paraffinic fraction with said butane in the presence of a catalyst of the aluminum chloride type to produce isobutane and predominantly branched chain hydrocarbons intermediate in boiling point between said butane and said predominantly paraffinic fraction, passing at least a substantial part of said isobutane together with at least a substantial part of said light fraction from said synthetic crude oil to an alkylation zone and contacting said isobutane and said last mentioned fraction with each other and with a catalyst of the aluminum chloride type to produce a highly branched chain alkylation product together with a normal butane fraction passing through said alkylation zone, passing at least a substantial part of said normal butane fraction and at least a substantial part of said fraction rich in butanes recovered from said rich absorber oil to said isomerization zone as at least a part of the butane contacted in said isomerization zone as aforementioned, passing at least a substantial part of said heavy naphtha fraction from said synthetic crude oil and at least a substantial part of said heavy naphtha fraction recovered from said rich absorber oil to a catalytic aromatization zone and contacting it in said zone with an aromatization catalyst of the metal oxide type in the presence of hydrogen to produce aromatic hydrocarbons and hydrogen, cycling at least a substantial portion of said produced hydrogen to said paraffin isomerization zone to increase the life of said catalyst of the aluminum chloride

type present in said isomerization zone, fractionating said aromatic hydrocarbons into at least one gasoline range fraction and at least one heavier-than-gasoline fraction, cycling at least a substantial part of said last mentioned fraction to the first mentioned contacting step as said heavy absorber oil, and blending selected gasoline range fractions of the products produced in said alkylation, isomerization and aromatization steps to produce a superior motor fuel of high anti-knock value.

4. A method for manufacturing high quality motor fuel from a stream of light and heavy hydrocarbon vapors comprising the combination of steps of contacting said stream with an absorber oil comprising aromatic hydrocarbons produced by a catalytic conversion, recovering from the rich absorber oil a heavy naphtha fraction, subjecting at least a substantial part of said heavy naphtha fraction to a catalytic conversion in the presence of a catalyst of the metal oxide type to produce aromatic hydrocarbons, recovering from the conversion products at least one fraction boiling in the motor fuel range and at least one heavy fraction containing substantial amounts of aromatics, and supplying at least a part of said heavy fraction as the absorber oil in the contacting step.

5. A method for manufacturing high quality motor fuel from a mixture of light and heavy hydrocarbon vapors comprising the combination of steps of contacting said mixture with an absorber oil comprising aromatic hydrocarbons produced by subsequent catalytic conversion, recovering from the rich absorber oil a heavy naphtha fraction, recovering an unabsorbed predominantly methane fraction from said mixture and producing a mixture of hydrogen and oxides of carbon therefrom, preparing a synthetic crude oil by catalytic reduction of the oxides of carbon, fractionating the said synthetic crude oil to produce fractions including a predominantly paraffinic heavy naphtha fraction, subjecting at least a substantial part of said paraffinic heavy naphtha fraction from said synthetic crude oil to a catalytic conversion in the presence of hydrogen and a catalyst of the metal oxide type to produce aromatic hydrocarbons, recovering from the conversion products at least one fraction boiling in the motor fuel range and at least one heavy fraction containing substantial amounts of aromatics, and supplying at least a part of said heavy fraction as the absorber oil to the contacting step.

6. A method for manufacturing high quality motor fuel from a stream of light and heavy hydrocarbon vapors comprising the combination of steps of contacting said stream with an absorber oil comprising aromatic hydrocarbons produced by a catalytic conversion, recovering from the rich absorber oil a heavy naphtha fraction, producing a mixture of hydrogen and oxides of carbon from the unabsorbed gases and preparing a synthetic crude oil by catalytic reduction of the oxides of carbon, recovering from the said synthetic crude oil a fraction including a predominantly paraffinic heavy naphtha fraction, subjecting at least a substantial part of said paraffinic heavy naphtha fraction from said synthetic crude oil and said first mentioned heavy naphtha fraction to a catalytic conversion in the presence of hydrogen and a catalyst of the metal oxide type to produce aromatic hydrocarbons, recovering from the conversion products at least one fraction boiling in the motor fuel range and at least one heavy fraction containing substantial amounts of aromatics, and supplying at least a part of said heavy fraction as the absorber oil in the contacting step.

7. A method for manufacturing high quality motor fuel from a stream of light and heavy hydrocarbon vapors comprising the combination of steps of contacting said stream with an absorber oil comprising aromatic hydrocarbons produced by a catalytic conversion, recovering from the rich absorber oil a fraction rich in butanes and a heavy naphtha fraction, producing a mixture of hydrogen and oxides of carbon from the unabsorbed gases and preparing a synthetic crude oil by catalytic reduction of the oxides of carbon, fractionating the said synthetic crude oil to produce fractions including a light olefinic fraction and a predominantly paraffinic heavy naphtha fraction, catalytically alkylating said butanes and said light olefinic fraction to produce hydrocarbons boiling in the motor fuel range, subjecting at least a substantial part of said paraffinic heavy naphtha fraction from said synthetic crude oil to a catalytic conversion in the presence of hydrogen and a catalyst of the metal oxide type to produce aromatic hydrocarbons, recovering from the conversion products at least one fraction boiling in the motor fuel range and at least one heavy fraction containing substantial amounts of aromatics, and supplying at least a part of said heavy fraction as the absorber oil in the contacting step.

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