

July 13, 1943.

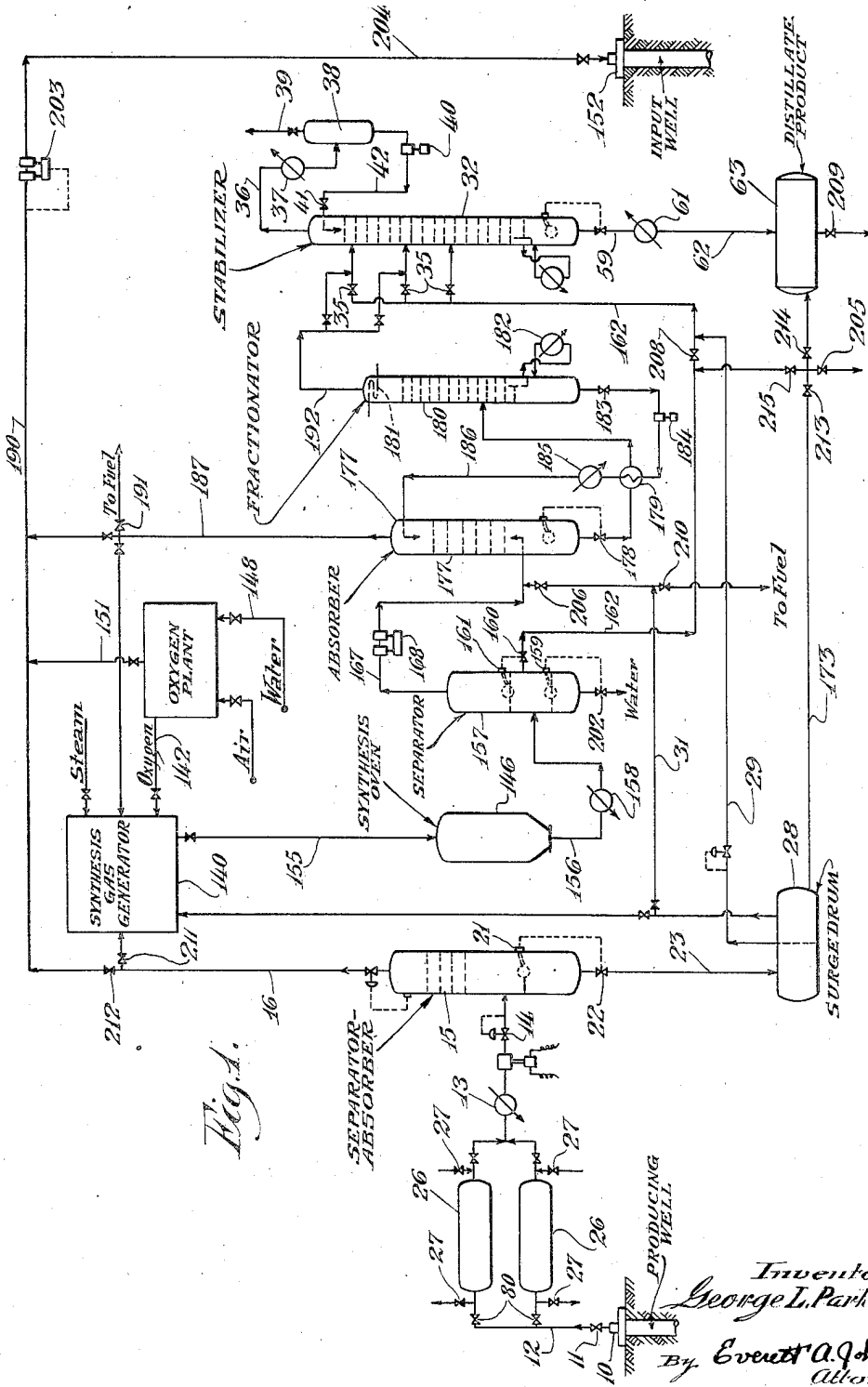
G. L. PARKHURST

2,324,172

PROCESSING WELL FLUIDS

Filed Oct. 31, 1940

3 Sheets-Sheet 1



Inventor:  
George L. Parkhurst  
By: Everett A. Johnson  
Attorney.

July 13, 1943.

