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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements relating to the Production of Hydrocarbon Motor Fuel

We, PRICESS MANAGEMENT COMPANY, Inc., a Corporation organised under the laws of the State of Delaware, United States of America, of 120, East 41st 5 Street, New York City, New York, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascer-10 tained in and by the following state-

ment:

This invention relates to the production of normally liquid hydrocarbons from a gaseous mixture consisting essentially of 15 carbon monoxide and hydrogen, or from a gaseous stream which can be converted into a mixture consisting essentially of curbon monoxide and hydrogen. More particularly, the invention relates to the 20 production of normally liquid hydrocarbons, including products in the motor fuel boiling range, from normally gaseous hydrocarbons of low molecular weight, such as methane and ethane. More par-25 ticularly, the invention relates to the production of normally liquid hydrocarbons from carbon monoxide and hydrogen and the treatment thereof to produce a gasoline of high anti-knock value.

The normally liquid hydrocarbons pro-

duced by the reaction of carbon monoxide and hydrogen ordinarily include substantial proportions of hydrocarbons in the gasoline boiling range. However, the 35 fraction corresponding to the gasoline boiling range recovered from the synthesis reaction products is very low in antiknock value and therefore generally unsuitable as such as gasoline motor fuel. 40 The treatment of this material by application of clevated conditions of tempera-ture and pressure to improve its anti-knock value results in the production of large quantities of gas and accompanying 45 low recovery of useful products. The improvement in anti-knock value by this means may not justify the losses involved in the process. This may be caused by the relative absence of aromatic constituents

in the reaction products of carbon 50 monoxide and hydrogen, this condition being also responsible, in part at least, for the initial low anti-knock value of the

motor fuel fraction.

The invention contemplates the treat- 55 ment of a gaseous stream consisting of carbon monoxide and hydrogen preferably in the ratio of approximately 1:2 in the presence of a suitable catalyst under known conditions of temperature and pres- 60 sure to cause the synthesis of hydrocarbons including normally liquid hydrocarbons. Normally liquid hydrocarbons thus produced are then treated conjointly with normally gaseous hydrocarbons of 65 two or more carbon atoms per molecule at a temperature of 750°—1500° F, to effect conversion of both to motor fuel of high anti-knock value.

According to one modification of the in- 70 vention a stream of normally gaseous hydrocarbons consisting chiefly of hydro-carbons having 3 and 4 carbon atoms per molecule is heated under conditions of temperature and pressure to promote 75 cracking and conversion to hydrocarbons of greater molecular weight including

normally liquid hydrocarbons.

This may be done by subjecting the gases to conditions of high temperature 80 and low pressure whereby conversion to aromatic hydrocarbons occurs or by sub-jecting them to conditions of high pressure and lower temperature whereby conversion to aliphatic hydrocarbons is the 85 predominating reaction. The gaseous stream so heated is admixed with the reaction products of the carbon monoxidehydrogen reaction whereby the hot gases are cooled and the carbon monoxide-hydrogen 90 reaction products are heated in admixture with the hot gases and their conversion reaction products with the result that the production of undesirably heavy products in the conversion reaction is in- 95 hibited and the carbon monoxide-hydrogen reaction products are improved in quality as motor fuel by conversion re-

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actions which may include cracking, polymerization, dehydrogenation and other reactions

When the gaseous hydrocarbon stream
is heated under high pressure, cracking
and conversion apparently proceed simultaneously, and the carbon monoxidehydrogen reaction products preferably are
added near the end of the heating operation, although a soaking period may be
compleyed thereafter to permit conversion
reactions to proceed and during this
period heat may be applied to maintain
the temperature of the mixture above a

When the gaseous stream is heated to a high temperature under low pressure substantial cracking apparently occurs prior to substantial conversion or polymerization. In this case, therefore, it is preferable to add the carbon monoxide hydrogen reaction products to the heated gaseous stream prior to substantial conversion whereby the heat developed by the subsequent exothermic conversion reactions promotes conversion of normally liquid hydrocarbons to motor fuel constituents of higher anti-knock value and conversion of gaseous hydrocarbons to normally liquid products.

The mixture is thereafter fractionated to separate therefrom gasoline and other liquids, and the remaining gases are fractionated to recover a fraction consisting.

35 essentially of C_s and C₄ hydrocarbons and the remaining gases which may include hydrogen, methane, and any ethane and ethylene undesired in the fraction for thermal conversion may be withdrawn for use in producing the carbon monoxide-

hydrogen mixture. The invention also contemplates, according to another modification of the invention, which may be preferable be-45 cause of its relative simplicity, the separation of a gasoline fraction from the reaction products of carbon monoxide and hydrogen and the subjection of the gasoline fraction to a temperature of 750— 50 1500° F. and elevated pressure in the presence of a substantial proportion of convertible normally gaseous hydrocarbons produced in the process, having three and four carbon atoms per molecule, hereafter 55 referred to as C. and C. hydrorarbons, to effect conversion of the normally liquid and normally gaseous constituents to motor fuel of high anti-knock value. The gasoline fraction and the normally 60 gaseous hydrocarbons may be admixed at a temperature below that at which conversion takes place and the mixture then

heated to the reaction temperature, or the normally gaseous hydrocarbons may be

65 preheated, prior to admixture with the

gasoline fraction, at the reaction temperature. The conditions of temperature and pressure preferably are sufficiently drastic to effect cracking of normally liquid constituents, and the reactions which result 70 in the production of high anti-knock motor fuel probably are, in addition to cracking, polymerization of normally gaseous constituents, dehydrogenation of paraffinic constituents, cyclization of ali- 75 phatic constituents and dehydrogenation of the resulting products to form aromatics, alkylation reactions between gaseous constituents and between gaseous and normally liquid constituents, etc., although the invention is not to be limited by such theoretical considerations. The reaction products are treated to separate therefrom a gasoline fraction and a normally gaseous fraction predominating in 85 C_s and C_s hydrocarbons which are in part least admixed with the normally liquid fraction undergoing conversion treatment as described. C. hydrocarbons and lighter products may be recovered 90 and converted to a carbon monoxide-hydrogen mixture by suitable catalytic oxidation.

The carbon monoxide-hydrogen mixture may be produced in any suitable way, but 95 in the preferred manner of this invention a stream of hydrocarbons, such as methane and ethane, is catalytically exidized to produce a mixture of carbon monoxide and hydrogen in the desired proportions. The 100 raw material will consist ordinarily chiefly of methane because of the relative abundance of that hydrocarbon in natural gas. refinery gases resulting from oil cracking and in lighter cases resulting from the 105 thermal polymerization of higher molecular weight hydrocarbons, any of all of which constitute the preferred raw material for the process of the present invention, although carbon monoxide and 110 hydrogen from any suitable sources may

be employed. The invention contemplates the catalytic oxidation of a gas consisting essentially of methane, ethane, or ethylene to 115 produce a mixture of carbon monoxide and hydrogen. To such a gascous stream undergoing oxidation may be added the gases from the polymerization or conversion reaction products which are un- 120 suitable for recycling to the polymerization or conversion reactions and any similar gases occurring in the reaction products of carbon monoxide and hydrogen, which may include some unconverted 125 carbon monoxide and hydrogen. The catalytic oxidation products of such a mixture may contain too much of one or the other of the desired components so that it may be necessary to provide a separate 130

source of one or the other for addition to the guscous stream after the catalytic oxidation reaction. For example, the gases from the polymerization reaction 5 may contain excess hydrogen whereby the oxidation reaction products will contain hydrogen in excess of the desired proportion. Carbon monoxide from a separate source may therefore be added to adjust 10 the ration of the essential components.

