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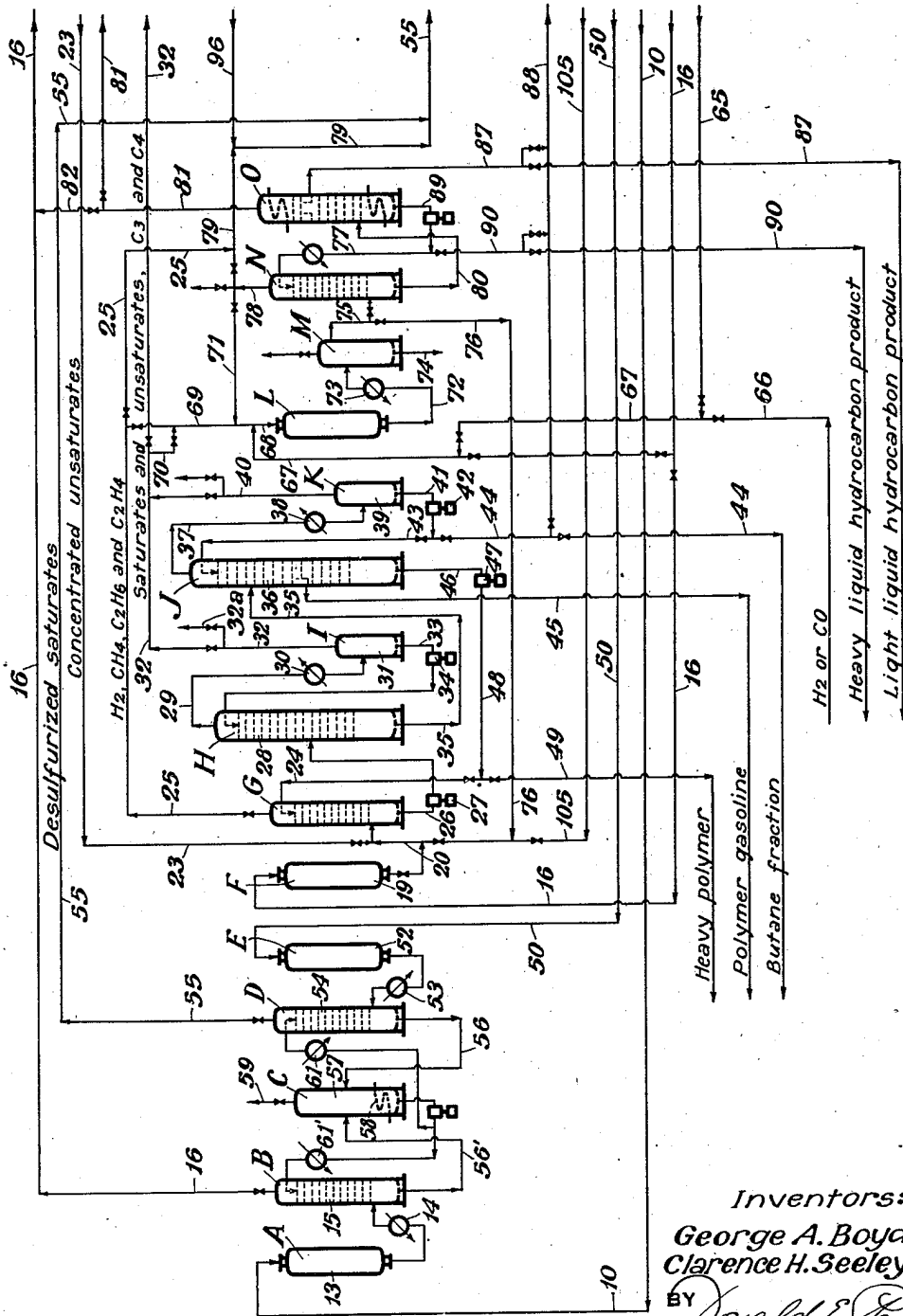
G. A. BOYD ET AL

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HYDROCARBON CONVERSION PROCESS