G. L. PARKHURST  
PROCESSING WELL FLUIDS

2,324,172

Filed Oct. 31, 1940

3 Sheets-Sheet 2

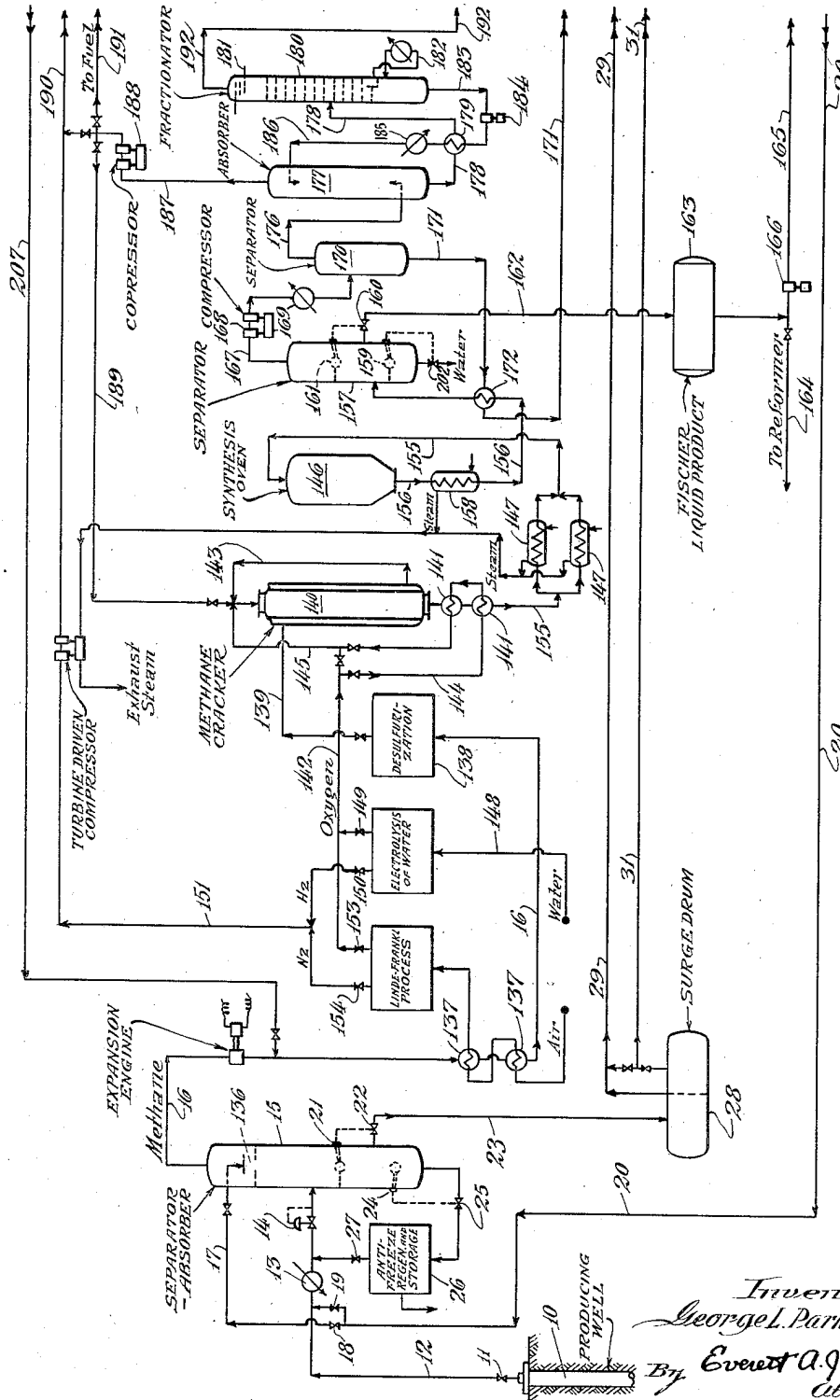


Fig. 2.

Inventor:  
George L. Parkhurst  
By: Everett A. Johnson  
Attorney.

July 13, 1943.

G. L. PARKHURST

2,324,172

PROCESSING WELL FLUIDS

Filed Oct. 31, 1940

3 Sheets-Sheet 3

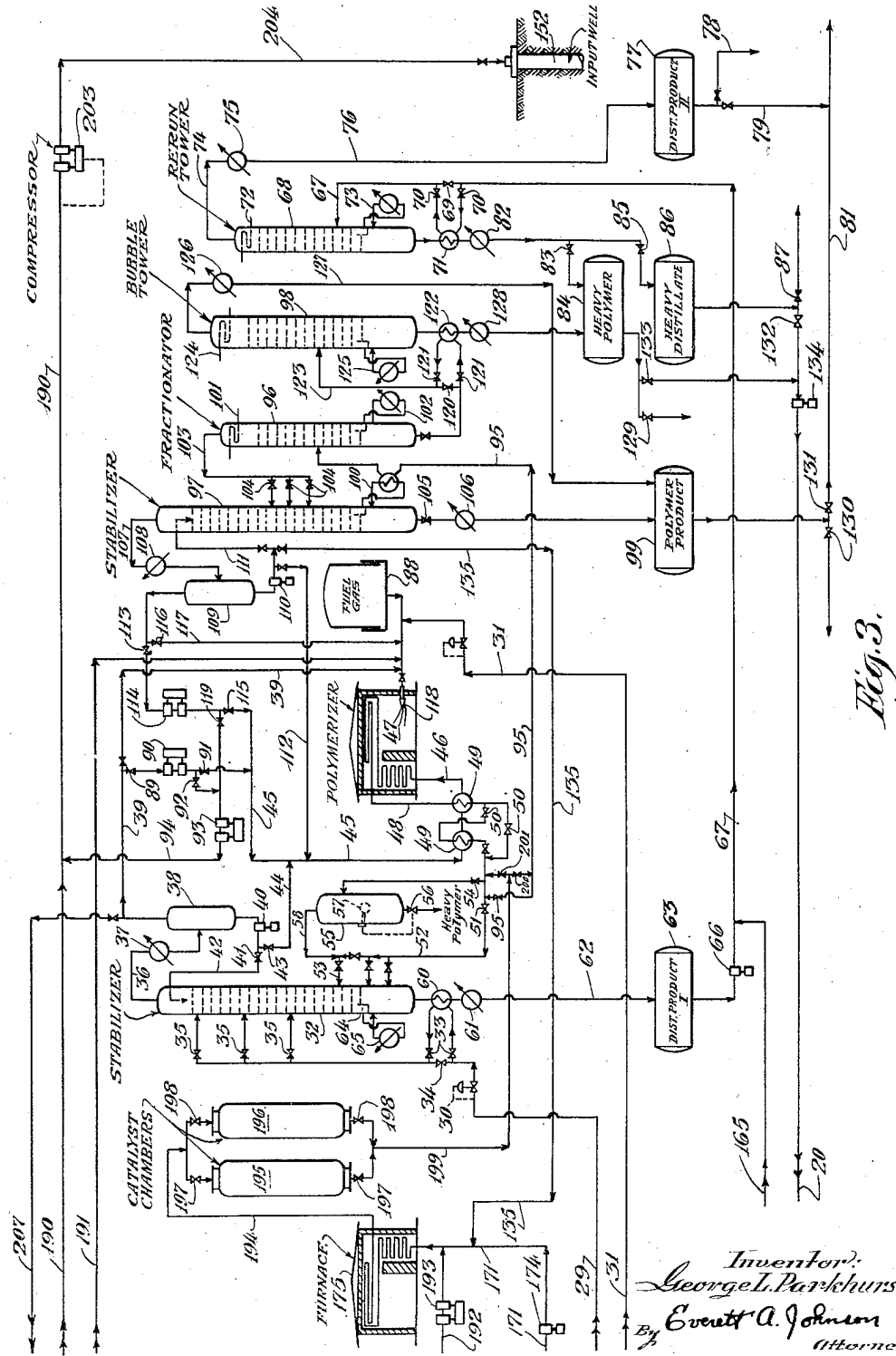


Fig. 3.

Inventor:  
George L. Parkhurst  
By: Everett A. Johnson  
Attorney

# UNITED STATES PATENT OFFICE

2,324,172

## PROCESSING WELL FLUIDS

George L. Parkhurst, Chicago, Ill., assignor to  
Standard Oil Company, Chicago, Ill., a corpo-  
ration of Indiana

Application October 31, 1940, Serial No. 363,737

3 Claims. (Cl. 44—50)

This invention relates to methods of hydrocarbon conversion and recycle which are particularly applicable for use in connection with wells of the so-called distillate or condensate type. The method is applicable also in connection with production from other types of wells when it is desired to cycle gas to repressure an underground formation. More particularly this invention relates to a combination of distillate recovery and the Fischer or Fischer-Tropsch process.

Production from certain deep hydrocarbon reservoirs of the so-called distillate type is wholly or largely in the vapor phase although these vapors contain substantial amounts of normally liquid hydrocarbons commonly including gasoline hydrocarbons and hydrocarbons boiling somewhat above the gasoline range. The existence of these hydrocarbons in the vapor phase in the sub-surface reservoir is due to the high pressure existing in the formation which brings into play the so-called retrograde phenomena, whereby a hydrocarbon system which would exist as a liquid phase plus a vapor phase at moderate pressures exists as a single dense vapor or super-critical phase.