The accompanying drawings are diagrammatic views in elevation of apparatus suitable for carrying out the present invention. The invention will be further 15 described with reference to the specific combodiments illustrated by the drawings but it is to be understood that the invention is not limited thereby but is capable of other embodiments which may be be-20 youd the physical limitations of the apparatus illustrated.

In the drawings, Figure 1 illustrates the modification of the invention last described above and Figure 2 illustrates the

25 first-mentioned modification.

In the preferred embodiment of the invention as illustrated in Figure 1 the carbon monoxide-hydrogen mixture is produced by the catalytic oxidation of hydrogen gases, particularly methane and Ca hydrocarbons, it being understood that the invention is not limited to the treatment of hydrocarbons produced by the reaction of a mixture of carbon monoxide 35 and hydrogen obtained in any particular manner. Referring to Figure 1, a stream of gaseous hydrocarbons predominating in methane and C2 hydrocarbons is introduced to the system through pipe line 1 provided with valve 2. A second pipe line 3 provided with valve 4 is provided for the introduction of oxygen. Lines 1 and 3 join to form line 5, and the mixture of oxygen and hydrocarbon gases suitable to 45 produce the desired mixture of carbon monoxide and hydrogen is produced by suitable manipulations of valves 2 and 4. Line 5 connects with a catalytic oxidation chamber 6 which may consist of a plur-50 ality of tubes arranged in parallel between suitable headers and containing a mixture of 90 parts nickel oxide and 10 parts of a promoter such as thoria on a suitable carrier such as fire clay or mag-55 nesia. The temperature for maximum oxidation will vary with the catalyst employed but ordinarily should be in the range of 900° to 1500° F. Ordinarily atmospheric pressure is employed. The 60 oxidation reaction is only slightly exothermic so that it may be necessary to maintain the reaction temperature by a suitable insulation of the reaction chamher. Preferably, however, the catalyst is 65 suitably maintained in tubes 3 through

which the reaction mixture is passed to permit the passage of heating or cooling fluids as necessary on the outside of the tubes to maintain the desired reaction temperature and to obtain maximum con- 70 tact of the catalyst and gaseous mixtures through the subdivision of the gaseous stream in the plurality of tubes 8 of the oxidation chamber. Preheating of the gaseous mixtures entering oxidation 75 chamber 6 as desired may be effected by the provision of heater 7 in line 5.

The oxidation reaction products emerge from chamber 6 by means of line 9 and may be treated to remove undesirable com- 80 ponents such as sulphur compounds and to adjust the ratio of carbon monoxide to hydrogen, by means not shown. The oxidation reaction products suitably may pass through a heat exchanger 10 located 85 in line 9 wherein they pass in indirect contact with a hydrocarbon stream produced in the system to effect cooling of the uxidation reaction products and heating of the hydrocarbon stream. If necessary 90 they may be further cooled to the exact temperature required for the succeeding operation by passage through cooler 11, also located in line 9.

After emerging from cooler 11 the 95 oxidation reaction products, which consist essentially of carbon monoxide and hydrogen in the desired ratio, are passed through a synthesis chamber 12 for the production of hydrocarbons by the re- 100 action of carbon monoxide and hydrogen.

Synthesis chamber 12 suitably consists of a plurality of tubes 13 arranged in parallel between suitable headers and maintained in a fluid bath which serves 105 the purpose of maintaining the proper reaction temperature. The tubes 13 are preferably rectangular in cross section with one cross sectional dimension greatly in excess of the other whereby a relatively 110 narrow passageway is provided in each. The tubes 13 are provided with a suitable catalyst for the conversion of the carbon monoxide and hydrogen to hydrocarbons. For example, the catalyst may consist of 115 metallic cobalt deposited on a carrier such as kieselguhr together with a promoter such as thoria. The gases should be maintained at a temperature of approximately 365° to 415° R. at atmos- 120 pheric pressure for maximum conversion. The reaction is exothermic, and the tubes 13 are immersed in a bath of oil or other suitable fluid which serves to remove the exothermic heat of reaction. Means not 125 shown are provided to circulate and cool the bath of oil, etc. to maintain the desired temperature.

The rate of this reaction is relatively low whereby it is necessary to provide a 130 relatively long time of contact to secure complete conversion of the carbon monoxide and hydrogen. This may be done by providing a single large chamber 5 or, preferably by providing a plurality of chambers with removal of liquids formed from the stream after passage through each chamber. For purposes of illustration the present drawing includes two such 10 chambers, but it is to be understood that any suitable number may be employed without departing from the method of

, operation illustrated.

The reaction products from synthesis 15 chamber 12 may be withdrawn therefrom through line 14 which connects with a fractionator 15. In fractionator 15 conditions of temperature and pressure may be maintained to effect condensation of normally liquid hydrocarbons and a desired portion of the normally gaseous hydrocarbons. To facilitate fractionation superatmospheric pressure may be maintained in fractionator 15. In this case a compressor 16 is provided in line 14 to force the gases therein into the fractionator 15. Heating means such as a heating coil 17 and cooling means such as cooling coil 18 may be provided in the bottom and top, respectively, of fractionator 15 to effect the desired separation.

The gases uncondensed in fractionator 15 are withdrawn from the upper portion of fractionator 15 through line 19 prosided with control valve 20. Heating means 21 is interposed in line 19 to the desired reaction temperature, of from about 365° to 415° F. Beyond heating means 40 21 line 19 connects with a second synthesis chamber 22 which may be identical

in construction with synthesis chamber 12 including the same type of catalyst in a plurality of tubes so that no detailed de-45 scription of this chamber will be given. Synthesis chambers 12 and 22 represent the first and last of a series of such chambers which may exceed two in number.

the additional chambers being connected 50 in series between chambers 12 and 22 with provision for removal of liquid products after each chamber in the manner illustrated in connection with chamber 12.

The reaction products are withdrawn 55 from chamber 22 through line 23 and consist of any unreacted hydrogen and carbon monoxide, normally liquid hydrocarbons formed in chamber 22, normally gaseous hydrocarbons formed in chamber 60 22 and normally gaseous hydrocarbons formed in chamber 12 and not removed by condensation in fractionator 15. Line 23 connects with a fractionator 24, and the

reaction products from chamber 22 are in-65 troduced therein for separation as desired. Superatmospheric pressure may be employed in fractionator 24 to facilitate the desired separation, and in this case a compressor 25 is provided in line 23 to force the reaction products from line 23 into 70 fractionator 24. Line 26 provided with a pump 27 connects the bottom of fractionator 15 with an intermediate point in fractionator 24 whereby the liquid fraction separated in fractionator 15 is intro-75 duced into fractionator 24 for further treatment therein.

