

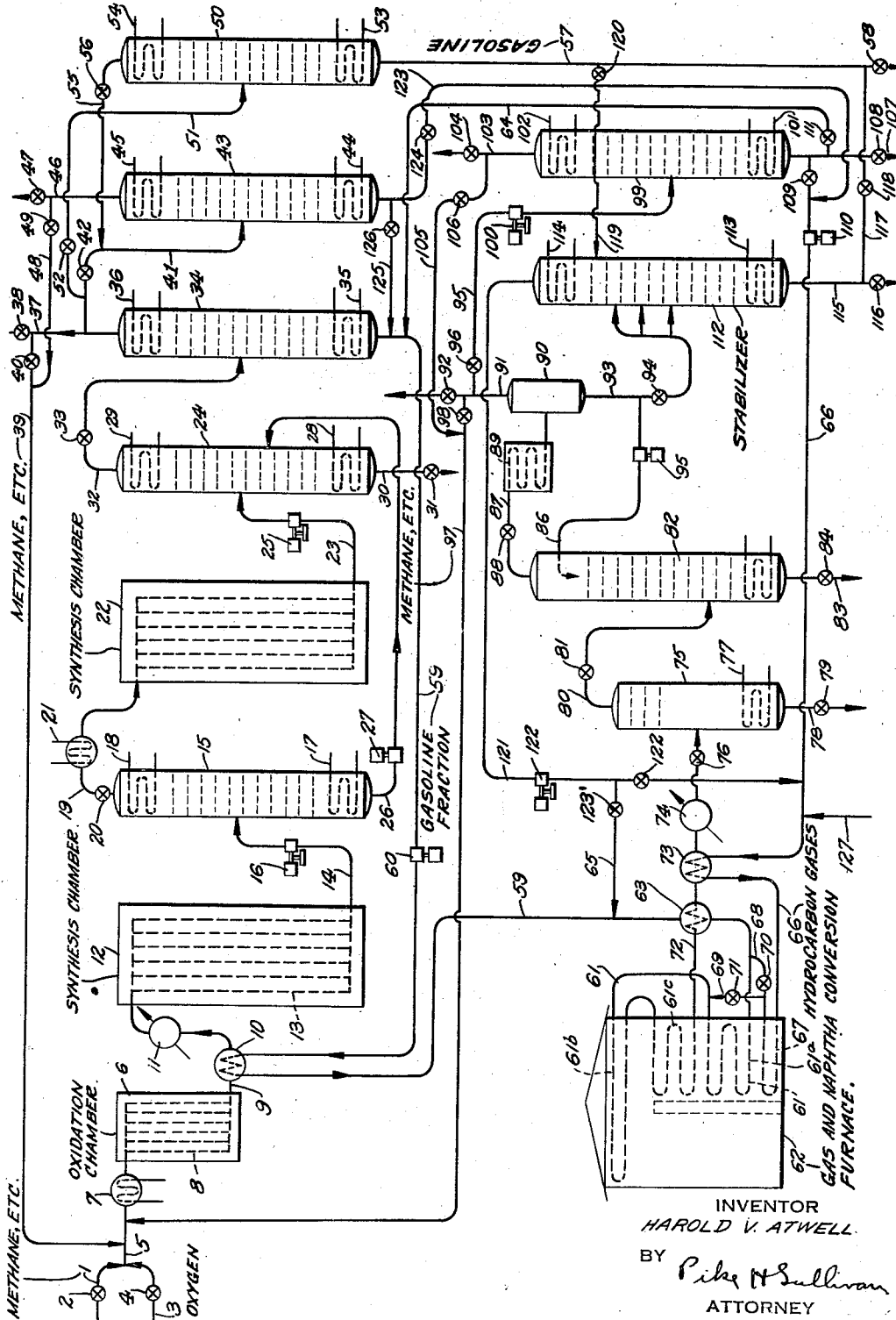
Oct. 14, 1941.