If gases coming from these extremely high pressure wells, e. g. at pressures of the order of 2000 to 4000 pounds per square inch, are reduced in pressure to pressures of the order of 700 to 1200 pounds per square inch, a distillate or condensate is formed. In handling the production from such reservoirs the well fluids are reduced in pressure and sometimes cooled to bring about the phenomenon of retrograde condensation, whereby a large part of the normally liquid hydrocarbons and also a substantial part of three and four carbon atom hydrocarbons are thrown out in the liquid phase and separated. This liquid phase can then be stabilized or flashed to atmospheric pressure. The gases originally separated, and sometimes those resulting from the stabilization or flashing operation are recycled to the underground formation from which they were produced, thereby maintaining the pressure in such formation and preventing retrograde condensation therein, thus greatly improving the ultimate recovery from the reservoir. In some instances, these gases are used for the maintenance of the pressure in or the repressuring of an underground formation other than that from which they originated.

It has been proposed to recover the liquid components of high pressure well fluids of the type described by a high pressure absorption or high pressure adsorption process followed by recycling

of the gases to the same or another sub-surface reservoir for pressure maintenance or repressuring purposes.

Although the present invention is particularly applicable to production from high pressure wells of the distillate type, it is also applicable to ordinary gas wells, particularly where natural gasoline is present in the gas and to wells producing a liquid phase as well as a gas phase at the well head.

It is an object of my invention to increase the quantity of motor fuel produced from well fluids of the distillate type. Further, it is an object of this invention to provide repressuring gases having an increased ability to promote retrograde vaporization or prevent retrograde condensation in the reservoir. It is also an object to provide a process in which increased quantities of motor fuel are obtained from well fluids of the distillate type and in which the quantity and quality of the repressuring gases are increased. A more particular object is to provide a process in which at least a part of the gases remaining after a distillate recovery operation are so treated as to produce a synthetic crude oil which can be further processed to motor fuel. Other objects will appear hereinafter.

The production from distillate wells normally includes a large amount of methane and lesser amounts of higher paraffinic hydrocarbons. Ordinarily this includes a substantial amount of C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> hydrocarbons, with a substantial amount of hydrocarbons within the gasoline boiling range, i. e. up to about 400° F., and usually some still heavier hydrocarbons in varying amounts. In distillate recovery, whether by retrograde condensation or high pressure absorption, it is customary to recycle practically all of the C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> hydrocarbons and often a large part of the C<sub>4</sub> hydrocarbons to the underground formation. The desirable normally liquid hydrocarbons are recovered and are not available for recycling. Therefore, because of the diminished supply of recycle gas, pressure maintenance is not ordinarily completely successful. The process of my invention, however, uses certain of these lower hydrocarbons for the production of additional amounts of hydrocarbons boiling in the motor fuel range without seriously diminishing the initial supply of fixed hydrocarbon gases available for recycling, and in addition introduces to the system considerable amounts of hydrogen and/or nitrogen under high pressure which improves the function of the gases in the sub-surface retrograde phenomena.

The above and other objects are accomplished by subjecting to catalytic oxidation certain of the light hydrocarbons present in the dry gas resulting from a distillate recovery operation to produce a synthesis gas comprising carbon monoxide and hydrogen. This synthesis gas is subjected to a Fischer or Fischer-Tropsch process, and high pressure nitrogen and/or hydrogen is cycled to the input well.

Briefly, this method is followed by first separating the distillate from gases by retrograde condensation or by high pressure absorption at pressures of about 1000 pounds per square inch or more. These gases are processed as outlined below. The distillate is separated into a predominantly C<sub>3</sub> and C<sub>4</sub> fraction, a light naphtha in the gasoline boiling range and a heavy naphtha. The normally gaseous C<sub>3</sub> and C<sub>4</sub> hydrocarbons may be subjected at high temperatures and preferably at high pressures to a thermal polymerization process which produces not only a large amount of gasoline range hydrocarbons but also an amount of gas of even greater volume than the gaseous volume of the hydrocarbons going to the polymerization operation. These gases are available for recycling. The thermal polymerization process involves, among other reactions, the dehydrogenation of C<sub>3</sub> and C<sub>4</sub> hydrocarbons and of ethane to some extent, and the polymerization of the olefinic hydrocarbons thus produced to form normally liquid hydrocarbons ordinarily boiling largely in the gasoline range but including a heavy polymer fraction, which is very useful in connection with a high pressure absorption operation. The overhead from the initial Fischer product separation comprising mainly C<sub>3</sub> and C<sub>4</sub> olefins can be subjected to catalytic polymerization and the polymer combined with the product from the distillate C<sub>3</sub>-C<sub>4</sub> thermal polymerizer. This combined stream is further fractionated and cycled as described in detail in connection with the drawings.

In a preferred process the normally gaseous hydrocarbons remaining after recovery of the liquid hydrocarbons from the high pressure well fluids and comprising predominantly methane are desulfurized and subjected to cracking in the presence of oxygen to produce a synthesis gas comprising carbon monoxide and hydrogen.

The methane or gas fraction can be cracked to produce the synthesis gas mixture consisting largely of carbon monoxide and hydrogen by any of a variety of processes. Thus it can be reacted with steam or with oxygen. Preferably the dry gas is cracked in the presence of oxygen produced either by electrolysis of water or by a low temperature distillation process from air. For example, the oxygen necessary for this gas-cracking step can be produced by the Linde or Linde-Franks process. This results in a volume of high pressure nitrogen which theoretically will be equal to twice the volume of methane cracked, since one-half mol of oxygen will theoretically be used for each mol of methane and about two mols of nitrogen will be produced for each half mol of oxygen. This nitrogen is available at an elevated pressure and can be used directly for recycling to the formation, preferably by boosting its pressure by pumping it as a liquid, since this is much less expensive than compressing it as a gas.

An advantage connected with either electrolysis of water or oxygen concentration from air is that both processes produce gases other than oxygen which can advantageously be injected

into an underground reservoir to increase or maintain its pressure and displace the hydrocarbons in that reservoir towards the outlet well or wells. Thus electrolysis yields hydrogen and the oxygen concentration yields nitrogen under high pressure.

Alternatively or additionally the tail gases from the Fischer or Fischer-Tropsch process can be compressed and recycled through the formation or sent to another formation to displace the hydrocarbon fluids en masse towards the output well or wells and to prevent the precipitation of liquids within the reservoir which would result from a pressure drop. These tail gases not only contain hydrogen as the principal component but also contain nitrogen, carbon monoxide and light hydrocarbons and enhance the operation of the retrograde phenomena.

If the gas cracking is carried out with steam rather than oxygen, an excess of hydrogen will exist in the synthesis gas and in the tail gas from the Fischer process. These tail gases particularly high in hydrogen are highly beneficial for cycling to a sub-surface reservoir to increase or maintain the pressure in the reservoir thus increasing the ultimate recovery of valuable hydrocarbons from the reservoir.