In contrast with the conditions obtaining in fractionator 15 fractionator 24 is maintained under conditions of tempera- 80 ture and pressure suitable to effect separation and collection of a liquid fraction consisting of those reaction products belling above the boiling range of the frac-

tion desired for further treatment in the 85 process to produce a high anti-knock motor fuel. For example, fractionator 24 may be operated under conditions suitable to effect condensation and separation of constituents boiling substantially above 90

400° F., or the fractionator may be operated to effect the passage overhead of a gaseous and vaporous mixture including an appreciable proportion of constituents boiling above 400° F. In any case, how- 95

ever, the mixture of vapors and gases passing overhead from fractionator 24 should be limited in the amount of material higher boiling than 400° F. whereby a normally liquid condensate 100 produced therefrom contains not more

than a small proportion of constituents boiling above the gasoline boiling range. To effect the desired fractionation of the reaction products introduced into fractionator 24 through lines 28 and 26, heating means such as heating coil 28 and

cooling means such as cooling coil 29 may be provided in the lower and upper portions, respectively, of fractionator 24. The 110 liquid condensate which collects in the hottom of fractionator 24 may be withdrawn therefrom and from the system for

drawn therefrom and from the system for further treatment elsewhere through line 30 provided with valve 31.

The vaporous and gaseous fraction passing overhead from fractionator 24 is withdrawn therefrom through line 32 provided with control valve 33. Line 32 connects with a fractionator 34 wherein the said 120 gaseous and vaporous fraction is treated to effect the separation and collection therein of a normally liquid fraction desired for further treatment in accordance with the process of the invention. Ordinarily the 125 liquid fraction condensed in fractionator 34 will include substantially all the constituents introduced therein which are in

stituents introduced therein which are in the motor fuel boiling range and may include normally gaseous hydrocarbons such 130 as C_s and C_s hydrocarbons in substantial proportions. However, if desired, the liquid condensate separated in fractionator 34 may be limited to liquids in the 5 upper portion of the gasoline boiling range. For example, the liquid condensate may be limited to exclude substantially all constituents boiling below 300° F. To effect the desired separation heating means such as heating coil 35 and cooling means such as cooling coil 36 may be provided in the bottom and top, respectively, of fractionator 34.

The disposal of the uncondensed frac-

15 tion from fractionator 34 will depend upon the conditions of operation of fractionator 34. The uncondensed gases and any accompanying uncondensed vapors are withdrawn from fractionator 34 through line 37 provided with control valve 38. When the conditions of operation of fractionator 34 are controlled to effect inclusion in the liquid fraction of substantially all convertible normally 25 gaseous hydrocarbons such as C₂ and C₄ hydrocarbons the remaining gases taken

drawn from the system for use elsewhere, for example, as fuel; or since these gases 30 consist essentially of methane and C. hydrocarbons and may include unreacted carbon monoxide and hydrogen all or a portion thereof may be diverted from line 37 through line 39 provided with valve

everhead through line 37 may be with-

35 40. Line 39 connects with line 5 whereby the mixture of hydro-carbon gases and carbon monoxide and hydrogen are admixed with the oxygen-hydrocarbon mixture in line 5 for passage to oxidation 40 chamber 6. Suitable adjustment of the

or the proportions of hydrocarbon gases and oxygen introduced through lines 1 and 3, respectively, may be effected by means of valves 2 and 4 to maintain the proper ratio 45 of oxygen and hydrocarbon gases being

introduced into exidation chamber 6.

When fractionator 34 is operated to effect condensation and collection of a liquid consisting substantially essentially 50 of normally liquid hydrocarbons, leaving substantial proportions of C₂ and C₄ hydrocarbons uncondensed, the gases passing through line 37 may be diverted wholly or in part through line 41 prostided with valve 42. Line 41 connects with a fractionator 43 wherein the gases are fractionated to effect separation of a condensate, consisting of convertible hydrocarbons such as C₂ and C₄ hydrocarbons together with any desired proportion of the C₂ hydrocarbons. To effect the desired fractionation heating means such as heating coil 44 and cooling or liquefaction means such as cooling coil 45

65 may be provided in the bototm and top,

respectively, of fractionator 43. Gases uncondensed in fractionator 43 are withdrawn overhead therefrom through line 46 provided with control valve 47. These gases may be withdrawn from the system 70 for use elsewhere, for example, as fuel; or all or a portion thereof may be returned to the process through line 39 as described above by diversion through line 48 which is provided with a valve 49 and connects 79 lines 46 and 39.

When fractionator 34 is operated to effect condensation and collection of a liquid consisting substantially essenti-ally of the relatively high boiling constituents of the motor fuel fraction, for example, those boiling above 300° F., the uncondensed portion withdrawn through line 37 will contain a substantial proportion of the motor fuel product of the process. To provide separate recovery of this portion of the motor fuel product a separate fractionator 50 is provided. Fractionator 50 is connected with line 37 by means of line 51 which is provided with a valve 52. Line 51 connects with fractionator 50 at a middle point thereof and with line 41 at a point between valve 42 and line 37. By closing valve 42 and opening valve 52 the overhead product from fractionator 34 passing through line 41 is diverted to fractionator 50. In fractionator 50 conditions of temperature and pressure are maintained to effect the separation of that portion of the vapors de- 100 sired in the motor fuel product. Fractionator 50 may be provided with heating means such as heating coil 53 and cooling means such as cooling coil 54 in the bottom and top, respectively, thereof to effect 105 the desired fractionation. Gases uncondensed in fractionator 50 are withdrawn therefrom through line 55 provided with valve 56. Line 55 connects with line 41 between valve 42 and fractionator 43 110 whereby the latter may be used to effect separation in the manner described above of convertible gaseous hydrocarbons from the mixture passing through line 55. The gasoline constituents collected as liquid in 115 the bottom of fractionator 50 are with-drawn therefrom through line 57 provided with a valve 58.

The liquid motor fuel fraction col-

The liquid motor fuel fraction collected in the bottom of fractionator 34 is 120 withdrawn therefrom through line 59 by means of pump 60 located in line 59 for further treatment in accordance with the process of the invention. Line 59 includes heat exchanger 10 whereby the normally 125 liquid fraction is preheated by heat exchange with the hot oxidation reaction products from chamber 6. Line 59 connects with the inlet of a heating coil 61 located in a furnace 62. If desired a heat 130