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2,258,839

MOTOR FUEL PRODUCTION

Filed Oct. 30, 1937



## UNITED STATES PATENT OFFICE

2,258,839

## MOTOR FUEL PRODUCTION

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Application October 30, 1937, Serial No. 171,919

4 Claims. (Cl. 196—9)

This invention relates to the production of normally liquid hydrocarbons from a gaseous mixture consisting essentially of carbon monoxide and hydrogen. More particularly, 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 produced by the reaction of carbon monoxide and hydrogen ordinarily include substantial proportions of hydrocarbons in the gasoline boiling range. However, the fraction corresponding to the gasoline boiling range recovered from the synthesis reaction products is very low in anti-knock value and therefore generally unsuitable as such as gasoline motor fuel. The treatment of this material by application of elevated conditions of temperature and pressure to improve its anti-knock value results in the production of large quantities of gas and accompanying 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 monoxide and hydrogen, this condition being also responsible, in part at least, for the initial low anti-knock value of the motor fuel fraction.

It is an object of the present invention to provide a means for treating normally liquid products obtained by the reaction of carbon monoxide and hydrogen to produce therefrom a gasoline motor fuel of high anti-knock value, with maximum recovery of useful products.

The invention contemplates the separation of a gasoline fraction from the reaction products of carbon monoxide and hydrogen and the subjection of the gasoline fraction to elevated conditions of temperature and 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 referred to as C<sub>3</sub> and C<sub>4</sub> hydrocarbons, to effect conversion of the normally liquid and normally gaseous constituents to motor fuel of high anti-knock value. The conditions of temperature and pressure preferably are sufficiently drastic to effect cracking of normally liquid constituents, and the reactions which result 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 aliphatic constituents and dehydrogena-

tion 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 C<sub>3</sub> and C<sub>4</sub> hydrocarbons which are in part at least admixed with the normally liquid fraction undergoing conversion treatment as described. C<sub>2</sub> hydrocarbons and lighter products may be recovered and converted to a carbon monoxide-hydrogen mixture by suitable catalytic oxidation.

The accompanying drawing is a diagrammatic view in elevation of apparatus suitable for carrying out the present invention. The invention will be further described with reference to the specific embodiment illustrated by the drawing, but it is to be understood that the invention is not limited thereby but is capable of other embodiments which may be beyond the physical limitations of the apparatus illustrated.

In the embodiment of the invention as illustrated in the drawing the carbon monoxide-hydrogen mixture is produced by the catalytic oxidation of hydrocarbon gases, particularly methane and C<sub>2</sub> 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 and hydrogen obtained in any particular manner. Referring to the drawing, a stream of gaseous hydrocarbons predominating in methane and C<sub>2</sub> 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 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 plurality 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 magnesia. 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 oxidation reaction is only slightly exothermic so that it may be necessary to maintain the reaction temperature by a suitable insulation of the reac-

tion chamber. Preferably, however, the catalyst is suitably maintained in tubes 8 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 contact of the catalyst and gaseous mixture through the subdivision of the gaseous stream in the plurality of tubes 8 of the oxidation chamber. Preheating of the gaseous mixture entering oxidation 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 components 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 in line 9 wherein they pass in indirect contact with a hydrocarbon stream produced in the system to effect cooling of the oxidation reaction products and heating of the hydrocarbon stream. If necessary 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 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 reaction 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 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 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 of greater molecular weight. For example, the catalyst may consist of metallic cobalt deposited on a carrier such as kieselguhr together with a promoter such as thorium. The gases should be maintained at a temperature of approximately 365° to 415° F. at atmospheric 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 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 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 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 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 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 provided with control valve 20. Heating means 21 is interposed in line 19 to raise the gaseous mixture in line 19 to the desired reaction temperature, e. g., 365° to 415° F. Beyond heating means 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 description 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 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 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 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 introduced 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 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 introduced into fractionator 24 for further treatment therein.