The normally gaseous hydrocarbons heavier than methane, i. e. C<sub>2</sub> and/or C<sub>3</sub> and/or C<sub>4</sub> hydrocarbons, can be separated wholly or in part in one or more fractions from the products of the Fischer synthesis oven, which can be operated in one or two or more stages with or without an intermediate product recovery step. All or part of the normally gaseous products can be recycled to the gas-cracking step or can be compressed and cycled to the input well. Likewise, some of the gaseous hydrocarbons from the Fischer process can be cycled to fuel. It will be apparent to those skilled in the art that the ultimate disposition of the gases remaining after the various separations will vary depending not only upon the composition of the well fluid undergoing recovery but also upon the manner in which the various steps are operated. Various economic considerations will enter to determine further what is to be done with the various gas fractions other than the methane fraction from the distillate recovery. Ordinarily the methane fraction is cracked to synthesis gas and the hydrogen, nitrogen and Fischer tail gases ordinarily are sent to an underground formation under pressure, the hydrogen and nitrogen being under considerable pressure.

In a preferred process, the gases comprising the methane fraction remaining after recovery of liquid hydrocarbons from the well fluids are cracked to produce a synthesis gas mixture made up largely of carbon monoxide and hydrogen. Any of a variety of processes can be used, for example, the gases can be reacted with steam or with oxygen. Some hydrocarbons of higher molecular weight than methane can be included in the methane fraction separated from the well fluid, particularly where their presence serves to produce a better balanced synthesis gas mixture and the synthesis gas can, if desired, be made entirely from C<sub>2</sub> and C<sub>3</sub> or C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> hydrocarbons, thus retaining the methane for sub-surface recycle purposes. The cracked gases are subjected to the synthesis conditions and the synthesis products subjected to further treatment.

In a manner similar to that used for the distillate recovery, the normally gaseous hydrocar-

bons heavier than methane, i. e., the C<sub>2</sub> and/or C<sub>3</sub> and/or C<sub>4</sub> hydrocarbons, can be separated wholly or in part in one or more fractions from the liquid products of the Fischer synthesis. The recovered gases can be recycled in whole or in part to the gas-cracking step or the synthesis gas step or they can be thermally or catalytically polymerized. An intermediate fraction of the Fischer synthesis product can be thermally or catalytically polymerized to liquid hydrocarbons either separately or along with the distillate hydrocarbons. Hydrogen produced by either the thermal or catalytic treatment of the hydrocarbons can, of course, be forced down a well to repressure an underground formation.

In order that the invention may be better understood, reference is made to the accompanying drawings which show in Figures 1, 2 and 3 flow diagrams illustrating my invention and forming a part of this specification.

Referring first to Figure 1, a producing well 10 furnishes well fluids from a sub-surface reservoir which is normally a deep high pressure well of the distillate type. The well fluids pass through valve 11 and line 12 to one or the other of driers 26. These driers may contain any desired drying material, for example, calcium chloride. The particular drier used at any particular time is controlled by the operation of valves 20. Normally one drier is onstream and the other is being regenerated by passing hot gases there-through by means of valves 27. The purpose of the drying operation is to remove water which would otherwise form natural gas hydrates on reduction of the temperature and pressure, thereby interfering with the operation of the subsequent apparatus. However, if the temperature and pressure of the separation step are such that hydrate formation is not objectionable, the drying step can be omitted.

The well fluids pass through cooler 13 and pressure reduction valve 14 to separator 15. The cooler and pressure reduction valve are controlled to give a temperature and pressure in the separator 15 which may be varied within considerable limits depending on the desired operation and the particular character of the well fluids. However, they are such as to give a substantial recovery of liquid hydrocarbons by virtue of the retrograde condensation phenomenon.

The gas phase from separator 15 is predominantly methane but also includes ethane and minor amounts of heavier hydrocarbons. This gas phase passes through line 16 to methane cracker or synthesis gas generator 140, where it undergoes an exothermic catalytic oxidation. (If necessary the gases from separator 15 may be reduced in pressure prior to introduction to the methane cracker 140.) The liquid phase formed in separator 15 and withdrawn through line 23 by valve 22 controlled by float 21, includes a major part of normally liquid hydrocarbons present in the well fluids and normally gaseous hydrocarbons, particularly C<sub>3</sub> and C<sub>4</sub> paraffinic hydrocarbons. These gases may be recovered by known means and the fraction in the gasoline boiling range passed from surge drum 28 by line 173 to Fischer Process gasoline storage tank 63.

The synthesis gas generator 140 is supplied with oxygen produced by electrolysis of water with by-product hydrogen under high pressure, for example, about 4000 pounds per square inch, or by the Linde-Franks process with nitrogen under high pressure as a by-product. The hydrogen or nitrogen is cycled via line 151 to input well

152 and oxygen passes to methane cracker 140 by line 142. The synthesis gas comprising largely hydrogen and carbon monoxide is withdrawn from methane cracker 140 by line 155 and introduced in synthesis over 146. In oven 146 the carbon monoxide and hydrogen are reacted to produce higher molecular weight hydrocarbons largely of the gasoline boiling range. This step is well known in the art and it is contemplated that it may be carried out under any one of the variety of conditions under which it is known to operate. Thus it may be carried out at pressures ranging from about atmospheric up to about 150 pounds per square inch or somewhat higher, and within the temperature range of between above 300° F. and 400° F., although somewhat higher and somewhat lower temperatures may be selected.

The synthesis product containing substantial amounts of olefins is removed from oven 146 by line 156 to separator 157. If desired, cooler or waste heat boiler 158 may be placed on line 156 between synthesis oven 146 and separator 157 to cool reaction products prior to introduction to the separator 157.

Considerable quantities of water are produced in the hydrocarbon synthesis from carbon monoxide and hydrogen and this water ordinarily is removed from the hydrocarbons and discarded from the system by valved line 202 in response to float control 159. When the process is operated to produce a predominantly synthesis gasoline, it is drawn off by valved line 162 and passed to stabilizer 32, the bottoms from stabilizer 32 being drawn off by line 59 through cooler 61 and thence to product tank 63.

The gas phase from separator 157 is pumped to absorber 177. Alternatively, the gas phase can be sent to fuel via valved line 206 and valve 210. The gases removed from absorber 177 via line 187 may be recycled to the input well or may be used as fuel. The liquid product from absorber 177 is withdrawn as bottoms by valved line 178, passed in heat-exchange relation with an absorber oil flowing in line 186 by means of heat exchanger 179 and introduced to fractionator 180. Fractionator 180 is provided with conventional dephlegmating means 181 and with reboiler 182. The bottoms from fractionator 180 is pumped via valved line 183 by pump 184 through heat exchanger 179 and cooler 185 and introduced as lean absorber oil in absorber 177 by line 186. The gases from absorber 177 comprising predominantly hydrogen are withdrawn by line 187 and may be compressed and recycled to the input well via line 190. Alternatively, the gases can be sent to fuel by valved line 191, or they may be recycled to the methane cracker or synthesis gas generator 140.

