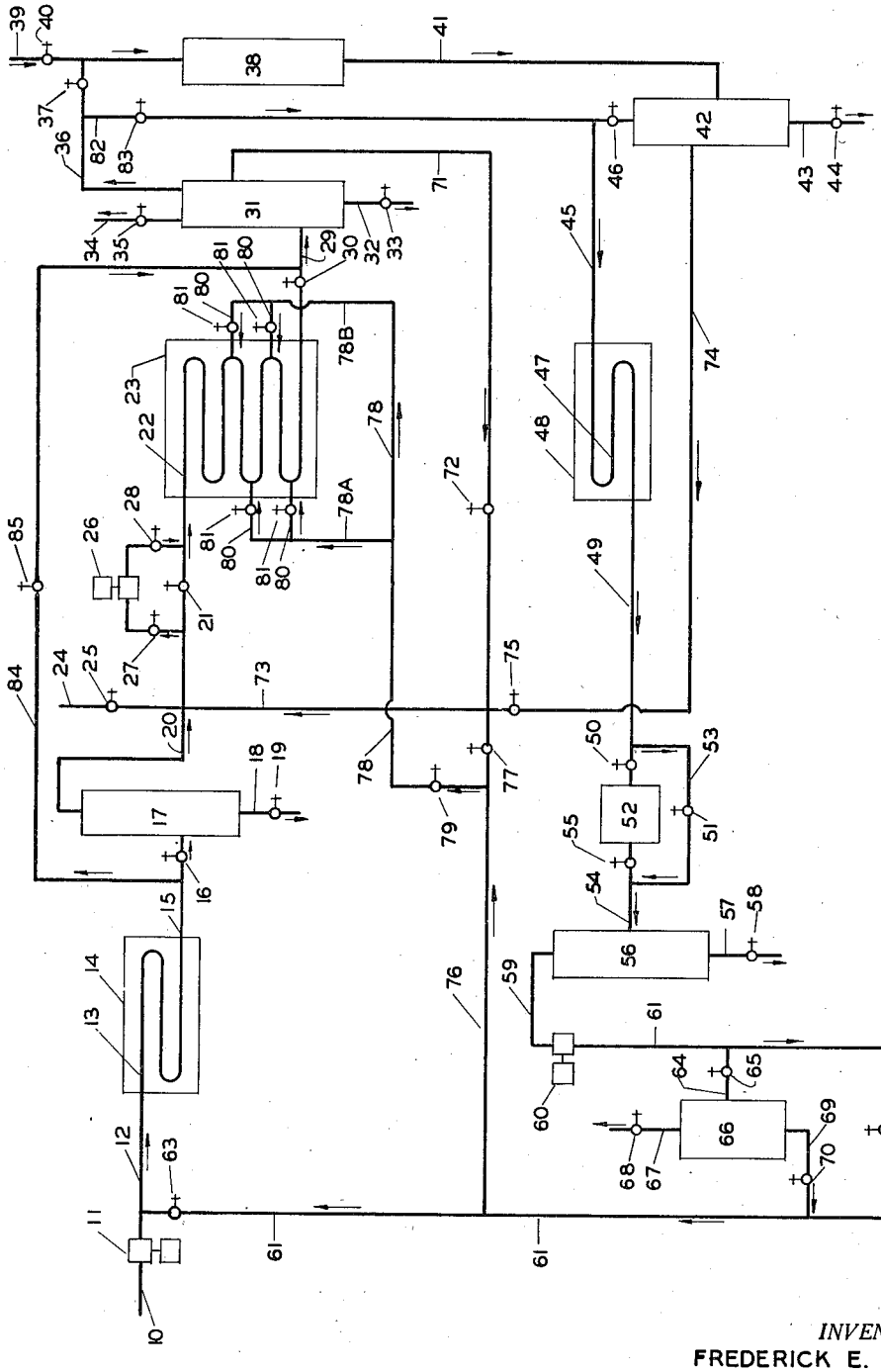
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PROCESS FOR CONVERTING HYDROCARBONS

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INVENTOR.
FREDERICK E. FREY

BY Hudson, Connor and Young
ATTORNEYS.