exchanger 63 may be provided in line 59 whereby the material passing there through is further preheated by heat exchange with the hot reaction products 5 passing from coil 61. Preferably, coil 61 is arranged in the furnace with a preheating section 61a, a radiant heating section 61b and a soaking section 61c in order to provide the desired application of heat to 10 the material passing therethrough. In accordance with the present invention normally gaseous hydrocarbons containing 2 or more carbon atoms, preferably C_s and C. hydrocarbons containing substantial 15 proportions of clefinic constituents, are admixed with the liquid products of the carbon monoxide-hydrogen reaction before or during the heat treatment provided in coil 61. If desired these gaseous 20 hydrocarbons may be admixed with the liquid material passing through line 59 prior to passage through heat exchanger For example, they may be introduced through line 64 which connects line 59 25 with a source to be described below. the gaseous hydrocarbons may be introduced into line 59 just previous to the passage of the liquid hydrocarbons through heat exchanger 63. For example, 80 the gaseous hydrocarbons may be introduced to line 59 through line 65 which connects line 59 with a source to be described below. If desired the gaseous hydrocarbons may 35 be separately preheated before admixture with the normally liquid hydrocarbons in line 59. For example, gaseous hydrocarbons may be introduced by means of line 66 to the inlet of a separate heating 40 coil 67 located in a convection section of The preheated normally furnace 62. gaseous hydrocarbons emerge from the outlet of coil 67 through line 68 which connects with line 59 near the inlet of coil 45 61. If desired, all or a portion of the preheated gaseous hydrocarbons from line 68 may be diverted through line 69 which connects line 68 with heating coil 61 at a point between preheater section 61a and 50 radiant heating section 61b. Valves 70 and 71 may be provided in line 68 and 69, respectively, to afford the desired distribution of the preheated gaseous hydrocarbons to line 59 or through line 69. In 55 the passage of the mixture of normally liquid and normally gaseous hydrocarbons through sections 61b and 61c of coil 61 they are heated to a temperature of 750-1500° F. sufficient to effect conversion of 60 the gases to gasoline motor fuel constituents of high anti-knock value and conversion of normally liquid hydrocarbons to motor fuel constituents of improved anti-knock value. They may be heated to 65 a temperature of 950° to 1200° F., for example 1050° F., at a pressure of 400 to 3000 pounds per square inch, for example 1000 pounds per square inch, for a time sufficient to effect the desired conversion.

The outlet of the soaking section 61s which constitutes the outlet of coil 61 connects to line 72 through which the conversion reaction products from coil 61 are withdrawn. Line 72 includes heat exchanger 63 whereby the hot reaction products are partially cooled by heat exchange with the fresh feed passing through line 59. Partially cooled reaction products may be further cooled by passage through heat exchanger 73 located in line 72 and also, if necessary, by further means such as cooler 74 also located in line 72. It is to be understood, however, that the specific means of cooling the hot reaction products shown are merely for purposes of illustration, and other means such as the injection of cooling liquids directly into line 72 may be employed. Line 72 connects with an evaporator 75 which may be operated at the same pressure as maintained in coil 61 or at a reduced pressure, control valve 76 being provided in line 72 to effect any desired reduction.

In separator 75 the reaction products 98 are separated into a heavy condensate and uncondensed vapors and gases. The pre-liminary cooling of the reaction products and the operation of separator 75 are controlled to effect condensation and separa- 100 tion of relatively high-boiling liquids. For example, the material collected in separator 75 may have an initial boiling point of 600° to 650° F. To assist in the desired separation heating means such as 10: a heating coil 77 may be provided in the lower portion of separator 75. Suitable baffle means may be provided in the upper portion of separator 75 to remove liquids entrained in the uncondensed vapors and II(gases. The condensate collected in the bottom of separator 75 is withdrawn therefrom through line 78 which is provided with control valve 79. This material may be used elsewhere, for 116 example, as fuel.

Vapors and gases uncondensed in separator 75 are withdrawn therefrom through line 80 which may be provided with control valve \$1. Line 80 connects with a 120 fractionator 82 wherein the mixture of gases and vapors is treated to effect separation therefrom of normally liquid constituents higher boiling than the desired motor fuel product and undesired for inclusion therein. This liquid condensate collects in the hottom of fractionator 82 and is withdrawn therefrom through line 83 provided with a valve 84. This material may be subjected to further 130

treatment elsewhere as desired. For example, it may be subjected to elevated conditions of temperature and pressure to convert it to gasoline motor fuel. Heat-5 ing means such as heating coil 85 may be provided in the lower portion of frac-tionator 82 to assist in the desired fractionation. Also cooling means such as the introduction of reflux material in the 10 upper portion of fractionator 82 through

line 86 may be provided. The vapors and liquids uncondensed in fractionator 82 are withdrawn therefrom through line 87 which is provided with 15 control valve 88. Line 87 contains a cooler 89 and connects with a collector 90. In cooler 89 the gases and vapors are cooled to effect liquefaction of constituents desired for inclusion in the motor fuel 20 product of the process. In collector 90 separation of liquids and uncondensed material is effected, the latter being withdrawn through line 91 provided with control valve 92 and the liquids being with-25 drawn through line 98 provided with con-trol valve 94. A portion of the liquids in line 93 may be diverted therefrom for return as reflux to fractionator 82 through line 86 which connects with line 93 and is

80 provided with a pump 95. The gases separated in collector 90 and withdrawn therefrom through line 91 ordinarily consist of normally gaseous constituents including C₂ and lighter 35 hydrocarbons as well as some C4 hydrocarbons. These gases preferably are treated to effect separation therefrom of convertible constituents for further treatment in accordance with the process of 40 the invention. For example, all or a portion thereof may be diverted from line 91 through line 95 provided with valve 96; or all or a portion thereof may be diverted from line 91 (hrough line 97 provided with 45 a valve 98. Line 97 connects with line 5 whereby the gaseous hydrocarbons passing there through are admixed with the oxygen-hydrocarbon stream passing through line 5 to oxidation reaction 50 chamber 6. Suitable adjustment of the proportions of hydrocarbon gases and oxygen introduced through lines 1 and 3, respectively, may be effected by means of valves 2 and 4 to maintain the proper 55 ratio desired in the oxidation reactants.

Line 95 connects with the mid-point of a fractionator 99 wherein temperature and pressure conditions are maintained to effect separation of a condensate consist-60 ing of convertible normally caseous hydrocarbons such as C₃ and C₄ hydrocarbons. If necessary a compressor 100 may be provided in line 95 to transfer the gases through line 95 into fractionator 99. 65 fractionator 99 fractionation is effected by

means of any suitable heating means such as heating coil 101 provided in the lower portion of fractionator 99 and cooling means such as cooling coil 102 provided in the upper portion thereof. The uncondensed gases, which consist of methane, hydrogen and any C. hydrocarbons undesired in the condensate in fractionator 99 are withdrawn therefrom through line 103 provided with control valve 104. These gases may be withdrawn from the system for use elsewhere, for example, as fuel; or all or a portion thereof may be diverted from line 103 through line 105 provided with valve 106. Time 105 connects line 108 with line 97 whereby the uncondensed gases from fractionator 99 may be passed to admixture with the oxidation reactants in line 5 as described above.

The condensate which collects in the 85 bottom of fractionator 99 will consist for the most part of normally gaseous convertible hydrocarbons such as C, and C. hydrocarbons and will include substantial proportions of olefins formed as a result of the reactions occurring in coil 61. This material is withdrawn from fractionator 99 through line 107 provided with control valve 108. Line 66 which connects with the inlet of coil 67 and includes heat exchanger 73 connects at its other end with line 107 between fractionator 99 and valve 103. Line 66 is provided with a control valve 109 and a pump 110 whereby, by manipulation of valves 108 and 109, any 100 desired proportion of the condensate from fractionator 99 may be diverted through line 66 for passage through heat exchanger 73 and coil 67 as described above.

Line 64, which connects with line 59, 105 connects at its other end with line 107 between valve 108 and fractionator 99. Line 64 is provided with a control valve 111 whereby all or a portion of the condensate from fractionator 99 may be ad- 110 mixed with the condensate from fractionator 34, as described above.