Filed June 19, 1937

2 Sheets-Sheet 1



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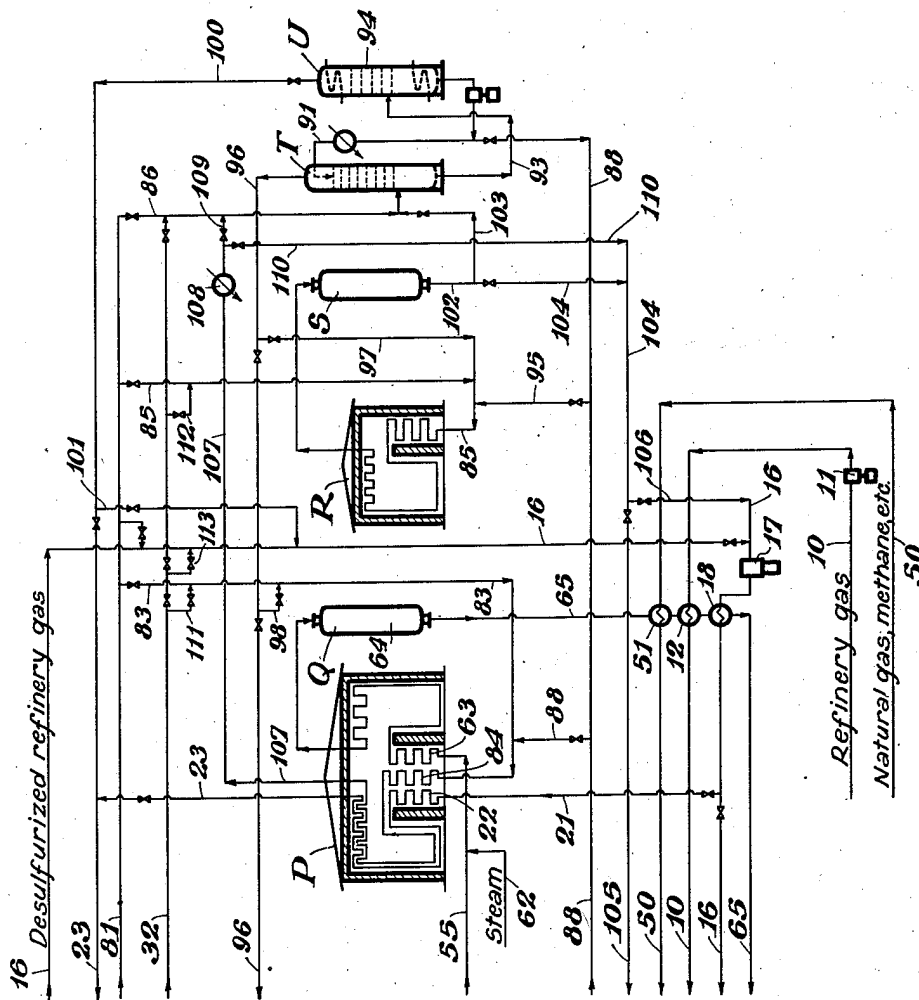
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# UNITED STATES PATENT OFFICE

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## HYDROCARBON CONVERSION PROCESS

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2 Claims. (Cl. 196—10)

This invention relates to hydrocarbon conversion processes and it pertains more particularly to processes for making high quality gasoline out of refinery gases, natural gases and other gaseous hydrocarbons. An object of our invention is to increase the yield of gasoline and other valuable products obtainable from gaseous hydrocarbons by conversion processes. More particularly, our object is to provide a more efficient and effective method and means for utilizing the so-called fixed gases such as hydrogen, methane, ethane and ethylene in the manufacture of high quality motor fuel.

A further object of our invention is to modify and combine hydrocarbon conversion processes in such a way that each process supplements and cooperates with the other processes in a more efficient and more effective manner, and in such a way that the combined processes operate as a unit to effect the conversion of light hydrocarbon gases into motor fuel.

Gas polymerization processes are relatively ineffective on fixed gases and, in fact, they actually produce fixed gases from condensibles such as propane, propylene, butanes, butylenes, etc. An object of our invention is to combine a gas polymerization process with one or more supplementary gas conversion processes for utilizing the so-called fixed gases (tail gases) therefrom, converting said gases directly into motor fuel and/or converting them into such form that they may be polymerized or reacted in other parts of our system to form high quality motor fuel.