In contrast with the conditions obtaining in fractionator 15 fractionator 24 is maintained under conditions of temperature and pressure suitable to effect separation and collection of a liquid fraction consisting of those reaction products boiling above the boiling range of the fraction desired for further treatment in the 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 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, however, 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 produced therefrom contains at most a minor proportion of constituents boiling above the gasoline boiling range. To effect the desired fractionation of the reaction products introduced into fractionator 24 through lines 23 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 liquid condensate which collects in the bottom of fractionator 24 may be withdrawn 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 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 liquid fraction condensed in fractionator 34 will include substantially all the constituents introduced therein which are in the motor fuel boiling range and may include normally gaseous hydrocarbons such as C<sub>3</sub> and C<sub>4</sub> hydrocarbons in substantial proportions. However, if desired, the liquid condensate separated in fractionator 34 may be limited to liquids in the 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 fraction 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 gaseous hydrocarbons such as C<sub>3</sub> and C<sub>4</sub> hydrocarbons the remaining gases taken overhead through line 37 may be withdrawn from the system for use elsewhere, for example, as fuel; or since these gases consist essentially of methane and C<sub>2</sub> 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 40. Line 39 connects with line 5 whereby the mixture of hydrocarbon gases and carbon monoxide and hydrogen are admixed with the oxygen-hydrocarbon mixture in line 5 for passage to oxidation 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 ratio of oxygen and hydrocarbon gases being introduced into oxidation chamber 6.

When fractionator 34 is operated to effect condensation and collection of a liquid consisting substantially essentially of normally liquid hydrocarbons, leaving substantial proportions of C<sub>3</sub> and C<sub>4</sub> hydrocarbons uncondensed, the gases passing through line 37 may be diverted wholly or in part through line 41 provided 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 C<sub>3</sub> and C<sub>4</sub> hydrocarbons together with any desired proportion of the C<sub>2</sub> hydrocarbons. To effect the desired fractionation heating means such as heating coil 44 and cooling or liquefaction means such as cooling coil 45 may be provided in the bottom and top, respectively, of fractionator 43. Gases uncondensed in frac-

tionator 43 are withdrawn overhead therefrom through line 46 provided with control valve 47. These gases may be withdrawn from the system 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 lines 46 and 39.

When fractionator 34 is operated to effect condensation and collection of a liquid consisting substantially essentially 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 desired 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 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 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 the bottom of fractionator 50 are withdrawn therefrom through line 57 provided with a valve 58.

The liquid motor fuel fraction collected in the bottom of fractionator 34 is 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 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 exchanger 63 may be provided in line 59 whereby the material passing therethrough is further preheated by heat exchange with the hot reaction products 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 the material passing therethrough. In accordance with the present invention normally gaseous hydrocarbons preferably predominating in C<sub>3</sub> and C<sub>4</sub> hydrocarbons and containing substantial proportions of olefinic 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 hydrocarbons may be admixed with the liquid material passing through line 59 prior to passage through heat exchanger 10. For example, they may be introduced through line 64 which connects line 59 with a source to be described below. Or the gaseous hydrocarbons may be introduced into

line 59 just previous to the passage of the liquid hydrocarbons through heat exchanger 63. For example, 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 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 coil 67 located in a convection section of furnace 62. The preheated normally gaseous hydrocarbons emerge from the outlet of coil 67 through line 68 which connects with line 59 near the inlet of coil 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 61c and radiant heating section 61b. Valves 70 and 71 may be provided in lines 68 and 69, respectively, to afford the desired distribution of the preheated gaseous hydrocarbons to line 59 or through line 69. In 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 sufficient to effect conversion to gasoline motor fuel constituents of high anti-knock value. They may be heated to 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 61c 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 are separated into a heavy condensate and uncondensed vapors and gases. The preliminary cooling of the reaction products and the operation of separator 75 are controlled to effect condensation and separation 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 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 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 example, as fuel.