The condensate from fractionator 29 withdrawn therefrom through line 107 and undesired for passage through line 64 115 or line 66 may be withdrawn from the system for use elsewhere, for example, as fresh feed to a thermal or catalytic polymerization process. This material is particularly useful for such a process or for 120 processes involving alkylation reactions since it includes substantial proportions of elefining constituents. The decomposition of normally liquid paraffinic hydrocarbons incidental to the treatment of such 125 material in coil 61 promotes the decomposition of normally gaseous paraffinic hydrocarbons admixed therewith whereby the resulting reaction products contain substantial proportions of normally 130

gaseous elefinic hydrocarbons. This promotion effect of the normally liquid hydrocarbons on normally gaseous paraffins may be utilized further by the addition to coil 5 61 through line 127 of paraffinic normally gaseous hydrocarbons such as propane from an extraneous source to effect decomposition thereof.

Line 93 connects with a stabilizer 112 at 10 a plurality of points. Stabilizer 112 is provided with heating means in the lower portion thereof such as heating coil 118 and cooling means in the upper portion thereof such as cooling coil 114 to effect 15 fractination of the motor fuel product

introduced through line 93 and produce a motor fuel containing the desired proportion of light ends and normally gaseous constituents. The stabilized gasoline 20 collected in the bottom thereof is withdrawn through line 115 provided with valve 116 and may be withdrawn to storage. If desired, this material may be

blended with the motor fuel product with-25 drawn from fractionator 50 through line 57 by means of line 117 which is provided with a suitable control valve 118 and con-

nects line 115 and line 57.

The operation of stabilizer 112 will de-30 pend upon the results desired and upon the operation of other parts of the pro-cess. Ordinarily, it will be operated to effect the production of a stabilized motor fuel including the desired proportion of 35 normally gaseous constituents. However, it may be desired to include in the gases passing overhead all normally gaseous constituents and even a portion of the lower boiling normally liquid constituents 40 of the motor fuel product. This latter method is particularly advantageous when the liquid fed to heating coil 61 includes only the heavier portion of the liquid constifuents of the vapors treated in frac-tionator 34 and where it is desired to blend the liquid condensate from stabilizer 112 with the condensate from fractionator 50, which latter condensate will ordinarily maintain an excessive propor-50 tion of light ends.

It may also be advantageous to introduce into stabilizer 112 all or a portion of the condensate from fractionator 50 to effect the production therein of a stabi-55 lized motor fuel. For example, line 119 provided with valve 120 may be provided to connect line 57 with stabilizer 112 at

an intermediate point thereof,

The mixture of gases or gases and 60 vapors produced in stabilizer 112 is withdrawn from the upper portion thereof through line 121 which is provided with a compressor 1221. Line 121 connects with line 66 whereby the gases with accompany-65 ing vapors may be preheated in coil 67

and introduced into coil 61 as described above; or all or a portion of the gases and any accompanying vapours passing through line 121 may be diverted therefrom through line 65 which connects line 70 121 with line 59 as described above whereby the gases so diverted are admixed with the liquids passing through line 59. Valves 122 and 123 are provided in lines 121 and 65, respectively, to provide the 75 desired distribution to lines 66 and 59.

The normally gaseous hydrocarbons separated as a condensate in fractionator 43 may be employed in the process in addition to those produced in fractionator 80 99 or stabiliser 112. For example, the condensate from fractionator 43 may be withdrawn therefrom through line 123 provided with valve 124. Line 123 connects with line 66 between pump 110 and 85 valve 109 whereby the normally gaseous hydrocarbons from fractionator 48 may be passed through line 66 and coil 67 as described above. If desired all or a portion of the normally gaseous hydrocarbons 90 may be diverted from line 128 through line 125 which is provided with a valve 126 and connects with line 59 between pump 60 and fractionator 34 whereby normally gaseous hydrocarbons so diverted 95 are admixed with the condensate with-drawn from fractionator 34 for passage through line 59 to coil 61.

It is to be understood that the various fractionators 15, 24, 34, 43, 50, 82, 99 and 100 112 are provided with suitable gas and liquid contact means such as bubble trays to assist in the desired fractionation. is to be understood, furthermore, that the functions of the fractionators illustrated 105 may be carried out in a lesser number of fractionators with the provision of suitable trap-out trays for withdrawal of side streams. However, for simplification in presenting the subject matter the present 110 arrangement is adopted for purposes of

illustration.

Referring to Figure 2, a gaseous stream which consists essentially of carbon monoxide and methane and may include 115 ethane and ethylene is introduced to the system through line 201 and passes to a catalytic exidation chamber 202 which is provided with a heater 203 for maintaining the proper temperature conditions for 120 the exidation reaction.

The oxidation reaction products emerge from the exidation chamber 202 by means of line 2031 and may be treated to adjust the ratio of carbon monoxide to hydrogen 125 and to remove undesirable components such as sulphur compounds. The oxidation reaction products may suitably pass through heat exchanger 205 wherein they are cooled after which they may be passed 130

through a cooler 206 whereby the exact temperature required for the succeeding operation is obtained. From the cooler 206 the exidation reaction products are 5 passed through a synthesis chamber 207 which suitably consists of a plurality of tubes 208.

The reaction products from synthesis chamber 207 may be withdrawn from 10 chamber 207 through line 209 and will contain unconverted carbon monoxide and hydrogen and hydrocarbons including normally liquid hydrocarbons. This mixture is suitably passed to a cooler 210 15 wherein it is cooled to a temperature sufficient to condense the normally liquid hydrocarbous and any desired portion of the normally gaseous hydrocarbons suitable for polymerization such as hydro-20 carbons having 3 and 4 carbon atoms per molecule. The thus cooled reaction products are passed through line 211 to a fractionator 212 wherein the liquid constituents are collected in the bottom of the 25 fractionator, and the constituents which it is desired to maintain in the gaseous form pass overhead. To facilitate fractionation superalmospheric pressure may be maintained in fractionator 212. In

30 this case a compressor 209a may be provided in line 211 to force the gases therein into the fractionator 212. For example, conditions of temperature and pressure may be maintained in the fractionator 212 35 whereby only the normally liquid hydrocarbons are condensed or whereby a por-

tion of the heavier normally gaseous hydrocarbons such as those having 3 and 4 carbon atoms per molecule are condensed 40 together with the normally liquid hydro-carbons. The uncondensed gases pass overhead from fractionator 212 through line

213 and a cooler 214 wherein they may be cooled to condense a portion thereof 45 after which the stream passes to a separator 215 in which liquefied components are separated and returned to the fractionator 212 as reflux through line 216 by means of pump 217. The uncondensed

gases pass overhead from the separator 215 through line 218 and a heat-exchanger or heater 219 which is provided with a source of heat which suitably may be a steam coil 220.

From the heat exchanger 219 the gases are passed at the desired temperature through line 221 to synthesis chamber 223 which may be identical with synthesis chamber 207. In synthesis chamber 222 60 substantially all the carbon monoxide and

hydrogen remaining in the gaseous stream The reis converted to hydrocarbons. action products may be withdrawn from chamber 222 through line 228.