An object of our invention is to provide a method and means for fractionating gases in various parts of our system and subsequently combining and utilizing the component parts of said gases in systems particularly designed for handling them most effectively.

A further object of our invention is to provide new and improved combinations and sub-combinations of refinery processes such as desulfurization, polymerization, synthesis, cracking, dehydrogenation, hydrogen production, gas fractionation and olefin concentration systems.

A further object of our invention is to improve the efficiency of gas conversion processes by providing unique combinations thereof with other processes, utilizing heat from one process to carry out other processes, using common gas lines for tying the various processes together so that the various types and fractions of gases may be properly combined or segregated and conveyed to the proper part of the system. A

further object is to provide a combination gas conversion plant which will be characterized by maximum flexibility of operation and which will be omnivorous as to charging stocks.

Other objects of our invention will be apparent as the detailed description proceeds.

We provide a combination of conversion processes which are so integrated and interrelated that each supplements the other in the most efficient manner to produce maximum yields of high quality motor fuel from any and all types of hydrocarbon gases. Our system includes the desulfurizing of different types of feed gases, the catalytic or thermal polymerization or alkylation of condensible gases (particularly olefins), the production of carbon monoxide, hydrogen and condensible gases (particularly olefins) from fixed gases, natural gas, etc., the utilization of this carbon monoxide and hydrogen for the synthesis of motor fuel and of condensible gases containing olefins, the segregation of gaseous olefins from said synthesis step and from other olefin-producing steps, the recycling of the olefins to the gas polymerization step and the recycling of fixed gases to the hydrogen-carbon monoxide-producing step, the synthesis step and condensible saturates to olefin production steps.

We first convert the sulfur compounds in our feed gases into hydrogen sulfide by treatment with catalysts and we remove all hydrogen sulfide thus produced so that there will be no sulfur in the gas streams to poison subsequent catalysts. If the desulfurized gases contain polymerizable fractions they may be subjected to catalytic or thermal polymerization. The natural gas is preferably treated with an oxidizing agent such as steam for the production of carbon monoxide and hydrogen which are then catalytically reacted to form motor fuel and condensible gases containing olefins, the latter being charged to the polymerization step. The gases from the synthesis step and gases from other parts of the system may be fractionated on the basis of molecular weight and on the basis of saturates and unsaturates, the unsaturates being polymerized and the saturates being converted into unsaturates by dehydrogenation, cracking or the carbon monoxide-hydrogen synthesis.

The drawing which forms a part of this disclosure is a flow diagram of our improved process which because of its size and complexity has been drawn on two sheets which should be placed together and read as a single figure or drawing.

Before describing the details of our system we will give a brief outline which will assist in

the understanding of the process as a whole. Refinery gas is passed through catalytic chamber A to convert sulfur compounds to  $H_2S$ , the  $H_2S$  is removed in tower B and the desulfurized gases are then passed to catalytic conversion chamber F or thermal conversion coil in furnace P. Natural gas or high line gas is desulfurized by passing through catalytic tower E and  $H_2S$  scrubber D, the scrubbing liquid for towers B and D being regenerated in the common tower C. The desulfurized natural or high line gases are then passed through a coil in furnace P and reacted in chamber Q with an oxidizing agent for converting said gas into carbon monoxide and hydrogen. This reaction is at a temperature of approximately  $1500^\circ F.$ , and the sensible heat of the reaction products is utilized for furnishing heat to the desulfurizing and catalytic conversion processes which require temperatures of about  $750$  and  $480^\circ F.$  respectively. The carbon monoxide and hydrogen formed in chamber Q are then reacted in synthesis catalytic chamber L, together with tail gases from the polymerization system. Water is condensed out of the reaction products in trap M, fixed gases are removed in tower N and condensibles are removed in tower O.

Both the catalytic and thermal polymerization systems use common absorber G from which fixed gases are separated, and from which condensibles and heavier products are introduced into stabilizer H. Condensibles from this stabilizer are withdrawn from collector I to the synthesis step L, to a gas cracking coil in furnace P, to heater R and dehydrogenation catalyst chamber S or to olefin absorber tower T, the olefins being withdrawn from the absorber liquid in tower U and returned to the catalytic or thermal polymerization process.