Returning to the fractionator 180, the gas phase withdrawn overhead by line 192 may be introduced to stabilizer 32 by either of valved lines 35. Reflux in addition to that resulting by the use of the cold material from the product separator 157 can be furnished by passing the off-gases from stabilizer 32 through partial condenser 37 to separator 38 from which a part of the liquid phase can be pumped by means of pump 40 through valve 41 back into the top of stabilizer 32. The off-gases from separator 38 can be recycled to methane cracker 140 or used as fuel.

Although the simple flow diagram and arrangement of apparatus shown in Figure 1 is advantageous in many respects, it is also desir-

able in some instances to use more extensive processing and equipment. This is particularly true where large production is available and where the characteristics of the formation in well fluids are such that the production of the well or wells declines only very slowly, justifying a high capital investment in obtaining increased efficiency. Figures 2 and 3 taken together illustrate some of these possibilities.

Referring to Figures 2 and 3 in more detail, the production from one or more producing wells 10, which are preferably of the distillate type, passes through valve 11 and line 12 into cooler 13 and pressure reduction valve 14 to a separator absorber 15 which, if valves 18 and 19 are closed and no absorber oil is introduced by lines 20 and 17, operates as a retrograde condensation separator similar to that shown in Figure 1. One difference, however, is that Figure 2 shows the use of an antifreeze system as one method of preventing natural gas hydrate trouble. A fluid antifreeze material, for example, calcium chloride brine, can be circulated with the well fluids through pressure reduction valve 14 and this serves to prevent the formation of natural gas hydrates. In the case of liquid antifreeze material, the antifreeze separates at the bottom of the separator absorber 15 and is withdrawn by valved line 25 under control of float 24 which floats at the interface between the antifreeze and the hydrocarbons. The antifreeze is withdrawn to a regeneration, storage and recycling system from which it goes back into the line either preceding or following cooler 13. In Figure 2 the regenerated antifreeze is returned by valved line 27 between the cooler 13 and pressure reduction valve 14.

It will be understood, however, that some of these apparatus arrangements may be omitted depending upon the character of the well fluids and the character of the subsequent operations. Thus, for example if the well fluids are available at moderate pressures, for instance 1500 to 3000 pounds per square inch, a pressure reduction ordinarily will not be needed and is not desirable when the distillate recovery is effected by absorption. If the product is very low in water content or if the separator-absorber 15 is operated at a temperature above that at which hydrates form under the particular conditions involved, the antifreeze step can be omitted. An alternative method of avoiding the natural gas hydrates is shown in Figure 1, wherein the well fluids are dried by passing them through a drier containing a solid contact mass such as calcium chloride for example.

The well fluids enter the high pressure separator-absorber 15 and the gases, chiefly methane, are withdrawn from separator 15 by line 16. The liquid hydrocarbons in separator 15 are withdrawn through valve 22 under the control of float valve 21 and passed by means of line 23 to surge drum 28. This surge drum can be operated at about the same pressure as separator 15 in which case it serves only as the surge drum. Or it may be operated at a pressure intermediate that of separator 15 and that of stabilizer 32, in which case it serves not only as a surge drum but also as a separator. Thus, for example, the distillate recovery vessel 15 can be operated at 1200 pounds per square inch, the surge drum 28 at 600 pounds per square inch, and stabilizer 32 at 300 pounds per square inch. Valved line 31 leading from surge drum 28 to fuel gas system 88 is provided.

Thus when surge drum 28 is operated as a separator, some of the gases can be removed to fuel.

The liquid present in surge drum 28 passes through line 29 and pressure reduction valve 30 into stabilizer 32. Before entering the stabilizer 32 all or part of the liquid can be used to cool the stabilized product by wholly or partially closing valve 34 and opening valves 33, thereby passing this cooled stream from the surge drum 28 through heat exchanger 60. On the other hand it is often desirable to utilize the low temperature of this material from the surge drum not as indirect heat-exchange material in heat exchanger 60 but rather as refluxing material in stabilizer 32. When the stream from the surge drum is not routed through the heat exchanger 60 prior to introduction into the stabilizer, the point of introduction preferably is the one corresponding to the upper of the three alternative valved lines 35.

In stabilizer 32 hydrocarbons lighter than butane are removed and the stabilizer is preferably operated at such pressure, reflux ratio, and top temperature as to eliminate a portion of the C<sub>4</sub> hydrocarbons not desired in the finished motor fuel. Reflux in addition to that resulting by the use of the cold material from the surge drum 28 can, if desired, be furnished by passing the off-gases from the stabilizer 32 via line 36 through partial condenser 37 to separator 38 from which a part of the liquid phase can be pumped by means of pump 40 through valve 41 and line 42 back into the top of stabilizer 32. If the hot material from polymerizer 47 is introduced into stabilizer 32 through line 53, as will be discussed hereinafter, little or no reboiling is necessary. However, if this is not the case, i. e. if a separate fractionator apparatus is used for the polymerization products, reboiling can be furnished by means of trapout plate 64 and heater 65. Some heating at this point may be desirable, even if the hot polymerization products are discharged into the stabilizer.

Stabilized material from stabilizer 32 can be cooled by heat exchanger 60 and/or cooler 61 and then passed to intermediate products storage tank 63. Since the material in this intermediate products storage tank normally contains a considerable amount of hydrocarbons boiling above the gasoline range, it can be rerun. Therefore, it is withdrawn by means of pump 66 and passed through line 67 to rerun tower 68. When desired, the liquid product from the Fischer process may be rerun with the bottoms from stabilizer 32 which may include gasoline, polymers and distillate hydrocarbons.

Rerun tower 68 can be operated at low pressure and is a conventional piece of equipment. If cooler 61 has been used, the material from intermediate product storage tank 63 can be used to cool the hot bottoms from rerun tower 68 by closing valve 69 and opening valves 70, thus passing this relatively cold stream through heat exchanger 71. In any event the material to be rerun enters the rerun tower 68 by line 67. The tower is provided with dephlegmating coil 72 and reboiling equipment 73. Stabilized gasoline of the desired end point is taken off through line 74, passed through condenser 75 and then passed via line 76 to storage tank 77 which with proper control may contain the final gasoline produced directly from the distillate. If the liquid product from the Fischer process has not been rerun with the intermediate product from stabilizer

32, this gasoline can be withdrawn through valved line 78 for shipment or for further treatment. Alternatively, it may be withdrawn through valved line 79 and blended in line 81 with the gasoline produced in the polymerization operation, and this is in general desirable since the polymer gasoline has a relatively high knock rating and the distillate gasoline has a relatively high volatility so that the two together make an excellent blended motor fuel.