Reaction products passing from cham-

ber 222 through line 223 may be suitably cooled in cooler 224 and passed through line 225 to fractionator 226 wherein a separation of liquid and gases is obtained. If superatmospheric pressure is main. 70 tained in fractionator 226 a compressor 223a may be provided in line 225. For example, conditions of temperature and pressure may be maintained in fractionator 226 whereby the normally liquid 76 hydrocarbons, and the normally gaseous hydrocarbons suitable for thermal polymerization such as those having 3 and 4 carbon atoms per molecule, are condensed and collected in the bottom of the frac- 80 tionator. The uncondensed gases pass overhead from fractionator 226 through line 227 and cooler 228 wherein partial condensation occurs. The cooled gases are then passed to separator 229 wherein 85 occurs separation of liquefied constituents which are collected and returned as reflux to the fractionator 226 through line 230 by means of pump 231. Uncondensed gases pass overhead from the separator 90 229 through line 232.

Heating means 233 are provided in the bottoms of the fractionators 212 and 226 to maintain the liquids collected therein at the temperature necessary to prevent 95 the inclusion of undesired constituents. The liquids collected in fractionators 212 and 226 are withdrawn therefrom through lines 234 and 235, respectively, and pass through line 236 to admixture with 100 gascous hydrocarbons which have been heated under conditions of temperature and pressure to cause cracking and conversion thereof to hydrocarbons of greater molecular weight.

Simultaneously with the synthesis of hydrocarbons from carbon monoxide and hydrogen in the synthesis chambers 207 and 222, as described above, a stream of normally gaseous hydrocarbons, compris- 110 ingressentially those having 3 and 4 carbon atoms per molecule but including also, if desired, those having 2 atoms per mole-cule, is passed through line 237 to thermal conversion means. These hydrocarbons 115 may consist entirely of those produced in the system or may include hydrocarbons added to the system, through line 238. By means of pump 239 this stream of hydrocarbons is passed through heat exchangers 120 240 and 205 wherein it passes in indirect contact with heated reaction products and serves to cool the reaction products while being itself suitably preheated. The pre-heated gases are then introduced to a 125 heater 241 wherein they are heated under suitable pressure and to a suitable tem-perature to cause cracking of paraffins and to promote conversion to hydrocarbons of greater molecular weight.

The gases may be heated under high pressure to promote the cracking of paraffins and the conversion of a portion of the gases to hydrocarbons of greater 5 molecular weight. Under such conditions the operation of the heater 241 is regulated whereby the gases receive substantially all the heating required to promote conversion within the heater. The heated 10 gases are then mixed with the reaction products from the synthesis of carbon monoxide and hydrogen which are introduced to the gases which emerge from the heater through line 242 by means of line 15 236 which is provided with a pump 292, if necessary, to overcome the pressure maintained in line 242. The resulting mixture is passed through line 243 to a reaction chamber 244 wherein intimate 20 contact of the constituents of the mixture is provided with resulting conversion of the normally liquid hydrocarbons produced by the synthesis of carbon monoxide and hydrogen, and conversion of normally 25 gaseons paraffins and olefins together with cooling of the hot gases to inhibit the production of undesired heavy products. The reaction chamber 244 may be dispensed with and the carbon monoxide-30 hydrogen reaction products admixed with the hol gases within the heater 241 in a portion of the coil located within a cooler part of the heater. If necessary, heat may be

applied externally to the reaction cham-35 ber 244 to maintain the temperature of the mixture therein above a desired minimum.

Under the conditions of operation, just mentioned above the heater 241 may be 40 operated to provide a temperature of 750° to 1100° F, in the hot gases leaving the heater under a pressure of 750 to 3000 pounds per square inch. The heater 241

may be operated under different conditions
45 to produce conversion products having
different characteristics. For example,
the heater 241 may be operated at a higher
temperature, for example, 1200° to 1500°
F. and at lower pressure, for example, 0 to

50 200 pounds per square inch to produce conversion products in which aromatic constituents predominate. Under these conditions of operation the heater 241 may be operated whereby the gases emerge 55 from heater 241 through line 242 before substantial conversion, such as polymerization of olefins, occurs. The heated gaseous hydrocarbons from such high-temperature.

low-pressure operation are then mixed 60 with the products from the synthesis of carbon monoxide and hydrogen in chambers 207 and 222 passing through line 236 which is provided with a pump 292. The resulting mixture is passed through line 65 243 to a reaction chamber 244 wherein the

exothermic heat of conversion maintains the mixture at temperatures between 750° F. and 1500° F. sufficiently high to effect conversion of liquid products of the carbon monoxide-hydrogen reaction to motor fuel 70 constituents of improved anti-knock value and the conversion of normally gaseous hydrocarbon products of the carbon monoxide-hydrogen reaction to normally liquid products.

liquid products.

The use of a reaction chamber, such as chamber 244, is not essential, if it is desired that the conversion reaction takes place in a portion of the coil of the heater. 241 located in a cooler part of the heater. In that case the relatively cool material passing through line 236 is introduced in the furnace into the coil at an intermediate point whereby the combined streams thereafter pass through a cooler part of the heater. If desired, the carbon monoxide-hydrogen reaction products may be preheated in heater 236a located in line 236 prior to admixture with the hot gases from heater 241 by heat exchange, for example, with hot gases or liquids from another

part of the system. The reaction products, including fixed gases, relatively heavy normally gaseous hydrocarbons, and normally liquid hydro- 95 carbons resulting from the synthesis of carbon monoxide and hydrogen and the conversion of normally gaseous hydro-carbons, emerge from the reaction chamber 244 through line 245 which, if neces- 10 sary, is provided with a pressure release valve 246 whereby the pressure on the reaction products is reduced to the desired degree. To reduce the temperature of the reaction products to inhibit further 10. reaction and prevent the formation of undesired heavy products, cooling liquid, such as gas oil, may be introduced into the reaction products before any reduction in pressure, for example, through line 11 247. After any reduction in pressure the reaction products pass through the heat exchanger 240 in indirect contact with the fresh feed for the heater 241 whereby the temperature of the reaction products is 11! further reduced. The reaction products are then passed through a cooler 248 to effect a further reduction in temperature and are then introduced into a third fractionator 249. If the gases are maintained 120 under low pressure in the heater 241 a compressor 245a may be provided in line 245 to force the gases into the fractionator 249 in case it is desired to maintain the fractionator 249 and succeeding fraction- 12: afors under superatmospheric pressure to facilitate fractionation. In the fractionator 249 conditions of temperature and pressure are maintained to liquefy constituents

heavier than those in the gasoline boiling 130

range and permit the passage overhead as a gaseous and/or vaporous stream of the hydrocarbons in the gasoline boiling range and those which are normally gaseous together with any fixed gases. The heaviest oils condensed in the fractionator 249 collect in the bottom thereof and are withdrawn from the system through line 256. A side stream consisting of clean 10 gas oil may be collected in a trap-out tray 251 located above the point of introduction of the reaction products in line 245. A portion of all of the gas oil in the trap-out tray 251 may be withdrawn through 15 line 252 by means of a pump 253 and passed through line 247 to admixture with the hot reaction products. Also a portion of the gas oil from the trap-out tray 251 may be passed through lines 252 and 254 20 to admixture with the hot gases from the heater 241 and the material from line 236. If desired, a portion of the gas oil collected by the trap-out tray 251 may be with-drawn from the system through line 255. The overhead gases in fractionator 249 pass from the fractionator through line 256 and are further cooled by passage through a cooler 257 whereby a portion thereof is liquefied. The cooled gases 30 pass from the cooler 257 to a separator 258 wherein liquefied constituents are collected and are returned to the fractionator 249 as reflux through line 259 by means of a pump 260. The uncondensed 35 hydrocarbons consisting of gasoline, lighter hydrocarbons, and fixed gases pass overhead from the separator 258 through line 261 and a cooler 262 wherein they are further cooled as a preliminary to their 40 introduction to a fourth fractionator 263. In fractionator 263 conditions of temperature and pressure are maintained to accomplish the condensation of the hydrocarbons in the gasoline boiling range and 45 to produce a stabilized gasoline which collects in the bottom of the fractionator 263 and is withdrawn from the system through line 264. The uncondensed gases, which consist of normally gaseous hydro-50 carbons and hydrogen, pass overhead from the fractionator 263 through line 265 and a cooler 266 to accomplish the condensation of a portion theref. The cooled gases are passed from cooler 266 to a separator 55 267 wherein liquefied constituents are collected and returned to the fractionator 263 as reflux through line 268 by means of a pump 269.