Stabilized gasoline from tower H is debutanized in tower J from which butane and light and heavy polymer gasoline are withdrawn. Similarly, scrubbed products from tower N are fractionated in tower O, from which light and heavy hydrocarbon products are withdrawn, and from which the saturated and unsaturated condensibles are passed to the polymerization systems, dehydrogenation system RS or olefin concentration system TU.

An important feature of our invention is the relation the  $CO-H_2$  conversion system LMNO bears to the rest of the system. The initial desulfurizing steps are necessary to protect the catalyst in chamber L. The catalytic conversion process in chamber L not only utilizes the products from catalyst chamber Q, but it utilizes the tail gases from the polymerization system, many of these gases being actually converted in the  $CO-H_2$  synthesis step into higher molecular weight, olefinic and paraffinic products. Thermal polymerization, gas cracking and dehydrogenation invariably lead to the production of large amounts of fixed gases which, by our process, are converted into  $CO-H_2$  and then into condensible and polymerizable hydrocarbons. The saturates removed from the gases in the olefin concentration system TU are likewise converted via the  $CO-H_2$  synthesis route and/or the steps of dehydrogenation or gas cracking, into polymerizable gases which can be converted either thermally or catalytically into motor fuels. The  $CO-H_2$  synthesis step therefore acts to tie together the system as a whole and to utilize the by-products of other conversion processes for

the production of feed stocks for the other processes.

Our invention will be described as applied to the conversion of ordinary refinery gases into gasoline where there is also a source of natural gas or fixed gas. The refinery gases are those which contain appreciable amounts of propane, propylene, butylene, iso-butylene, butane, etc., and fixed gases are those which contain hydrogen, methane and perhaps ethane and ethylene. The analyses of these gases may, of course, vary within wide limits and the operation of our system will be modified accordingly, as hereinafter described.

Refinery gas from line 10 is passed by pump 11 through heat exchanger 12 to catalyst chamber 13 wherein it is contacted with a catalyst mixture of equal parts of copper oxide and lead chromate moistened with a partially hydrolyzed solution of commercial ethyl ortho-silicate in toluol. Here the organic sulfur compounds are converted into hydrogen sulfide, the conversion being effected at about atmospheric pressure and at a temperature of about  $700$  to  $750^\circ F.$  It should be understood, of course, that we may employ other known catalysts for this conversion and other operating conditions known to those skilled in the art for effecting the conversion of organic sulfur into  $H_2S$ . The hydrocarbons and  $H_2S$  are then passed through cooler 14 to reduce the mixture to room temperature or higher, after which it is introduced into the base of scrubber tower 15 (B), in which practically all of the  $H_2S$  is removed from the gases by means of sodium phenolate or the like. We prefer to reduce the sulfur content of the gas to less than .1 grain per 100 cu. ft.

The sulfur-free gases are then passed through line 16, compressor 17 and heat exchanger 18 to catalytic polymerization chamber 19 under a pressure of about 100 to 600 or preferably 300 pounds and at a temperature of about  $300$  to  $600$ , or preferably  $480^\circ F.$  The catalyst in this chamber is preferably phosphoric acid on kieselguhr, and the time of contact is preferably about 100 seconds. It should be understood, of course, that any other suitable catalyst may be employed for effecting the polymerization of the olefins to gasoline, examples of which are sodium-aluminum chloride, boron trifluoride or other metallic halides, sulphuric acid, etc. No claim is made to the use of any of these particular catalysts, per se, because their use and the operating conditions which they require are well-known to those skilled in the art. Polymerization products from catalyst chamber 19 are withdrawn through line 20 to absorber G.

Instead of employing the catalytic polymerization process we may pass the refinery gas from compressor 17 thru heat exchanger 18, line 16 and line 21 to thermal-polymerization coils 22 in furnace P, operated at a pressure of about 500 to 3000 pounds and a temperature of about  $800$  to  $1300^\circ F.$  with a time of contact of about 20 to 200 seconds. Here again the particular polymerizing conditions for any gas will be dependent upon the composition of that gas, and since these conditions are known to those skilled in the art they will not be described in further detail. Polymerization products from coils 22 are passed through line 23 to line 20 and thence to absorber G. It should also be understood that the conversion products from coils 22 and/or from catalyst chamber 19 may be quenched or

cooled prior to or at the time of their introduction into absorber G.