The bottoms from the rerun 68 may be cooled in heat exchanger 71 and/or cooler 82 and then passed by valved line 83 to tank 84 and blended with the heavy polymer which as hereinafter will appear is normally the main product passing to this tank. In some instances the heavy distillate tank 86 can be omitted and all the heavy distillate can be passed along with the heavy polymers in tank 84. The heavy polymers separately accumulated in tank 84 is the best absorber oil for use in distillate separator 15. Therefore, when the separator 15 is operated as a high pressure absorber, the heavy distillate can be collected in storage tank via valved line 85 and removed by valved line 87.

Returning now to separator 38 in connection with stabilizer 32, the liquids from this separator alternately are passed by pump 40 through valve 43, line 44, line 45, heat exchangers 48 and line 46 into the coils of the polymerization furnace 47.

The gases from separator 38 on the other hand can be utilized in a variety of ways which will depend for the most part upon their composition. Their composition in turn depends on the pressures chosen for various parts of the apparatus and on the composition of the original well fluids. If gases from the surge drum 28 are not used as fuel, gases from separator 38 can be used as part or all of the fuel for polymerizer 47. Fuel gas storage tank 88 normally floats on the line. The gases from separator 38 normally contain a substantial amount of polymerizable components and it is therefore desirable to pass all or a part of them from valved line 39 through valve 89, compressors 90, valve 91, line 45, heat exchangers 49 and line 46 to the coils of a polymerization furnace 47. The third possibility which is desirable when fuel gases are available from other sources and when, as is ordinarily the case, the gases from separator 38 do not contain large amounts of polymerizable hydrocarbons, is to pass all or a part of these gases through valve 89, compressors 90, valve 92, compressors 93, line 94, line 190, compressors 203, and line 204 to input well 152. I prefer, particularly when polymerizer 47 discharges into stabilizer 32, to cycle the greater part of the gas from separator 38 to the input well or wells 152. Gases from downstream points can be picked up and recycled to a point in the Fischer process. For example, valved line 207 can be provided for that purpose.

Referring now in more detail to polymerizer 47, the hydrocarbons entering it are preheated by means of heat exchangers 49, or by one of them if so desired, by control of flow of product by valves 50, and then pass with any desired routing through the coils of the polymerization furnace 47. This polymerizer is preferably operated at a temperature of between about 950 and 1150° F., for instance about 1025° F., and at a pressure of 1000 to 3000 pounds per square inch, for example 1500 pounds per square inch.

Other types of polymerizers may be used, preferably high temperature thermal polymerization

systems, but also including thermal and catalytic systems in which the gases are first dehydrogenated and then polymerized in a separate operation. Such a polymerization can be applied to the synthetic crude produced by the Fischer process as will be described below. Although the operation of polymerization involves dehydrogenation as well as polymerization, in the strict sense of the latter term, I refer to the combined reactions, whether occurring together or in separate steps, as polymerization. This is in accordance with the usage in the art.

The reaction products from the polymerizer 47 pass out through line 48 and heat exchangers 49 and thence through valved lines 51, 54, or 95. If desired, the hot polymerization products from polymerizer 47 can enter separator 55 by valved line 54 in which case valve 51 is closed. The heavy polymer may be withdrawn by valved line 56 in response to float control 57. The remaining vapors then pass by valved line 58 and one of valved lines 53 to stabilizer 32. This has the advantage of using a single column for two purposes and utilizing the hot stream from the polymerizer and the relatively cold stream from the distillate recovery operation to good advantage in eliminating or cutting down the amount of reflux and reboiling necessary in connection with this tower. When this operation is carried out in this fashion, tanks 63, 77 and 86 will, of course, contain the polymer product as well as the distillate product, and stabilizer 97, fractionator 96, bubble tower 98 and tanks 84 and 99, together with the associated equipment, can be eliminated.

On the other hand, it is sometimes advantageous to keep the polymerization products entirely separate from those of the distillate recovery operation, and when this is desired valves 51 and 54 can be closed and valve 95 opened, thus sending the products from the polymerizer 47 to a separate fractionation system. Another possibility is to utilize a separate fractionation system only for such part of the polymer products as it is desired to keep separate and to retain the advantages of single tower operation insofar as the bulk of the polymer products is concerned. This can, of course, be accomplished by proper control of valves 51, 54 and 95.

The material, if any, passing through valved line 95 can be used, if so desired, to heat reboiler 100, whereupon it enters fractionating column 96 which is operated under such conditions that the gases and a portion of the gasoline is taken overhead and a portion of the gasoline and the heavy polymers is eliminated as bottoms. Fractionator 96 can be provided with dephlegmator 101 and reboiling apparatus 102. The overhead from this fractionator 96 passes into stabilizer 97 through line 103 and one of the three alternative valved lines 104. The bottoms from the stabilizer is withdrawn through valve 105 and passed through cooler 106 to storage tank 99 as part of the stabilized polymer gasoline product. The overhead from stabilizer 97 passes through line 107 and partial condenser 108 to separator 109. A portion of the liquid phase from this separator can be passed by pump 110 through valved line 111 to serve as reflux in stabilizer 97. Likewise all or a portion can be recycled by valved line 112, line 45, heat exchangers 49 and line 46 to the coils of the polymerization furnace 47 to produce higher ultimate yields of polymer gasoline. Alternatively, all or a portion of the liquid phase from separator 109 may be routed by valved line



135 and line 171 to furnace 175 and subsequently subjected to catalytic polymerization together with the synthetic crude produced by the gas-cracking and hydrocarbon synthesis steps.

The gas phase from separator 109 may be handled in any one or more of the three alternative ways discussed in connection with the gas phase from separator 38. Thus it may be passed through valve 113, compressors 114, valve 115, line 45, etc. to the coils of the polymerizer 41; or through valve 116 and line 117 to burner 118 or fuel gas storage 88; and/or it may be passed by valved line 113, compressors 114, valve 119, compressors 93, line 94, line 190, compressors 203, and line 204 to one or more input wells 152. This latter is a highly desirable operation, since it is important to keep up the amount of gas available for recycling to the formation and this gas being rich in hydrogen is a particularly desirable material for recycling. In many instances, it will be possible to eliminate part of the compressors referred to, since it will not be desired to utilize all of these possible alternative arrangements shown.

Reverting now to the bottoms from the fractionator 96, these can be used, if desired, to cool the bottoms from bubble tower 98 by closing valve 120 and opening valves 121, whereby the hot stream passes through heat exchanger 122 and thence through line 123 into the bubble tower 98. This bubble tower is conventionally equipped with dephlegmating means 124 and reboiling means 125. It is so operated as to eliminate a heavier than gasoline bottoms and a gasoline overhead. The latter is passed through condenser 126 and line 127 to polymer product tank 99 while the bottoms pass through heat exchangers 122 and/or cooler 128 to heavy polymer tank 84.

The heavy polymer can be withdrawn from tank 84 for any desired purpose through valved line 129 and the heavy distillate from tank 96 similarly can be withdrawn through valved line 87. However, it is advantageous to use one or both of these materials as an absorber oil and to operate vessel 15 as a high pressure absorber rather than merely as a retrograde condensation separator, since the recovery of distillate can ordinarily be increased quite substantially by so doing.