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PROCESS FOR CONVERTING HYDROCARBONS

Frederick E. Frey, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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This invention relates to the conversion of normally gaseous hydrocarbons into normally liquid motor fuel, and more specifically to processes for obtaining increased efficiency and economy by the use of non-catalytic and catalytic conversion steps in cooperative relationship whereby a mixture of normally gaseous hydrocarbons are fractionally treated and converted to obtain an optimum yield at a minimum expense of motor fuel with high anti-detonating qualities.

A number of processes are in use today for the production of hydrocarbon motor fuels such as gasoline by subjecting higher boiling hydrocarbons to decomposition temperatures. In all of these processes a more or less large amount of normally gaseous hydrocarbons are produced of varying composition, which if not utilized represent wasted natural resources. In so called liquid phase cracking processes there are produced gaseous hydrocarbons of a substantial olefin content and in so called vapor phase cracking processes there are produced hydrocarbon gases essentially more olefinic in nature, and in larger yields. Processes have been proposed to subject these normally gaseous hydrocarbons to conversion steps to produce liquid hydrocarbon motor fuels, the processes depending upon the composition of the gases converted. In connection with the operation of most modern refineries there is a vapor recovery plant, which collects vapors from over liquids confined in storage tanks and subjects them to processes for the recovery of heavier constituents to serve as liquid motor fuels. The residue gases from such a treatment contain little methane and large amounts of hydrocarbons between methane and the lightest constituent of the motor fuel product. If cracking operations are employed in the refinery, these gases will also contain unsaturated hydrocarbons in amounts which may vary considerably from time to time. In many cases there may be natural gasoline plants operated in conjunction with or in the neighborhood of refineries, and these plants will have residue gases high in methane, but with substantial proportions of other heavier gaseous hydrocarbons, essentially paraffinic in nature. Any of these stocks of normally gaseous hydrocarbons are suitable for conversion processes of one type or another to produce hydrocarbons of higher boiling range, either with or without separation of some components. Successful economic use of any process will in general be dependent on two factors; (1) volume sufficient to justify investment in a conversion process and insure a profit over operating costs and (2) reasonable constancy of composition to render a given process operative over a considerable period of time.

It is easily conceivable that the composition of any one type of charge stock for a given process might not be available in quantities sufficient to justify one of the existing conversion processes, or that variations in operating conditions or charge stock of a refinery might produce variations in a gaseous stock to penalize or prohibit the use of a fixed conversion process. This invention has to do with a novel and cooperative arrangement of conversion processes as steps in a larger unified process, so that various gaseous hydrocarbon mixtures such as those mentioned above may be used to advantage, and variations in relative amounts of one or more mixtures, or in their compositions or in the nature of the final products may be taken care of within this invention.

An object of this invention is to provide a novel process for obtaining increased yield and output from a conversion plant of hydrocarbons of a motor fuel range and of high antiknock value by means of new and novel cooperation of the steps to be described.

A further object of this invention is to obtain a motor fuel having a high antiknock value by processing a mixture of normally gaseous hydrocarbons containing both saturated and such unsaturated components, wherein the aforesaid gaseous mixture is so treated thermally and catalytically as to apply to best advantage economical conversion steps to both types of hydrocarbons.

Another object of this invention is to produce from any mixture or mixtures of normally gaseous hydrocarbons of limited methane content a motor fuel having high antiknock qualities and in a particularly high yield with reference to the hydrocarbons treated.

Still another object is to produce from a given conversion stock a normally liquid motor fuel whose volatility, saturate content and aromaticity may be varied at will.

Still a further object is to produce a liquid motor fuel economically, despite a fluctuating supply of gaseous hydrocarbons as conversion stock, or despite fluctuations in their composition.