As an absorber liquid in tower G we prefer to employ the heavy polymer from a subsequent tower, as will be hereinafter described. This or other scrubbing liquid such as gas oil, naphtha, light hydrocarbons down to and including butane, etc., is introduced through line 24 at the upper part of the absorber, and fixed gases such as hydrogen, methane, ethane and ethylene leave the top of the absorber through line 25. The heavier reaction products and scrubbing liquid leave the base of the absorber through line 26 and are passed by pump 27 into stabilizer tower 28. The absorber is preferably operated at a pressure of about 240 pounds per square inch, but it may be operated at full conversion pressure. The stabilizer tower is preferably operated at a pressure of about 325 pounds/sq. in., a top temperature of about 130° F. and a bottom temperature of about 440° F. The C<sub>3</sub> and C<sub>4</sub> fractions from the top of the stabilizer are withdrawn through line 29 through cooler 30 to collector or reflux drum 31 from which a part (containing both saturated and unsaturated C<sub>3</sub> and C<sub>4</sub> fractions) is withdrawn through line 32, and another part is returned through line 33 and pump 34 as reflux in the top of stabilizer 28 (H).

Stabilized liquid from the base of tower H is withdrawn through line 35 and introduced into the upper part of debutanizer tower 36 (J), which is preferably operated at a top temperature of about 150° F. and pressure of about 100 pounds per square inch and a bottom temperature of about 385° F. The butane fraction from the top of the tower is withdrawn through line 37, condensed in cooler 38 and introduced into collector 39 from which a part of it may be withdrawn through line 40 for admixture with the fractions in line 32. A portion of the butane fraction is returned through line 41 by pump 42 through line 43 to serve as reflux in the top of the debutanizer tower. A part of the butane fraction from collector 39 may also be withdrawn through line 44 for blending with motor fuel or for other purposes. If it is not desired to withdraw a butane fraction as through line 44 then, of course, tower H can be eliminated and line 26 can connect with tower J in the place of line 35. Towers H and J are necessary only when the butane cut is to be withdrawn.

From an intermediate point of the debutanizer tower a side stream of polymer gasoline is withdrawn through line 45 for storage or for further refining treatments with acid, doctor, doctor solution, clay, selective solvents, etc. Heavy polymer gasoline is withdrawn from the base of the debutanizer tower through line 46 and it is passed by pump 47 to line 48 to line 24 leading to absorber tower G or through line 49 leading to storage or to further refining processes, as hereinabove indicated.

Returning now to the beginning of our process, we introduce natural gas, high line gas (refinery gas vented at high pressure and containing chiefly hydrogen, methane, ethane and other difficultly condensable hydrocarbons), or hydrocarbon gases not readily polymerizable, said gas being introduced under pressure through line 50 and heat exchanger 51 into catalyst chamber 52 which is substantially a duplicate of catalyst chamber 13 and which operates under the same conditions and with the same catalyst. We employ a different catalyst chamber for these natural or high line gases, however, since we

desire to keep them segregated from polymerizable gases and since we wish to pass them directly to the hydrogen-carbon monoxide generator, as will be hereinafter described.

The gases and H<sub>2</sub>S from the base of chamber 52 are withdrawn through cooler 53 to the lower part of scrubber 54 wherein a scrubbing liquid such as sodium phenolate or the like removes all of the H<sub>2</sub>S from the gases, the sulfur-free gases being removed from the top of the scrubber through line 55. Scrubber liquid from the base of towers 54 and 15 are introduced through lines 56 and 56' respectively to tower 57 wherein the H<sub>2</sub>S is stripped from the scrubbing liquid by heater 58, the H<sub>2</sub>S being vented from the system through line 59. The regenerated scrubbing liquid is then returned through coolers 61 and 61' to the top of towers 15 and 54. While we employ two separate scrubbing towers, we effect a marked saving in installation and operating expense by employing a single regenerating tower which regenerates the scrubbing liquid for both scrubbing towers.

