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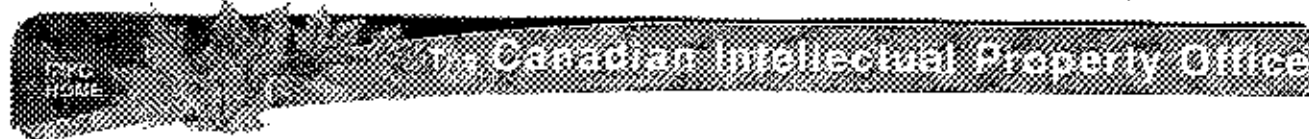
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(12) Patent:

(54) PROCESS FOR SYNTHESIZING HYDROCARBONS

(54) PROCEDURE DE SYNTHETISAGE D'HYDROCARBURES

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ABSTRACT

CLAIMS: [Show all claims](#)

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This invention relates to the catalytic synthesis of hydrocarbons and oxygenated hydrocarbons by interaction of carbon monoxide and hydrogen, and more particularly is directed to synthesis of liquid hydrocarbons predominately of the type adaptable for the use as motor fuel.

It has been known for sometime that liquid hydrocarbons, and oxygenated hydrocarbons, can be produced by the catalytic treatment of mixtures of hydrogen and carbon monoxide in the presence of a catalyst. The typical catalyst for this reaction comprises a metal of the iron group such, for example, as iron itself, nickel, cobalt or ruthenium, preferably associated with any one of the known activators or promoters such as compounds of the alkali metals or alkaline earth metals, or alumina (Al_2O_3).

The fresh feed gas or so-called synthesis gas is normally typified by a product composed essentially of hydrogen and carbon monoxide in the molar ratio of approximately two to one. In many instances, however, I prefer to operate at ratios substantially higher as for example, 2.5:1, or 3:1 or as high as 5:1. It has been found desirable in carrying out the catalytic reaction in question, to maintain as near as possible the predetermined molar ratio throughout the course of the reaction. This objective, however, presents some difficulty since the progress of the reaction does not appear to utilize the two reactants in their original proportions with the result that the molar ratio at points subsequent to the point of initial contact with the catalyst is progressively altered.

More specifically I have observed that in the types of operations with which I am familiar the molar ratio of

hydrogen to carbon monoxide of the residual unreacted gases tends to increase as the reactants move through the contact mass. This observation covers the normal type of operation wherein the synthesis gas is passed through a catalyst mass in conventional manner within the optimum temperature ranges of treatment and over the substantially full operating range of pressures. It appears it is also true in respect to the full range of hydrogen and carbon monoxide molar ratios of feed gas extending, for example, from a feed gas containing less hydrogen than carbon monoxide to those where the molar ratio is 5 and above. It is strikingly characteristic of operations employing iron catalysts although it may typify to a lesser extent, operation in the presence of cobalt, nickel, or other catalysts.

While it has been proposed to employ feed gases of very precisely determined composition and to adjust the composition, during the course of the reaction, by the addition of gases rich in one or the other of said reactants, this procedure demands the constant availability of gases of varying controlled composition and therefore introduces a particular burden upon economic operation of the process.

An object of the present invention is to provide a process wherein the composition of the gaseous reactants may be maintained substantially at or near the desired relative molar composition of hydrogen and carbon monoxide throughout by means which are economical to operate and which utilize products of the reaction. Another object contemplates the operation of the process as above in a manner such that adjustment is made for a wide variation in the composition of the feed gases thus permitting the use of gases which may

vary somewhat from optimum. Another object is the attainment of a high utilization efficiency in the conversion of feed gas to hydrocarbon or oxygenated hydrocarbon products.

In accordance with the present invention the process is controlled by adjusting the increased molar ratio between hydrogen and carbon monoxide in later stages of the reaction, with reformed products of reaction so proportioned as to compensate for the increase and thus approach optimum in later stages or zones of reaction. This is accomplished preferably by reacting effluent products, such as gaseous hydrocarbons and carbon dioxide to produce a synthesis make-up gas preferably of lower hydrogen to carbon monoxide ratio. At the same time the desired reaction products such as the higher hydrocarbons as well as by-product water vapor may be separated between stages and subsequent to the final stage of operation in order to enhance the reaction.