Vapors and gases uncondensed in separator 75 are withdrawn therefrom through line 80 which

may be provided with control valve 81. Line 80 connects with a 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 bottom of fractionator 82 and is withdrawn therefrom through line 83 provided with a valve 84. This material may be subjected to further treatment elsewhere as desired. For example, it may be subjected to elevated conditions of temperature and pressure to convert it to gasoline motor fuel. Heating means such as heating coil 85 may be provided in the lower portion of fractionator 82 to assist in the desired fractionation. Also cooling means such as the introduction of reflux material in the 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 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 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 withdrawn through line 93 provided with control 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 provided with a pump 95.

The gases separated in collector 90 and withdrawn therefrom through line 91 ordinarily consist of normally gaseous constituents including C<sub>3</sub> and lighter hydrocarbons as well as some C<sub>4</sub> hydrocarbons. These gases preferably are treated to effect separation therefrom of convertible constituents for further treatment in accordance with the process of 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 through line 97 provided with a valve 98. Line 97 connects with line 5 whereby the gaseous hydrocarbons passing therethrough are admixed with the oxygen-hydrocarbon stream passing through line 5 to oxidation reaction 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 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 consisting of convertible normally gaseous hydrocarbons such as C<sub>3</sub> and C<sub>4</sub> hydrocarbons. If necessary a compressor 100 may be provided in line 95 to transfer the gases through line 95 into fractionator 99. In 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<sub>2</sub> 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. Line 105 connects line 103 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 bottom of fractionator 99 will consist for the most part of normally gaseous convertible hydrocarbons such as C<sub>3</sub> and C<sub>4</sub> 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 108. Line 66 is provided with a control valve 109 and a pump 110 whereby, by manipulation of valves 108 and 109, any 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, 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 admixed with the condensate from fractionator 34, as described above.

The condensate from fractionator 99, withdrawn therefrom through line 107, and undesired for passage through line 64 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 processes involving alkylation reactions since it includes substantial proportions of olefinic constituents. The decomposition of normally liquid paraffinic hydrocarbons incidental to the treatment of such material in coil 61 promotes the decomposition of normally gaseous paraffinic hydrocarbons admixed therewith whereby the resulting reaction products contain substantial proportions of normally gaseous olefinic hydrocarbons. This promotion effect of the normally liquid hydrocarbons on normally gaseous paraffins may be utilized further by the addition to coil 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 a plurality of points. Stabilizer 112 is provided with heating means in the lower portion thereof such as heating coil 113 and cooling means in the upper portion thereof such as cooling coil 114 to effect fractionation 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 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 withdrawn from fractionator 50 through line 57 by means of line 117 which is provided with a suitable control valve 118 and connects line 115 and line 57.

The operation of stabilizer 112 will depend upon the results desired and upon the operation of other parts of the process. Ordinarily, it will be operated to effect the production of a stabilized

motor fuel including the desired proportion of 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 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 constituents of the vapors treated in fractionator 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 proportion 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 stabilized 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 vapors produced in stabilizer 112 is withdrawn from the upper portion thereof through line 121 which is provided with a compressor 122. Line 121 connects with line 66 whereby the gases with accompanying 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 vapors passing through line 121 may be diverted therefrom through line 65 which connects line 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 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 99 or stabilizer 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 valve 109 whereby the normally gaseous hydrocarbons from fractionator 43 may be passed through line 66 and coil 67 as described above. If desired all or a portion of the normally liquid hydrocarbons may be diverted from line 123 through line 125 which is provided with a valve 126 and connects with line 59 between pump 60 and fractionator 34 whereby normally liquid hydrocarbons so diverted are admixed with the condensate withdrawn 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 112 are provided with suitable gas and liquid contact means such as bubble trays to assist in the desired fractionation. It is to be understood, furthermore, that the functions of the fractionator illustrated 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 arrangement is adopted for purposes of illustration.

The present invention provides a method for the treatment of the reaction products of the carbon monoxide-hydrogen reaction to produce therefrom motor fuel of high anti-knock value under conditions of maximum efficiency and maximum recovery of useful products. The invention has been described with reference to specific combinations of steps, but it is to be un-

derstood that such reference is for the purpose of illustration only, the invention not being necessarily limited thereto. This application is a continuation-in-part of my prior application Serial No. 119,178, filed January 6, 1937.