Sulfur-free gases in line 55 are admixed with steam through line 62 and the mixture is passed through coils 63 in furnace P wherein they are heated to a temperature of about 1200 to 1500° F. The hot gaseous mixture is then passed over a catalyst such as nickel in catalyst chamber 64 (Q), which is operated at atmospheric pressure or higher. It should also be understood that the catalyst chamber itself may be heated to the desired temperature and the gases introduced at a temperature below that required for conversion, picking up the remaining necessary heat in the chamber. Other suitable catalyst may be employed for the conversion of hydrocarbons and steam to carbon monoxide and hydrogen. It should also be understood that instead of steam we may employ other oxygen-containing gases or commercially pure oxygen, the catalyst and conditions for operating the CO and H<sub>2</sub> generation being varied accordingly. Also, we may react the hydrocarbons with metal oxides to produce the carbon monoxide and hydrogen. Our invention is not specific to any particular type of CO and H<sub>2</sub> generation and any well-known process may be used for accomplishing this result.

The mixture of CO and H<sub>2</sub> from catalytic chamber 64 is at the high temperature of at least 1200° F., and it is important that the heat of these gases be utilized. We therefore pass the hot gases by line 65 through heat exchangers 51, 12 and 18 so that the heat put into the gases for CH-H<sub>2</sub> generation is utilized for supplying at least a major part of the heat for the desulfurization catalytic reactions and for the catalytic gas polymerization. It should be understood, of course, that these exchangers may be supplemented by other heaters and other heat exchange systems may be employed for obtaining the necessary temperature conditions and desired heat economy.

The mixture of CO and H<sub>2</sub> from line 65, after cooling by the heat exchangers, may be supplemented by CO, H<sub>2</sub> or a mixture of CO and H<sub>2</sub> from line 66. This gas mixture is then passed through line 67 to line 68 wherein it is admixed with tail gases from lines 25 and 69 and/or with condensable gases from lines 32 and 70 also recycled gases through line 71. The mixture of these gases now having about 1 volume of CO to 1.4 volumes of H<sub>2</sub>, although the volumetric ratio may vary from 1:1 to 1:1.8, is introduced into

catalyst chamber L which is maintained at a temperature of about 400 to 700° F., preferably 475° F., and at a pressure of about 1 to 5 atmospheres, the time of contact being about 10 to 60 seconds, preferably about 30 seconds, the catalyst in chamber L preferably comprising eighth group metals, particularly cobalt or nickel, or a mixture of eighth group metals with metal oxides. Good proportions of metal to oxide are about 1:1 to 1:3, and the oxides may be of chromium, zinc, beryllium, rare earths, uranium, silicon, aluminum, magnesium and manganese. We prefer to use about 1 part of iron, cobalt or nickel with about 2 parts of chromic oxide. Combinations with palladium, copper and iron oxide (the latter with nickel and copper) may be used. Nickel on kieselguhr using thorium as a promoter has been found to give excellent results, the ratio of metals to kieselguhr being 1:1, 18% of the metal being thorium; in this case the metals are precipitated as carbonates and then reduced with hydrogen at 450° C. A catalyst may be prepared by dissolving aluminum or silicon from alloys to give a so-called Raney alloy skeleton. Raney catalysts of nickel-aluminum, nickel-silicon, cobalt-aluminum, cobalt-silicon and nickel-cobalt-silicon have been used in the reduction of carbon monoxide. A very excellent catalyst consists of nickel, manganese and alumina on kieselguhr or on kieselguhr and silica. Sodium or lithium may be used in very small amounts (less than 1%) with the eighth group metals or eighth group metal combinations.

The exact operating conditions and time of contact in catalyst chamber L, which may be called our catalytic synthesis chamber, will necessarily vary with the different gas mixtures charged thereto and with the different catalysts employed. We prefer to maintain the operating conditions so controlled as to yield a large quantity of olefins, particularly in the propylene-butylene range, since such olefins are particularly amenable to polymerization in catalytic chamber 19 or thermal coils 22.