The polymer product of gasoline boiling range can be withdrawn from tank 99 through valved line 130 for storage, further treatment or use, or can be, and preferably is, withdrawn through valve 131 for admixture with the distillate gasoline in line 81.

As has been pointed out above, the preferred absorber oil is the heavy polymer separately accumulated in tank 84 and this is one of the principal reasons for using a separate fractionating system on at least a part of the polymer products. In connection with small installations, it will be apparent that this fractionating system can be simplified considerably. In the preferred operation using heavy polymers as absorber oil, the heavy distillate is withdrawn from the system through valved line 87, valves 83 and 132 being closed, while such part of the heavy polymer as is needed for absorber oil passes through valve 133, pump 134, line 20 and one or both of valves 18 and 19 into the separator-absorber 15.

Referring more in detail to the processing of the methane fraction, the gases recovered from the separator-absorber 15 pass by line 16 to an organic sulfur removal unit 138, the desulfurized gases being passed to the methane cracker 140

by line 139. Ordinarily, the methane or gas fraction is passed concurrent to the flow through the unit as a cooling medium around the tubes. The methane fraction is then circulated by line 143 to the top of the methane cracker 140 and re-enters the unit with the oxygen in line 145. These combined gases enter the catalyst bed at about 900 F. and the product gases are removed from the bottom of the methane cracker 140 at about 1600° F. Heat exchangers 141 are provided on the product gas line to preheat the oxygen flowing via lines 142 or 144 and 145 to the stream entering the methane cracker. In passing through the methane cracker the methane is subjected to catalytic oxidation at a temperature of about 1600° F. and at a pressure of about 140 pounds per square inch. The methane fraction would be available at about this pressure and at about 375° F. from the organic sulfur removal process. The oxygen is available at about 60° F. The product gases should be cooled to about 400° F. before entering the synthesis oven 146. When desired, heat can be removed from oven 146 by recycling cold gas or by water tubes. The sensible heat content of the product gases between about 1600° F. and about 400° F. is removed before the synthesis gas reaches the synthesis oven 146. A portion of this heat is removed by heat exchanger 141 in preheating the oxygen and the heat above about 700° F. is recovered in waste heat boiler 147. The remainder of the heat may be discarded in a water cooler (not shown).

The oxygen for the catalytic oxidation of the methane fraction may be obtained by the electrolysis of water or by the Linde or the Linde-Fränk process from air. In the electrolysis of water, electrode pressure of the order of 1000 atmospheres of hydrogen may be obtained for cycling to the input well 152.

The electrolysis of the water as a source of oxygen produces a quantity of by-product hydrogen under very high pressure and this hydrogen may be cycled to the underground reservoir dispensing with the recompression of the gases. In Figure 2 the water enters the system by line 148, the oxygen being led to line 142 by valved line 149; the hydrogen passing via valved line 150 and line 151 to input well 152. When the oxygen necessary for the gas-cracking step is produced by the Linde or Linde-Fränk process, there results a volume of by-product nitrogen which is available at an elevated pressure. The air is passed through heat exchanger 137 and the recovered oxygen is led to line 142 by valved line 153, the recovered high pressure by-product nitrogen passing via line 154 to line 151 and ultimately to input well 152. Thus by my process there is no deficiency of recycled gas and an increased quantity of motor fuel is produced from the well fluids.

According to the preferred procedure, the methane fraction which may include selected higher hydrocarbons is subjected to catalytic oxidation at high temperature and under moderate pressure according to the known process. Suitable temperatures are of the range of 1450° F. to 1700° F. and pressures may range from atmospheric up to about 150 pounds per square inch.

A suitable catalyst for use in the synthesis oven are metals of the eighth group, i. e. iron, cobalt and nickel, with cobalt being particularly useful. The catalyst may be supported on kieselguhr, for example, and is rendered more active by the presence of small amounts of difficultly

reducible oxides such as alumina, thoria, zirconia, chromium oxide and the like. A particularly preferred catalyst is cobalt on kieselguhr promoted by small amounts of thoria and magnesia. This reaction is highly exothermic and heat is removed from the reaction products by waste heating boilers which produce steam, which in turn may be used as power for compressing the discard gases cycled to the input well.

Alternatively, the synthesis gas may be produced by reacting the methane with steam. This latter reaction is less desirable since it is not exothermic, as is the reaction between methane and oxygen, and further since it produces an excess of hydrogen, the mol ratio of hydrogen to carbon monoxide being about 3:1. This can be compensated by including some hydrocarbons higher than methane with the methane fraction or by introducing carbon monoxide from another source. The gaseous reaction products of the catalytic oxidation are, of course, carbon monoxide and hydrogen. From this carbon monoxide and hydrogen, hydrocarbons are synthesized by the Fischer process. A mol ratio of hydrogen to carbon monoxide of about 2:1 ordinarily is used to produce hydrocarbons predominating in paraffins. Decreasing the hydrogen content of the synthesis gas gives a more olefinic product. Thus a hydrogen to carbon monoxide ratio of about 1.5 to 1 yields more olefins.

The synthesis gas comprising largely hydrogen and carbon monoxide is withdrawn from methane cracker 140 by line 155 by which it passes to the synthesis oven 146. In oven 146 the carbon monoxide and hydrogen are reacted with each other and with any hydrocarbons present to produce higher molecular weight hydrocarbons largely of the gasoline boiling range. This step is well known in the art and it is contemplated that it may be carried out under any one of the variety of conditions under which it is known to operate. Thus it may be carried out at pressures ranging from atmospheric up to about 150 pounds per square inch, or somewhat higher, and within the temperature range of between about 300° F. and 400° F., for example 383° F., although somewhat higher and somewhat lower temperatures may be used if desired.

It is well recognized that the Fischer synthesis is highly exothermic and if uncontrolled the heat effect raises the temperature of the reaction to a point where methane and carbon are produced. At the same time it is necessary to keep the reaction temperature between narrow limits. The dissipation of the heat of reaction may be effected by circulation of water around the catalyst containers, thereby generating steam suitable for process use.

The synthesis product is removed from the oven 146 by line 156 to separator 157. If desired, waste heat boiler 158 may be on line 156 to cool the reaction product prior to introduction to the separator 157.

Considerable quantities of water are produced in the Fischer process and this water ordinarily is removed from the hydrocarbons and discarded from the system through valved line 202 in response to float-control 159. If the product separator 157 is operated under such conditions that a synthesis gasoline fraction is recovered, valve 160, operating in response to float-control 161, in line 162 provides a means for drawing it off to storage tank 163 or for further treatment.

The heavy liquid fraction from a Fischer synthesis frequently has a very low octane number and therefore it may be desirable to send the product to a reforming step by valved line 164. However, where a finished motor fuel is produced in the Fischer synthesis it may be pumped by pump 166, line 165 and line 67 to rerun tower 68.