It has been proposed to polymerize thermally an olefin rich hydrocarbon gas under heat and pressure to produce volatile, normally liquid hydrocarbons of the boiling range of gasoline and

also to effect thermal conversion of paraffin rich gases under pressure and at a temperature sufficiently high to cause the paraffins to react, the products being suitable for gasoline. It has further been proposed to react gaseous olefins, added in small proportions, to a paraffin rich gas under pressure and high temperature such that liquid hydrocarbons are produced by union of olefin with paraffin. Further it has been proposed to pyrolyze normally gaseous paraffins such as ethane, propane and butane at a low pressure and at a high temperature to produce gaseous olefins which may subsequently be converted by heat and pressure into gasoline. It has also been proposed to employ polymerization catalysts to effect the conversion of gaseous olefins into gasoline. Catalytic polymerization I have found to proceed more readily with propylene and butylene than with ethylene. The conversion of paraffin rich gases under heat and pressure can be accomplished efficiently under conditions which I have found lead to the production of a limited amount of ethylene and notable amounts of propylene and butylenes, which may to advantage subsequently be subjected to catalytic polymerization.

It has been shown that pentanes, butanes, and in some cases propane, can be converted efficiently under heat and pressure directly into higher molecular weight hydrocarbons but that operating conditions adapted to the conversion of the ethane present, and sometimes propane as well, decrease the conversion efficiency with respect to the first mentioned paraffins. By applying a separate thermal conversion to such ethane and propane at relatively high temperatures olefins may be produced and returned to the cooperating polymerization steps wherein they may be converted with particularly high efficiency.

A further advantageous cooperation in polymerization steps is obtained in the conversion of olefin rich light hydrocarbons by subjecting them to thermal polymerization under pressure whereby olefins are converted into motor fuel in high yield per thermal treatment, thereby producing a residual light hydrocarbon mixture relatively depleted in olefins and especially suitable for subsequent conversion of both olefins and paraffins contained therein into motor fuel in the multiple conversion steps heretofore described.

The nature of this invention is more fully disclosed in the following description, which deals with one mode of operation, and which brings out more clearly still further operative and economic advantages.

Reference will now be made to the drawing, which diagrammatically illustrates one type of apparatus by means of which the process may be practiced.

Hydrocarbon gas containing at least 20 per cent of olefins is charged through conduit **10**, pump **11** and conduit **12** at a pressure in excess of 500 pounds per square inch and forced into the reaction chamber or coil **13** contained in a suitable furnace **14** wherein temperatures of 700° to 1,000° F. are imparted to the mixture and olefin polymerization thereof takes place. The thermally treated hydrocarbons pass from the reaction coil **13** by way of conduit **15** and valve **16** to a separator **17** in which normally liquid hydrocarbons are separated from the mixture and discharged from the process by conduit **18** controlled by valve **19**. The normally gaseous hydrocarbons, still under pressure in the separator **17** pass therefrom by way of conduit **20** and valve **21** to a second reaction or conversion coil **22** contained in any manner of suitable furnace **23**.

The separation of the normally liquid from the normally gaseous hydrocarbon effected in the separator **17** may be effected by absorption in the usual manner with heavy absorption oil which dissolves the polymer products, while maintaining the reaction pressure and an elevated temperature equal to or somewhat lower than the reaction temperature attained in the coil **13**. With considerable reduction of temperature in the separator **17** the separation of polymers may be effected by condensation.

Effluents from separator **17** which are charged to the coil **22** will be more or less depleted in olefins and largely paraffinic in nature with considerable proportion of hydrocarbons containing three or four carbon atoms. Similar normally gaseous hydrocarbon mixtures, also largely or wholly paraffinic may be introduced into the process by means of conduit **24** controlled by valve **25**.

In the reaction or conversion coil **22** more drastic conversion conditions are maintained than in the coil **13**. The temperature in the coil **22** accordingly may be above 1,000° F. and when a pressure above that existing in separator **17** is desired it may be maintained by use of pump **26**, valve **21** being closed and valves **27** and **28** open. In this case a considerable part of the paraffins present, as well as surviving olefins, undergo a conversion so that some normally liquid hydrocarbons are produced along with a considerable proportion of unsaturated hydrocarbons containing chiefly 3 or 4 carbon atoms, the effluents being relatively much more depleted in ethylene, of 2 carbon atoms, in the conversion step conducted as described.