The reaction products and gases from the synthesis catalytic chamber L are withdrawn through line 72 through cooler 73 for condensing water, and the condensed water is withdrawn from trap M through line 74. Liquid and gaseous products from trap M are withdrawn through line 75 either to the base of the scrubber tower N or through line 76 to absorber G. Scrubbing liquid, which may be heavy hydrocarbons from the base of tower O, is introduced through line 77 near the top of tower N and fixed gases are removed from the top of the tower through line 78. These gases may contain considerable amounts of CO, H<sub>2</sub> and unreacted gas and may therefore be recycled through line 71, as hereinabove described. Alternatively, they may be passed through line 79 to line 55 for admixture with further amounts of gases and steam for the generation of further amounts of carbon monoxide and hydrogen.

Scrubbing liquid and products from the base of tower N are withdrawn through line 80 to a lower intermediate point of fractionator O, which is provided with a suitable reboiler coil at its base and a reflux coil at its top. This fractionator is operated to eliminate C<sub>3</sub> and C<sub>4</sub> saturates and unsaturates through line 81; these gases may be returned through line 82 to line 16 for admixture with the feed stream for gas polymerization processes, or it may be passed through line 83 to gas cracking coils 84 in furnace P, through

line 85 to dehydrogenation furnace R or through line 86 to olefin concentrator T.

A side cut of light liquid hydrocarbon product may be withdrawn from fractionator tower O through line 87, and if this stream has a low knock rating it may be passed through line 88 and line 83 to the gas cracking coil 84 for cracking and/or gas reversion. Heavy liquid from the base of fractionator O is withdrawn through line 89, a portion of it is cooled and introduced through line 77 as a scrubbing medium in tower N and the rest of it is withdrawn through line 90 as a heavy liquid hydrocarbon product, or is passed through line 88 to the gas cracking coils 84 or dehydrogenation furnace R.

As above indicated, lines 32 and 86 lead to olefin concentrator tower T, the gases being introduced near the bottom of tower T and a scrubbing liquid such as a selected solvent like B, B' dichlorethyl ether being introduced through line 91 at the top of said tower. Other selective solvents such as liquid sulfur dioxide, benzol, alcohols, ketones, etc., and even gas oil, naphtha or butane may be used as the scrubbing liquid. The scrubbing liquid absorbs most of the olefins and is withdrawn through line 93 to tower 94 where the olefins are removed. In tower 94 there is provided a suitable heater in the base thereof and a suitable reflux coil at the top for carrying out the olefin regeneration step. Excess amounts of butane or other hydrocarbon scrubbing liquid may be withdrawn through line 88 to gas cracking feed line 83 or to dehydrogenation feed line 95. Saturates from the top of tower T may be withdrawn through line 96 from which they may be passed through line 97 to the dehydrogenation furnace R, to line 98, to line 83 and the cracking tubes 84, or to line 79 to the carbon monoxide-hydrogen generator unit. Olefins from the top of tower U are withdrawn through line 100 to line 23, and thence to absorber G or through line 101 to line 16 for charging to either the thermal or catalytic polymerization system.

As previously indicated, dehydrogenation furnace R may obtain its feed stock or gases from lines 85, 97 or 95 and line 95 is supplied from line 88 which is connected to lines 44, 87 and 90 so that saturated liquids or condensable gases from all parts of the system may be charged to this dehydrogenation system for conversion to olefins. The conversion is effected in catalytic chamber S which is operated at about 800 to 1200° F., preferably 1000° F. at normal pressure or higher, using a chromic oxide catalyst. Other catalysts known to be effective for dehydrogenation may of course be used. Here again the exact operating conditions will depend upon the catalyst employed, and no claim is made to this specific step since it is well-known in the art.

Conversion products from chamber S are withdrawn through line 102 and line 103 to olefin concentrator tower T or through lines 102 and 104 either through line 105 to absorber G or through line 106 to line 16 for admixture with feed stock entering the thermal or catalytic processes.

We have already described the three coils in furnace P and it should be understood that instead of employing a single furnace we may employ a separate furnace for each coil. The hydrogen-carbon monoxide generator and the thermal polymerization system have been described. Products from the gas cracking coils 84 are led through line 107 to cooler 108 and

thence either through line 109 to line 86 and olefin concentrator tower T or through line 110 to line 104 which leads either to line 105 and absorber G or to line 106 for admixture with polymerization feed stock in line 16.