The uncondensed gases from the 60 separator 267, consisting of normally gaseous hydrocarbons and hydrogen, pass overhead through line 270 and a cooler 271 to a fifth fractionator 272.

In fractionator 272 conditions of tem-65 perature and pressure are maintained to

accomplish the condensation of the normally gaseous hydrocarbons desired for passage to the conversion heater 241. These ordinarily include the C₃ and C₄ hydrocarbons together with any desired 70 proportion of C₅ hydrocarbons. The condensate collects in the bottom of the fractionator 272 and is withdrawn through line 273 and passed through line 237 to the heater 241 after admixture with any fresh 75 feed introduced to the system through line 238.

The synthesis of hydrocarbons from carbon monoxide and hydrogen may be controlled in the ratio of carbon monoxide to hydrogen to produce reaction products mainly paraffinic in nature or to produce reaction products containing a substantial proportion of olefins. When the reaction products are low in olefinic content 85 it is preferable to operate the fractionators 212 and 226 under conditions of tempera-ture and pressure whereby normally liquid products are condensed therein and collected for passage through line 236 as 90 a cooling medium for the hot gases from the heater 241 and whereby normally gaseous hydrocarbons together with unconverted carbon monoxide and hydrogen pass overhead from fractionators 212 and 25 226 through lines 218 and 232, respectively.

When the reaction products of the synthesis of carbon monoxide and hydrogen are relatively rich in olefins it may be desired to condense all or a portion of the normally gaseous hydrocarbons, such as the C₂ and C₄ hydrocarbons, together with the normally liquid reaction products in the fractionators 212 and 226 for passage 105 through line 236 to admixture with the hot gases from the heater 241 whereby the normally gaseous clefins may be subjected to conditions promoting their conversion to products of higher molecular weight. 110

When the relatively heavy normally gaseous hydrocarbons, such as C_4 and C_4 hydrocarbons, in the reaction products of the synthesis of carbon monoxide and hydrogen are condensed in fractionators 115 212 and 226 along with the normally liquid constituents the gases passing overhead from the second fractionator 226 through line 232 will consist of unconverted carbon monoxide and hydrogen, 120 methane and any C_2 hydrocarbons undesired for passage to admixture with the hot gases from heater 241. These gases may be passed through lines 274 and 275 to admixture with the fresh feed being 125 introduced to the system through line 201. If desired these gases may be passed instead through line 276 by means of compressor 277 to admixture with the overhead gases from the fractionator 272 130

which pass therefrom by means of line 278. The overhead gases from fracfraction to pass overhead with the normally gaseous hydrocarbons. If it is tionator 272 together with any gases condesired that these light ends should not be further converted the overhead gases ducted through line 276 pass through a from the separator 229 may be passed through lines 232, 276, 284 and 286 to 5 cooler 279 wherein heavy constituents undesired in the recycle gases to the oxidacombine with the overhead gases from fractionator 263 whereby the gasoline constituents will be condensed in cooler tion chamber 202, or constituents desired in the recycle stream to the heater 241, The cooled gases pass are condensed. 10 from the cooler 279 to separator 280 where-266 and collected for return as reflux to fractionator 263 in separator 267. To in the liquefied constituents are separated and returned to the fractionator 272 as provide maximum recovery of any such reflux through line 281 by means of pump gasoline constituents it may be desired to 282. The uncondensed gases from the 15 separator 280 pass overhead through line provide means such as a line 288 for passing these overhead gases including gaso-line constituents to admixture with the 283 and are recycled to admixture with overhead gases from the separator 258 whereby they pass through cooler 262 and the fresh feed passing to exidation chamber 202 through line 275, as described above. If desired, all or a portion thereof line 261 directly to fractionator 263. 20 may be diverted from the system through It may be desired to use only a portion line 292. or a selected portion of the reaction produets of the synthesis of carbon monoxide Alternatively, all or a portion of the gases passing from the separator 229 and hydrogen for admixture with the hot through line 276 may be passed through 25 lines 284 and 285 to admixture with the gases from the heater 241. If only a portion is used the undesired portion may overhead gases from the separator 267 after which the mixture is passed through be withdrawn from the system from line 236 through line 289. If it is desired to cooler 271 and into the fractionator 272, use only a selected portion all of the said reaction products may be withdrawn through line 289 from line 286 and passed as described above. If the gases passing overhead from the separator 229 through line 276 contain any gasoline constituents which it is deto suitable fractionating means (not shown) after which the fraction desired for admixture with the hot gases may be reintroduced to the system through line sired to retain in the gasoline fraction they may be passed through lines 284, 85 286 and 287 to admixture with the gases passing overhead from the fractionator 263 through line 265 after which they pass through the cooler 266 wherein gaso-The fractionator 212 may be operated to recover any proportion of the C. and lighter hydrocarbons and any light ends line constituents are condensed, as deof the liquid fraction separated from 40 scribed above. hydrogen and carbon monoxide and the 10t If the fractionators 212 and 226 are heavier liquids as in a side stream, and means may be provided to collect and conduct such side stream to either fractionator 263 or 272, as desired, to increase operated to permit the passage overhead from separators 215 and 229 of the normally gaseous hydrocarbons such as C₃
45 and C₄ hydrocarbons all the overhead the concentration of hydrogen and carbon 110 gases from separator 229 will be passed through line 276 and be disposed of by monoxide in synthesis chamber 222 Heating means 291 may be provided in admixing them with the overhead gases the bottoms of fractionators 249, 263 and from fractionators 268 or 272 or separator 272 to maintain the desired temperature 50 267, as described above, whereby the relatively heavy normally gaseous hydrocarbons, such as Ca and Ca hydrocarbons, of the condensate collected therein and 115 prevent the inclusion of undesired constituents. The fractionators 212, 226, 249, 263 and 272 are provided with suitable trays will be collected in fractionators 272 and combined with the recycle stream passing or other fractionating equipment to facili- 120 55 through line 273. It may be desired to pass only the tate the stripping, condensation, absorpheavier liquid constituents of the reaction tion and evaporation steps incident to products from the synthesis of carbon monoxide and hydrogen to admixture fractionation. It is to be understood that the functions 60 with the hot gases from the heater 241. of fractionators 249, 263 and 272 may be 125 For example, the reaction products may assigned to a single fractionator having a unitary structure provided with suitable means for withdrawing side streams. However, a plurality of fractionators is be fractionated to include as the lightest component of the liquid fraction only the heavy ends of the naphtha fraction, per-65 mitting the lighter ends of the naphtha used here to simplify presentation of the 130 subject matter of the invention.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to 5 be performed, we declare that we are aware that in Patent Specification No. 406,326 there is described and claimed a method of treating hydrocarbon materials which are normally gaseous which consists in 10 passing the materials through a heated zone in which they are heated to cracking temporature and are converted to a limited degree to form dissociated pro-ducts capable of being polymerised to form 15 normally liquid products and treating a gasoline or maphtha stock of relatively low anti-knock value in a second or conversion zone (at a temperature of from 600° C. to 900° C.) in the presence of said 20 dissociated products so as to reform said gasoline or naphtha stock into a high anti-knock gasoline, but what we claim is:—
1. The process for producing hydro-