I claim:

1. The method for converting the normally liquid and normally gaseous hydrocarbon products of the reaction of carbon monoxide and hydrogen which comprises separating from the said reaction products a fraction predominating in normally liquid constituents and including at most a minor proportion of hydrocarbons boiling above the gasoline boiling range, admixing with said fraction a substantial proportion of normally gaseous hydrocarbons from a source set forth below, subjecting the resulting mixture to elevated conditions of temperature and pressure to effect conversion of normally liquid and normally gaseous constituents thereof to gasoline of high antiknock value, separating from the resulting conversion products gasoline constituents and a normally gaseous fraction predominating in  $C_3$  and  $C_4$  hydrocarbons, controlling the separation of the conversion products to effect inclusion in said normally gaseous fraction of a substantial proportion of the relatively low-boiling normally liquid constituents of the said conversion products and admixing at least a portion of said gaseous fraction with said first-mentioned fraction as described.

2. The method of producing motor fuel of high anti-knock value which comprises subjecting normally gaseous hydrocarbons consisting essentially of hydrocarbons containing less than three carbon atoms per molecule to catalytic oxidation to convert said hydrocarbons substantially to carbon monoxide and hydrogen, passing said carbon monoxide and hydrogen over a suitable catalyst and under suitable conditions of temperature and pressure to effect reaction of said carbon monoxide and hydrogen to form hydrocarbons heavier than methane and including normally liquid hydrocarbons, separating from the resulting reaction products a fraction predominating in normally liquid constituents and including at most a minor proportion of hydrocarbons boiling above the gasoline boiling range, admixing with said fraction a substantial proportion of normally gaseous hydrocarbons from a source set forth below, subjecting the resulting mixture to elevated conditions of temperature and pressure to effect conversion of normally liquid and normally gaseous constituents thereof to

gasoline of high anti-knock value, separating from the resulting conversion products gasoline constituents, a normally gaseous fraction predominating in  $C_3$  and  $C_4$  hydrocarbons and a fixed gas fraction predominating in hydrocarbons containing less than three carbon atoms per molecule, admixing at least a portion of said normally gaseous fraction with the fraction separated from the carbon monoxide-hydrogen reaction products as described, and admixing at least a portion of said fixed gas fraction with said first-mentioned normally gaseous hydrocarbons for processing therewith.

3. The method for converting the normally liquid and normally gaseous hydrocarbon products of the reaction of carbon monoxide and hydrogen which comprises separating from the said reaction products a fraction predominating in normally liquid constituents and including at most a minor proportion of hydrocarbons boiling in the upper portion of the gasoline boiling range and hydrocarbons boiling above the gasoline boiling range, separating from said reaction products a second fraction predominating in the normally liquid constituents and including at most a minor proportion of hydrocarbons boiling in the lower portion of the gasoline boiling range and hydrocarbons boiling above the gasoline boiling range, admixing with said second fraction a substantial proportion of normally gaseous hydrocarbons from a source set forth below, subjecting the resulting mixture to elevated conditions of temperature and pressure to effect conversion of normally liquid and normally gaseous constituents thereof to gasoline of high anti-knock value, separating from the resulting conversion products a gasoline fraction deficient in constituents boiling in the lower portion of the gasoline boiling range and a vaporous fraction predominating in  $C_3$  and  $C_4$  hydrocarbons and hydrocarbons boiling in the lower portion of the gasoline boiling range, suitably blending said last-mentioned gasoline fraction and said first fraction to produce therefrom a stabilized motor fuel of high anti-knock value and admixing at least a portion of said vaporous fraction with said second fraction prior to said conversion treatment.

4. The method in accordance with claim 2 wherein  $C_3$  and  $C_4$  hydrocarbon constituents of the products of the reaction of carbon monoxide and hydrogen are passed to said thermal conversion treatment to effect conversion thereof to gasoline of high anti-knock value.

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