The saturates and unsaturates from line 32 may be passed through line 111 to line 83 leading to the gas cracking coils, through line 112 leading to line 85 and the dehydrogenation system or to line 86 leading to the olefin concentrator tower T. We have also provided a line 113 for introducing these gases from line 32 directly to line 16, so that if these gases contain substantial amounts of polymerizable gas they may be returned directly to the gas polymerization systems.

While a certain number of pumps, valves, heat exchangers, etc., are shown in the drawings, it should be understood that the drawings are diagrammatic and that further pumps, valves, heat exchangers, connections, etc., will be required in commercial installations; we do not desire to complicate the already complex drawings by including further details which will be obvious to those skilled in the art. Operating conditions have for the most part been given and where they have been omitted, for instance with respect to olefin concentrator tower T, it is believed that those skilled in the art are sufficiently familiar with the details to arrive at the proper conditions for any given stock. We prefer, for instance, to operate tower T under a pressure of about 100 pounds absolute and at a temperature of about 180° F., but a wide range of operating conditions is permissible. Similarly, the conditions in the scrubber and fractionator N and O may be changed within wide limits and in fact, we may employ a recovery system similar to G, H and J in place of N and O. While we have described in detail a preferred embodiment of our invention it should be understood that we do not limit ourselves to any of said details except as defined by the following claims which should be construed as broadly as the prior art will permit.

We claim:

1. The method of preparing high anti-knock motor fuel which comprises subjecting substantially sulfur-free gaseous hydrocarbons to a controlled oxidation by contacting with steam and a catalyst comprising nickel at a temperature of about 1200 to 1500° F. to produce carbon monoxide and hydrogen, admixing said carbon monoxide and hydrogen with substantially unpolymerizable hydrocarbons, subjecting said mixture to a hydrocarbon synthesis step including con-

tacting said mixture with a catalyst comprising a metal of the eighth group at a temperature of about 400° F. to synthesize hydrocarbon gases, separating from said synthesized hydrocarbon gases a fraction containing substantially unpolymerizable fixed gases, recycling the recovered fixed gases to the first-mentioned high temperature controlled oxidation to produce additional carbon monoxide and hydrogen, separating from said synthesized hydrocarbon gases a second fraction containing polymerizable gaseous hydrocarbons, polymerizing at least a part of said synthesized hydrocarbon gases to form liquid hydrocarbons boiling within the motor fuel boiling range, fractionating the polymerization product to recover at least one fraction comprising unpolymerized hydrocarbons, admixing said carbon monoxide and hydrogen from the oxidation step with the unpolymerized hydrocarbons from the polymerization step and passing the mixture to the hydrocarbon synthesis step.

2. The method of manufacturing high anti-knock motor fuel which comprises subjecting hydrocarbon gases to controlled oxidation at a temperature of between about 1200° F. and 1500° F. in the presence of a catalyst to produce carbon monoxide and hydrogen, admixing said carbon monoxide and hydrogen with hydrocarbon gases, subjecting said mixture to a hydrocarbon synthesis by contacting with a synthesis catalyst at a temperature of about 400° F., fractionating the hydrocarbon synthesis product to recover normally gaseous olefins, unpolymerizable saturated condensible hydrocarbons, and a fixed gaseous fraction, recycling the fixed gaseous fraction to the said oxidation step to produce additional carbon monoxide and hydrogen, admixing the unpolymerizable saturated condensible hydrocarbons and the said carbon monoxide and hydrogen, conducting the said mixture to the hydrocarbon synthesis step to form additional normally gaseous olefins, polymerizing the normally gaseous olefins recovered by the fractionation of the hydrocarbon synthesis product, separating at least one polymer fraction comprising normally liquid hydrocarbons boiling within the motor fuel range and at least one fraction comprising unpolymerized hydrocarbons and recycling the said unpolymerized hydrocarbons to the hydrocarbon synthesis step with the normally gaseous hydrocarbons recovered from the hydrocarbon synthesis step.

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