1. The process for producing hydrocarbon motor fuel wherein carbon monoxide and hydrogen are reacted to produce normally liquid hydrocarbons including motor fuel constituents and normally gaseous hydrocarbons, characterized by 80 admixing normally liquid hydrocarbons thus obtained with normally gaseous hydrocarbons containing 2, 3 or 4 carbon atoms per molecule, and maintaining the resulting mixture at a temperature of 85 750—1500° F., to effect conversion thereof

to motor fuel of high anti-knock value.

2. The process of claim 1 characterized by heating normally gaseous hydrocarbons containing 2, 3, or 4 carbon 40 atoms per molecule to promote conversion thereof to normally liquid hydrocarbons, admixing normally liquid hydrocarbons from the carbon monoxide-hydrogen synthesis with said heated normally 45 gaseous hydrocarbons, and maintaining the resulting such as the carbon monoxide to the resulting such as the carbon maintaining the resulting such as the carbon maintaining the resulting such as the carbon maintaining the carbo

the resulting mixture at a temperature of 750—1500° F, to effect conversion thereof to motor fuel of high anti-knock value.

3. The process of claim I characterized

50 by admixing normally liquid hydrocarbons from the carbon monoxidehydrogen synthesis with normally gaseous hydrocarbons containing 2, 3 or 4 carbon atoms per molecule at a temperature below 55 that at which conversion of the gases would occur, and heating the resulting

would occur, and heating the resulting mixture to a temperature of 750—1500° F. to effect conversion thereof to motor

fuel of high anti-knock value.

4. The process of any of claims 1, 2, 60 and 3 characterized in that normally gaseous hydrocarbon products of the carbon monoxide-hydrogen synthesis are admixed with the normally liquid hydrocarbons as described.

5. The process of any of claims I, 2, and 3 characterized in that the conversion reaction products are fractionated to separate therefrom normally gaseous hydrocarbons containing 2, 3 or 4 carbon 70 atoms per molecule, and normally gaseous hydrocarbons thus obtained are admixed with the normally liquid products of the carbon monoxide-hydrogen synthesis as described.

6. The process of any of claims 1, 2, and 3 characterized in that the conversion reaction products are fractionated to separate therefrom normally gaseous hydrocarbons containing 2, 3 or 4 carbon atoms per molecule, and normally gaseous hydrocarbons thus obtained and normally gaseous products of the carbon monoxide-hydrogen synthesis are admixed with the normally liquid products of the carbon monoxide-hydrogen synthesis as described.

7. The process of any of claims 1, 2, and 3, characterized in that the conversion reaction products are fractionated to separate hydrocarbons having not more than two carbon atoms per molecule, and hydrocarbons thus obtained are catalytically oxidized to carbon monoxide and hydrogen for synthesis as described.

8. The process of any of claims 1, 2, and 3 characterized in that the normally liquid products of the carbon monoxide-hydrogen synthesis treated as described are limited to those boiling in the upper portion of the gasoline motor fuel boiling range.

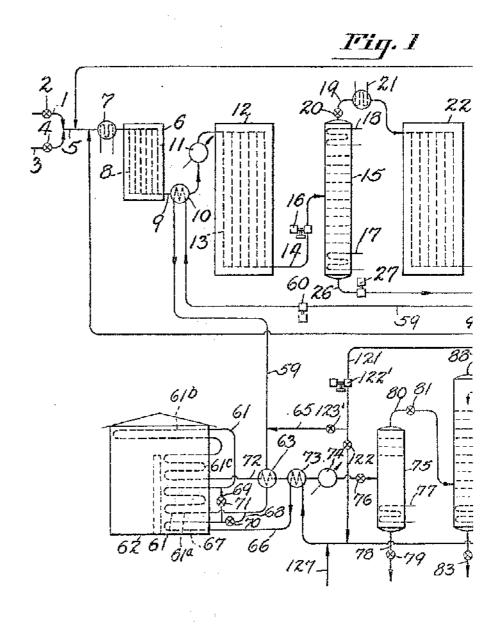
9. The process substantially as hereinbefore described with reference to Figure 1 and with reference to Figure 2 of the 105 accompanying drawings.

Dated this 5th day of January, 1938. For

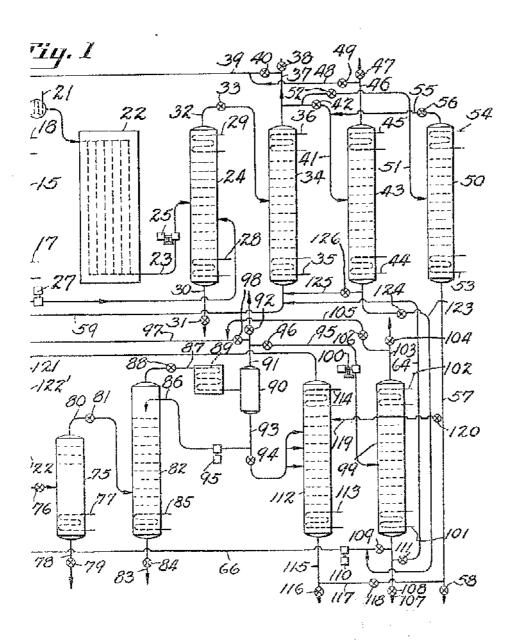
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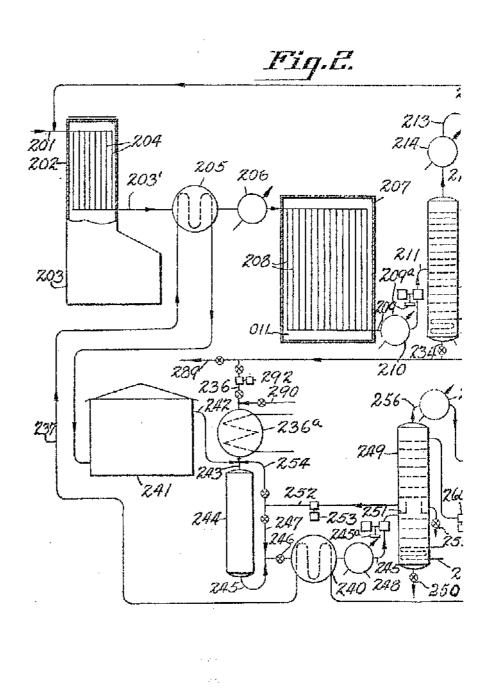
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