The thermally treated effluents from reaction coil **22** are passed through conduit **29** and valve **30** to the recovery element or separator **31** in which normally liquid hydrocarbons are separated from the mixture and discharged through the conduit **32** controlled by valve **33**. The normally gaseous hydrocarbons remaining in separator **31** will contain substantial quantities of propylene and butylenes and these gases with or without separating therefrom methane and lighter gases, which may be discharged through conduit **34** and valve **35**, pass from the separator **31** by conduit **36** and valve **37** to the polymerization chamber **38** wherein is contained a polymerization catalyst such as activated aluminum silicate, modified aluminum chloride, phosphoric acid or the like which will effect polymerization of proplylene and butylenes efficiently. In the polymerization chamber **38** the above mentioned olefins in the presence of paraffins are polymerized into hydrocarbons of the gasoline boiling range while subjected to a pressure suitably of about 200 to 500 pounds per square inch and a temperature of about 150° to 550° F.

Normally gaseous hydrocarbon mixtures containing olefins, suitably with propylene and butylenes predominating, may be introduced into the process by way of conduit **39** and valve **40**, and under necessary and suitable pressure and will undergo concomitant polymerization in polymerization chamber **38**.

The effluents from the polymerization chamber **38** are passed through conduit **41** to the recovery element or separator **42** in which normally liquid hydrocarbons are separated and discharged from the process by means of conduit **43** and valve **44**. Normally gaseous hydrocarbons which will be present in separator **42** comprise methane,

ethane, and also any propane or higher gaseous paraffins some of which are not to be returned to the pressure conversion step by means to be described. These lighter normally gaseous hydrocarbons pass from the separator 42 through conduit 45 and valve 46 to a pyrolysis chamber or coil 47, housed in a suitable furnace 48, and in which ethane and any propane or butane present are pyrolyzed at a relatively low pressure, less than 500 pounds per square inch, and at a temperature of 1200° to 1700° F. to produce gaseous olefins. The mixture is passed from the pyrolysis coil 47 through conduit 49 and valve 50, valve 51 being closed, to a reaction chamber or zone 52 in which the conversion of more or less of the gaseous olefins present into aromatic oils may be permitted by a continuation therein of the reaction. Pyrolysis in chamber or tube coil 47 may be carried out without the aid of separate reaction chamber 52 and in such a case the effluents from 47 pass through conduit 49 and conduit 53 controlled by valve 51 to conduit 54 thence passing to separator 56, valves 50 and 55 being closed. In either case the oils formed may be separated from the gaseous pyrolysis effluents by passing the said effluents from conduit 54 to the separator 56 and discharging therefrom the oils so formed through discharge line 57 and valve 58.

Gaseous effluents from the separator 56, containing substantial amounts of ethylene pass through the conduit 59 to the compressor 60, thence through conduit 61, valves 62 and 63 being open, to conduit 12 through which they may pass to the reaction coil 13 wherein the olefins present undergo polymerization conversion. However, if the olefins are desired in concentrated form, the pyrolyzed gases may pass from conduit 61, valve 62 being closed, through line 64 and valve 65 to the separator 66 in which methane and lighter gases are separated from the mixture and discharged through discharge pipe 67 and valve 68, and the remainder of the pyrolyzed hydrocarbons now of increased olefin content are passed through conduit 69 and valve 70 back into conduit 61 and thence through valve 63 into conduit 12 and reaction coil 13. The separation in separator 66 may be effected by oil absorption, low temperatures, partial liquefaction or other equivalent means.

Hydrocarbons of three or more carbon atoms per molecule may be removed from separator 31 and passed through conduit 71, valve 72 and conduit 73 into conduit 20 so that they may be reintroduced into reaction coil 22. It will more often be preferable to isolate the relatively more olefin depleted hydrocarbons of 3 and more carbon atoms from separator 42 and pass them through conduit 74 and valve 75 to conduit 73 and thence to conduit 20 and reaction coil 22. In some cases the conversion steps performed in 22, 38 and 47 may be operated cooperatively to best advantage while omitting the conversion in 13. Such a case may be the conversion of light hydrocarbons relatively low in olefins and correspondingly rich in paraffins. In such a case, and also, if desired, where conversion in 13 is employed, hydrocarbons passing through conduit 61 are passed with valves 63 and 79 being closed, through conduit 76 and valve 77 to conduit 73, and thence through conduit 20 to reaction coil 22.