The accompanying drawing is more or less diagrammatic representation of one form of apparatus capable of carrying out the present process. More particularly, referring to the drawing, a synthesis gas from any suitable source, not shown, passes through lines 2, 3 and 4 to the lower portion of a reactor 5 containing a mass of catalyst. The details of the reactor 5 form no part of the present invention and are therefore disclosed only symbolically. While various forms of reactors and conditions of contact mass may be utilized, it is advantageous to employ the so-called fluidized type of reactor wherein the reaction vessel contains a powdered mass of catalyst through which the reactant gases pass upwardly in such a manner that they suspend each particle of catalyst and yet permit "hindered settling" or slippage of the particles in the gases. Operating in this manner the catalyst under proper condition of reactant flow assumes a fluid-like, boiling condition of good thermal properties with an upper

surface in the nature of a pseudo liquid level. The reactor is advantageously cooled, preferably by cooling surfaces disposed in contact with the catalyst powder and supplied internally with a suitable coolant effective to hold the cooling surfaces at a predetermined temperature level. Under these conditions the reaction temperature throughout the mass may be closely controlled within a few degrees of predetermined optimum. Schematically, it is shown that reactor 5 is cooled by coil 5a, the coolant entering at the bottom and leaving at the top thereof.

The gasiform effluent from the top of reactor 5 passes through outlet conduit 6 into a separator 7 adapted to remove the more or less inevitable small quantities of entrained catalyst which are returned in a known manner to the catalyst bed by means of standpipe 8 controlled by valve 9 leading into the reactor 5 at a point below the normal level of catalyst therein. The catalyst-free effluent passes through conduit 10 to condenser 11 preferably operating at atmospheric or other convenient temperature suitable to condense normally less liquid products, thence are conveyed by pipe 12 to separator 13 where condensed water vapor and hydrocarbons separate, water being withdrawn through pipe 14 and oil through pipe 14a. This oil product from pipe 14a as well as similar products derived in later stages may be passed to apparatus for further separation, recovery or other treatment, the details of which steps form no part of the present invention.

The effluent gases from separator 13 pass by line 15 into inlet line 16 feeding the lower portion of a second stage reactor 17 which may be substantially identical in construction with the first stage reactor 5. It should be noted that the present arrangement necessarily contemplates

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operation of the process in a series of stages wherein only partial conversion of the reactants occurs in each stage. In the example illustrated by the drawing only approximately 50% of the reactants are consumed in the first stage. It may be further noted that, in view of the volume contraction between the two stages, reactor 17 may have advantageously a substantially smaller volume capacity than reactor 5. Excess heat of reaction in the fluidized mass of reactor 17 is carried away by a coolant flowing through coil 17a.

The feed gases supplied through line 16, and supplemented as will hereinafter appear more in detail, pass upwardly through the fluidized powdered catalyst in reactor 17, the effluent gaseous products passing through line 18 into a second separator 19 to remove entrained particles. Such particles as recovered are returned to the catalyst bed by way of standpipe 20 and control valve 21. The separated gasiform products pass through line 22, condenser 23 and line 24 to a separator 25 from which condensed water is removed through pipe 26 and normally liquid products are removed through pipe 26a. The gaseous effluent from separator 25 comprises largely or entirely carbon dioxide and hydrocarbon gases, especially methane, which pass upwardly through line 27, controlled by valve 28, into line 29 supplying a reformer or synthesis gas regenerator 30. The products of the reformer 30 consisting essentially of a synthesis gas mixture are delivered through a line 31 to supplement the second stage feed gases in line 16.

Referring more particularly to the reformer 30, I have indicated a synthesis gas regenerator which operates to convert a mixture of carbon dioxide and methane or other

hydrocarbons to a product containing carbon monoxide and hydrogen substantially in the molar ratio of 1:1. The regenerator is shown only diagrammatically or symbolically since devices of this class are well-known in the art. According to one method of operation the reaction takes place at approximately 2000°F. in the presence of a nickel catalyst supported on a clay of high alumina content, such as fire clay or alundum. This particular type of synthesis gas regenerator has been selected for the purpose of better illustrating facilities adapted to carry out the synthesis of hydrocarbons at a predetermined molar ratio of hydrogen to carbon monoxide in the range of about 2:1. Thus the specific regeneration or reforming step, which results in a product having a molar ratio of 1:1, is effective to adjust the relatively high molar ratio of the effluent gases in line 15.