The gaseous product of the synthesis is taken off overhead from separator 157 by line 167, compressed by compressors 168, and sent to cooler 169 before entering separator 170. The liquid fraction from separator 170 is withdrawn by line 171 and passed in heat-exchange relationship with the synthesis products going to the product separator 157. Heat exchanger 172 is provided for this purpose. The liquid fractions comprising substantial amounts of olefins are sent via line 171 and pump 174 to furnace 175. The gaseous products from separator 170 are withdrawn by line 176 and passed to absorber 177, wherein it is subjected to the action of a circulating absorber oil. The rich absorber oil is withdrawn from absorber 177 by line 178, passed through heat exchanger 179 and introduced to fractionator 180. Fractionator 180 is provided with a conventional dephlegmating means 181 and reboiler 182. The bottoms from fractionator 180 is passed via line 183 and pump 184 through cooler 185 and introduced as the lean absorber oil in absorber 177 via line 186. The tail gases from absorber 177 comprising predominantly hydrogen are withdrawn by line 187. These gases may be recycled to the methane cracker 140 by valved line 189. They may be compressed by compressors 188 and recycled to the input well by line 190, or the tail gases may be sent to fuel by valved line 191.

Reverting to fractionator 180, the gaseous fraction is withdrawn overhead by line 192, compressed by compressors 193, and passed to furnace 175. Thus the bottoms from separator 170 and the overhead from fractionator 180 are heated in the same furnace. The hot feed passes by line 194 to catalyst chambers 195 and 196, where polymers are formed.

The elevated temperature maintained in the polymerization zone is ordinarily in the range of 300 to 500° F. and the pressure usually is about 150 to 1500 pounds per square inch. The above conditions are for catalysts of the phosphoric acid-kieselguhr or metal pyrophosphate types. Sulfuric acid and aluminum halide may be used at lower temperatures. Valves 197 and 198 are provided whereby one catalyst chamber is on-stream, while the other is being regenerated. The reaction products are removed from the catalyst chamber by line 199, and can be passed by valved line 200 and valved line 95 to fractionator 96. Alternatively, the reaction products may be introduced by valved line 201 to valved lines 51 or 54 and blended with the reaction products from polymerizer 47.

Vessel 15 when operated as an absorber can usually be operated at a somewhat higher pressure and, if desired, at a slightly higher temperature than when operated as a retrograde condensation separator. More specifically as an absorber its pressure may range from 1000 to 4000 pounds per square inch, usually from 1200 to 3000 pounds per square inch, for instance 2000 pounds per square inch. The absorber oil in any desired ratio, for example two to six gallons per thousand cubic feet of gas, can be introduced above baffles 136, or part of it or even all of it can be passed through cooler 13 into the

absorber along with the well fluids. The absorber oil, of course, is removed from vessel 15 along with the distillate hydrocarbons and finds its way through surge drum 28 and stabilizer 32 to intermediate storage tank 63 and ultimately to heavy distillate storage tank 86. By this route the absorber oil becomes contaminated with the heavy distillate and in the preferred operation the newly produced heavy polymer is continuously sent to the absorber as an absorption medium, since its aromatic character and its high critical temperature make it possible to operate separator-absorber 15 at a higher pressure than would otherwise be the case. If desired, the material to be used as absorber oil may be fractionated. Thus for instance the heavy polymers in tank 84 could be fractionated and the desired fraction could be sent to the absorber 15. For economic reasons the operation at a higher pressure is more desirable.

It is to be understood, of course, that the various flow diagrams presented are merely illustrative of some of the possibilities and other alternative routings will occur to those skilled in the art in view of this description. Therefore my invention is not restricted to the details shown. Likewise, it will be understood that these flow diagrams are simplified for purposes of convenience and that various items of pumping and compressing equipment, insulation control devices, safety equipment, and various other details are not indicated.

Having described my invention what I claim is:

1. A method of effecting maximum recovery from a high pressure petroleum reservoir and of preparing liquid hydrocarbons from high pressure well fluids recovered therefrom comprising the steps of simultaneously generating oxygen and a by-product gas of the oxygen generation at about the pressure of the high pressure reservoir, injecting said high pressure by-product gas into a high pressure petroleum reservoir to effect maximum recovery of high pressure well fluids, separating said well fluids at a high pressure into at least one fraction rich in normally gaseous hydrocarbons and at least one fraction rich in distillate motor fuel hydrocarbons, generating a synthesis gas comprising carbon monoxide and hydrogen by treating said normally gaseous hydrocarbons at an elevated temperature in the presence of said generated oxygen, subjecting the said synthesis gas to an exothermic hydrocarbon synthesis step, fractionating the product from said hydrocarbon synthesis into at least one gas fraction and at

least one liquid fraction, said liquid fraction being rich in motor fuel hydrocarbons.

2. A method of effecting maximum recovery from a high pressure petroleum reservoir and of preparing liquid hydrocarbons from high pressure well fluids recovered therefrom comprising the steps of simultaneously generating oxygen and a by-product gas of the oxygen generation at about the pressure of the high pressure reservoir, injecting said high pressure by-product gas into a high pressure petroleum reservoir to effect maximum recovery of high pressure well fluids, separating said well fluids at a high pressure into at least one fraction rich in normally gaseous hydrocarbons and at least one fraction rich in distillate motor fuel hydrocarbons, cycling at least a portion of the high pressure normally gaseous hydrocarbons along with the high pressure by-product gas to the high pressure petroleum reservoir to enhance the retrograde vaporization effect of the pressuring gases, generating a synthesis gas comprising carbon monoxide and hydrogen by treating said normally gaseous hydrocarbons at an elevated temperature in the presence of said generated oxygen, subjecting the said synthesis gas to an exothermic hydrocarbon synthesis step, fractionating the product from said hydrocarbon synthesis into at least one gas fraction and at least one liquid fraction, said liquid fraction being rich in motor fuel hydrocarbons.

3. A method of effecting maximum recovery from a high pressure petroleum reservoir and of preparing liquid hydrocarbons from high pressure well fluids recovered therefrom the steps comprising simultaneously generating oxygen and a by-product gas of the oxygen generation at a high pressure of the magnitude of the pressure existing in a petroleum reservoir, injecting said high pressure by-product gas into the high pressure petroleum reservoir to effect maximum recovery of high pressure well fluids, separating said well fluids at high pressure into at least one fraction rich in methane and at least one fraction rich in distillate motor fuel hydrocarbons, generating a synthesis gas comprising carbon monoxide and hydrogen by cracking said fraction rich in methane in the presence of said oxygen, subjecting said synthesis gas to an exothermic hydrocarbon synthesis step, recovering from the product of said hydrocarbon synthesis step at least one synthesis fraction rich in motor fuel hydrocarbons, and blending said distillate motor fuel hydrocarbons and said synthesis fraction.

GEORGE L. PARKHURST.