It will often be preferable to operate reaction coil 22 at pressures in excess of 1,000 pounds per square inch and at temperatures between 800° and 1200° F. and under conditions whereby joint polymerization of paraffins and olefins is favored. Accordingly the olefin rich material from conduit 76 is passed through conduit 78 and valve 79, valve 77 being closed, and is introduced portionwise through branches 78—A and 78—B of pipe 78 into the latter part of reaction coil 22 through the several pipes 80, such introduction being controlled by proper manipulation of valves 81. Under these conditions light paraffinic hydrocarbons containing three and more carbon atoms are only slightly changed into unsaturated molecules, but are reacted or polymerized with unsaturated material, such as ethylene which is produced in reaction coil 47, to produce highly branched low boiling hydrocarbons of the gasoline boiling range which have excellent anti-detonating qualities. In such a case recycling of a large proportion of predominantly paraffinic light hydrocarbons containing 3 and more carbon atoms to the reaction coil 22 by means of conduits 73 and 20 may be desirable. If all of such material is returned to the reaction coil 22 it will be desirable to by-pass catalytic chamber 38 and separator 42 by means of conduit 82 and valve 83, valves 37 and 46 being closed. If relatively small amounts of olefins are introduced into the mixture to undergo cooperative polymerization reaction with paraffinic hydrocarbons, all of such introduction may take place through line 73, with valve 79 closed.

The objects and advantages of this invention will now be more apparent from the following additional explanation of the process. Highly olefinic gases are economically polymerized in the reaction coil 13 and polymers are separated therefrom in the separator 17 without the release of pressure, or with only a partial release of pressure, and the expense of subsequently recompressing the gas is thus minimized. The olefin depleted gaseous hydrocarbons with their pressure more or less elevated, if desired, by pump 26 are converted in the reaction coil 22, and in the effluents produced, from which gasoline is separated, there is sufficient propylene and butylenes present, though of a low content, after reducing to 500 pounds per square inch pressure or so for the separating step if desired, to effect efficient catalytic polymerization. Propane and butane from the catalytic polymerization effluents are returned to the reaction coil 22 and in the olefin depleted condition in many cases yield virtually as much gasoline per pass as if the propylene and butylenes had also been recycled, with the advantage then of added output from the economical catalytic polymerizing step. The catalyst used in the catalytic reaction chamber 38 may be a catalyst which does not polymerize ethylene effectively since ethylene has already been given an opportunity to produce gasoline in the reaction coils 13 and 22, wherein it is consumed more readily and completely than the higher olefins present.

Considerable ethane is formed in the thermal polymerization steps and with ethane originally present it cannot ordinarily be efficiently converted therein, but can be pyrolyzed in the reaction coil 47 and subjected as ethylene to reaction in coils 13 or 22. When sufficient quantities of ethylene are thus produced, reaction coil 22 may be operated preferably at higher pressures and somewhat less elevated temperatures within the given range, and the ethylene be introduced portionwise through the several pipes 80 so that polymerization involving paraffin-ethylene juncture is favored and the effluents from the reaction

coil 22 will contain only a small amount of unsaturated constituents. Propylene and butylene survive however, to be subjected to catalytic polymerization, to which they respond particularly readily.

Reaction coil 13 is most valuable as a part of the process when olefin rich gases in considerable volume and with large amounts of ethylene are available, which would result in overloading the steps in reaction coil 22 and in some cases chamber 38. The separation of polymers in the separator 17 may be effected with reduction in pressure and at a temperature permitting partial condensation of normally gaseous hydrocarbons. Polymerization or reaction coil 13 may discharge into the separator or recovery element 31 by means of conduit 84 and valve 85, when valves 16 and 30 are closed.

Normally liquid hydrocarbons which have been produced in the various steps of the process and discharged therefrom by means of the valved conduits 18, 32, 43, and 57 may be further treated or refined in any desired manner and united in any combination or used separately as motor fuel or they may be united in any combination and further treated in such combination to make motor fuel to meet any given specifications.

Fixed gas discharged from the system by means of valved conduits 34 and/or 67 will be rich in methane and hydrogen and be suitable for fuel, or as a source of hydrogen for hydrogenation.

The thermal polymerization of olefin-rich gaseous hydrocarbons containing over 20 per cent of olefins to produce normally liquid hydrocarbons in reaction coil 13 is carried out under known conditions at pressures of 500 to 2,000 pounds and more per square inch and a temperature of 700° to 1,000° F. By thermal polymerization of a part of the olefins will be understood herein and in the claims hereof to mean a conversion conducted under the conditions above set forth.

The thermal conversion of paraffins of 3 and more carbon atoms together with olefins to produce liquid hydrocarbons as conducted in reaction coil 22 is carried out under known conditions at a pressure of 500 to 5,000 pounds per square inch and more and at a temperature of 800° to 1,200° F. whereby extensive conversion of paraffins as well as olefins is effected. By thermal conversion of a paraffin-olefin mixture will be understood herein and in the claims hereof to mean a conversion conducted under the conditions above set forth.

The catalytic polymerization of simple olefins in the presence of paraffins to produce liquid hydrocarbons as conducted in reaction chamber 38 is carried out under known conditions at pressures of about 200 to about 500 pounds per square inch and temperatures of 150° to 500° F., the conditions appropriate to any selected catalyst being determinable by trial. By catalytic polymerization will be understood herein and in the claims hereof to mean a conversion conducted under the conditions above set forth.

The pyrolysis of hydrocarbon gases to produce gaseous olefins and more or less of oils as conducted in reaction coil 47 is carried out under known conditions at temperatures of 1,200° to 1,700° F. and pressure below 500 pounds per square inch and which may be atmospheric or below. By pyrolysis will be understood herein and in the claims hereof to mean a conversion conducted under the conditions above set forth.

Hydrocarbons suitable for conversion in the process constitute gaseous hydrocarbons essentially of the paraffin series together with olefins, which are of limited methane content and including hydrocarbons such as pentane and pentene. These latter 5 carbon atom hydrocarbons are treated when their presence in large amounts in the products will produce motor fuel of excessive volatility.

Example.—As an example of the operation of the process, a mixture of light hydrocarbons containing 50 per cent of ethylene and higher olefins, 20 per cent of ethane and 30 per cent propane, butane, and pentane, may be subjected to a temperature of 900° F. under 2,000 pounds per square inch pressure to produce normally liquid hydrocarbons from the olefins, leaving 15 per cent of olefins unconverted. After removing the liquid hydrocarbons produced the hydrocarbons are then subjected to 1,020° F. and 2,000 pounds pressure, together with the paraffins of 3 to 5 carbon atoms per molecule separated from a subsequent step of the process to produce additional liquid hydrocarbons plus a gas containing 8 per cent of propylene, plus butylenes and only 2 per cent ethylene. After removing the liquids the gases are subjected to catalytic polymerization at a temperature of 400° F. and 500 pounds pressure with the aid of hydrous aluminum silicate to produce additional polymer and light paraffins containing 3 per cent olefins. From the light hydrocarbons a fraction containing 3 to 5 carbon atoms per molecule is returned to the second conversion step above mentioned, and the remaining light hydrocarbon gas, predominantly ethane, is subjected to pyrolysis at 1500° F. and 30 pounds pressure to produce olefins, chiefly ethylene, which are passed to the first and second conversion steps mentioned.

Although preferable modes of operation have been outlined in the above description, it is to be understood that my invention is not to be limited by the same, but may be varied in any desirable manner as might be required by variations in the charge stock and which variations would readily be ascertained by one skilled in this art.

What I claim and desire to secure by Letters Patent is:

1. A multistage process for converting a normally gaseous hydrocarbon mixture containing both paraffins and olefins into normally liquid hydrocarbons suitable for motor fuel, which comprises subjecting a hydrocarbon mixture containing both paraffins and olefins to thermal treatment under pressure to effect polymerization of a major portion of the olefins, separating from the thermally polymerized mixture the normally liquid hydrocarbons produced and discharging them from the process, subjecting the remaining predominantly paraffinic portion of said thermally polymerized mixture to heat and pressure to effect thermal conversion thereof and the production therefrom of gaseous olefins and additional normally liquid hydrocarbons, separating said additional normally liquid hydrocarbons from the said remaining thermally converted mixture and discharging them from the process, subjecting said thermally converted mixture remaining after said last separation to catalytic polymerization to produce in part normally liquid hydrocarbons, separating from the effluents of said catalytic polymerization a first fraction consisting of normally liquid hydrocarbons and removing the same from the process, separating also from the said effluents of said catalytic polymerization a second fraction consisting of three

and more carbon atoms per molecule and returning said second fraction to said thermal conversion step, and subjecting at least a part of the remaining effluents from said catalytic polymerization to pyrolysis conditions independent of said first mentioned polymerization to produce olefins and passing said olefins to said thermal conversion step.

2. A multistage process for converting a normally gaseous hydrocarbon mixture containing both paraffins and olefins into normally liquid hydrocarbons suitable for motor fuel, which comprises subjecting a hydrocarbon mixture containing both paraffins and olefins to thermal treatment under pressure to effect polymerization of a major portion of the olefins, separating from the thermally polymerized mixture the normally liquid hydrocarbons produced and discharging them from the process, subjecting the remaining predominantly paraffinic portion of said thermally polymerized mixture to heat and pressure to effect thermal conversion thereof and the production therefrom of gaseous olefins and additional normally liquid hydrocarbons, separating said additional normally liquid hydrocarbons from the said converted mixture and discharging them from the process, subjecting said thermally converted mixture remaining after said last separation to catalytic polymerization to produce in part normally liquid hydrocarbons, separating from the effluents of said catalytic polymerization a first fraction consisting of normally liquid hydrocarbons and removing the same from the process, separating also from the said effluents of said catalytic polymerization a second fraction consisting of three and more carbon atoms per molecule and returning said second fraction to said thermal conversion step, and subjecting at least a part of the remaining effluents from said catalytic polymerization to pyrolysis conditions independent of said first mentioned polymerization to produce olefins and passing said olefins to the aforesaid thermal polymerization step.

3. A multistage process for converting a normally gaseous hydrocarbon mixture containing both paraffins and olefins into normally liquid hydrocarbons suitable for motor fuel, which comprises subjecting in a first stage a predominantly paraffinic hydrocarbon mixture to heat and pressure effecting thermal conversion thereof and the production therefrom of olefins and of normally liquid hydrocarbons, separating said normally liquid hydrocarbons from the thermally converted mixture and discharging them from the process, passing the remaining hydrocarbon mixture to a second stage where other normally liquid hydrocarbons are produced by catalytic polymerization, separating from the effluents of said second stage a first fraction consisting of normally liquid hydrocarbons and discharging said normally liquid hydrocarbons from the process, separating also a second fraction consisting of hydrocarbons of three and more carbon atoms per molecule and returning said second fraction to the aforesaid first conversion stage, subjecting a part of the remaining effluents from said second stage to pyrolysis in a third stage to produce olefins by pyrolysis, and finally passing said olefins to the aforesaid first stage.

4. A multistage process for converting a normally gaseous hydrocarbon mixture containing both paraffin and olefin hydrocarbons into normally liquid hydrocarbons of motor fuel boiling range which comprises contacting said normally gaseous mixture with a polymerization catalyst at a temperature between 150 to 500° F. under a pressure between 200 and 500 pounds per square inch to convert a portion of said olefins to normally liquid hydrocarbons in the motor fuel boiling range, separating said liquid hydrocarbons from the effluent of the polymerization step and removing them from the system, separating the remaining effluent into a first fraction composed largely of paraffin hydrocarbons of three and more carbon atoms per molecule and a second fraction composed largely of hydrocarbons of less than three carbon atoms per molecule, subjecting said second fraction to pyrolysis at a temperature between 1200 and 1700° F. under a pressure less than 500 pounds per square inch thereby forming ethylene, subjecting said first fraction to thermal conversion in the presence of ethylene produced in the pyrolysis step, at a reaction temperature between 800 and 1200° F. under a pressure between 500 and 5000 pounds per square inch producing thereby normally liquid hydrocarbons and normally gaseous olefins, separating said normally liquid hydrocarbons from the gaseous effluent of said thermal conversion and removing them from the process and passing the remainder of the gaseous effluent into contact with said polymerization catalyst.

5. A multistage process for converting normally gaseous hydrocarbon mixtures into hydrocarbons in the motor fuel boiling range, which comprises subjecting in a first stage a normally gaseous hydrocarbon mixture of limited methane content and containing paraffin hydrocarbons and at least 20 per cent of olefin hydrocarbons under a pressure between 500 and 2000 pounds per square inch to a thermal polymerization at a temperature between 700 and 1000° F. whereby normally liquid hydrocarbons in the motor fuel boiling range are produced, separating from said reacted mixture normally liquid hydrocarbons and removing them from the process, adding to the remaining hydrocarbons a normally gaseous hydrocarbon mixture consisting predominantly of paraffin hydrocarbons of at least three carbon atoms per molecule and subjecting said resultant mixture in a second stage under a pressure between 500 and 5000 pounds per square inch to a thermal conversion at a temperature between 800 and 1200° F. whereby normally liquid hydrocarbons in the motor fuel boiling range and normally gaseous olefin hydrocarbons are produced, separating normally liquid hydrocarbons from the converted mixture and removing them from the process, passing the remaining hydrocarbon mixture to a third stage and therein contacting said mixture under a pressure between 200 and 500 pounds per square inch at a temperature between 150 and 500° F. with a polymerization catalyst whereby said normally gaseous hydrocarbons react forming normally liquid hydrocarbons in the motor fuel boiling range, separating from the effluents of said third stage a first fraction consisting of a normally liquid hydrocarbon mixture and removing it from the process, separating also as a second fraction a normally gaseous mixture consisting of hydrocarbons of three and more carbon atoms per molecule and passing said second fraction to aforesaid second stage, subjecting at least a part of the remaining effluents of said third stage under a pressure less than 500 pounds per square inch in a fourth stage to a temperature between 1200 and 1700° F. whereby ethylene is produced and passing a controlled amount of said ethylene to said second stage and the rest of said ethylene to said first stage.

6. A multistage process for the conversion of normally gaseous hydrocarbons to normally liquid hydrocarbons in the motor fuel boiling range, which comprises subjecting in a first stage a normally gaseous hydrocarbon mixture consisting predominantly of paraffin hydrocarbons of at least three carbon atoms per molecule, in admixture with controlled amounts of ethylene produced in a subsequent stage of the process, under a pressure in excess of 1000 pounds per square inch to a conversion temperature between 800 and 1200° F. whereby normally liquid hydrocarbons in the motor fuel boiling range and normally gaseous olefin hydrocarbons other than ethylene are produced, separating normally liquid hydrocarbons from the converted mixture and removing same from the process, passing the remaining hydrocarbon mixture to a second stage under a pressure between 200 and 500 pounds per square inch and therein contacting said mixture under said pressure at a temperature between 150 and 500° F. with a polymerization catalyst whereby aforesaid normally gaseous olefin hydrocarbons other than ethylene react forming normally liquid hydrocarbons in the motor fuel boiling range, separating from the effluents of said second stage a first fraction consisting of a normally liquid hydrocarbon mixture and removing it from the process, separating also as a second fraction a normally gaseous fraction consisting of hydrocarbons of three and more carbon atoms per molecule and passing said second fraction to said stage and subjecting a least a part of the remaining effluents of said second stage under a pressure less than 500 pounds per square inch to a temperature between 1200 and 1700° F. whereby ethylene is produced, and adding said ethylene to said hydrocarbon mixture in said first stage.

7. The process of claim 3 wherein a normally gaseous hydrocarbon mixture containing olefin hydrocarbons is added to the hydrocarbon mixture passed to said second stage where other normally liquid hydrocarbons are produced by catalytic polymerization.

8. The process of claim 4, wherein a normally gaseous hydrocarbon mixture composed largely of paraffin hydrocarbons of three and more carbon atoms per molecule is mixed with the hydrocarbon fraction subjected to thermal conversion in the presence of ethylene.

FREDERICK E. FREY.