In its broadest aspect, however, the invention is not so limited, but enables the adjustment of reactant feeds to any desired range and in the case of specially conducted processes wherein the molar ratio of hydrogen to carbon monoxide becomes excessively low may even be used to raise the ratio. Thus, where an abnormally low ratio of effluent gas is to be adjusted upwardly, regenerator effluent of higher hydrogen to carbon monoxide ratio is usable.

To this end, the regeneration step may be modified by the addition of oxygen or even steam, which function to produce a product, respectively, of a 2:1 and 3:1 ratio of hydrogen to carbon monoxide. In fact, I prefer to provide for the addition of steam, and oxygen if desired, through pipe 32, from a source not shown in order to permit some desirable control of the process. More specifically,

controlled quantities of steam may be introduced, or not, as required to maintain the system in balance depending, of course, upon the rate of carbon dioxide and methane production and other factors.

In operation of a typical hydrocarbon synthesis process, gas, containing predominately hydrogen and carbon monoxide in molar ratio 2:1 normally with a small quantity of carbon dioxide and methane and advantageously free of nitrogen and other inert diluents, is fed to the first stage reactor 5 and partially reacted therein with an iron catalyst. The working temperature of the reactor normally falls within the range of 500° to 700°F. with a pressure of about 100 to 500 pounds per square inch, advantageously about 200 pounds per square inch gauge. With other catalysts the conditions of temperature and pressure will be varied to those characteristically optimum. In the case of cobalt catalyst, for example, the operating temperature may be about 400°F. and the pressure atmospheric or slightly thereabove.

The separated effluent gases, approximately 50% reacted and with the normally liquid reaction products removed, have a hydrogen to carbon monoxide ratio of approximately 3:1. These gases pass into the bottom of the second stage reactor through line 16 together with advantageously an equal quantity of regenerated synthesis gas from the line 31 wherein the molar ratio of hydrogen to carbon monoxide is approximately 1:1. The flow of reformed gases is advantageously controlled insofar as possible to adjust the relatively high molar ratio of the gases in line 16 to an average value approximating a ratio of 2:1. Accordingly, the catalytic reaction progresses in the second stage reactor 17 under the same feed conditions as in stage 1.

Preferably the other conditions of reaction are similarly maintained within identical ranges and the effluent by-products are conveyed to the regenerator or reformer 30 to complete the cycle.

In accordance with one desirable modification of the present invention, means is provided to recycle a portion of the gaseous reaction products from the final stage through either or both of the reaction chambers. This comprises a branch line 34 supplying the respective reactor feed inlets through a booster pump 35 and inlet pipes 36, 4 and 37. Valves 38 and 39 may be provided to control such recycle.

With this direct recycling of tail gases, additional advantages are available. The build-up of carbon dioxide and/or lower hydrocarbons in the feed gas exerts a beneficial influence in inhibiting undesired side reactions. However, of additional importance, is the fact that the tail gases, usually containing some hydrogen, may be used to supplement the hydrogen to carbon monoxide ratio of the fresh feed gas. In particular where the effluent gases from the final stage still contain some unreacted hydrogen and carbon monoxide, as is frequently the case, the recycle stream may be so controlled as to enable operation at higher ratios than normal. This follows from the fact, indicated above, that the unreacted gases in the effluent from the catalyst mass will generally have a higher ratio of hydrogen to carbon monoxide than the inlet feed.

In applying these principles, a fresh synthesis gas having a hydrogen to carbon monoxide ratio of 2:1 may be built up to a ratio of 2.5:1 or even 3:1 in the inlet pipes 4 and 37 by means of such recycle of a portion of the tail gas. The corresponding ratio in the effluent gases from the

first stage reactor will be higher, as for example, a ratio of 4.5:1. This will be adjusted down to the desired ratio by addition of so-called reformer or regenerator synthesis gas before introduction into the second stage reactor.

In connection with the foregoing 1 may secure a further degree of control by providing a branch pipe 40 supplied through valve 40a from the synthesis gas inlet pipe 2 and provided with several lateral branches 41 feeding through valves 42 into the contact mass at spaced points along its vertical dimension. By this expedient it will be apparent that the gaseous reactants in the contact mass, tending to rise in hydrogen to carbon monoxide ratio with the progress of the reaction, are adjusted downwardly to the proper pre-determined value of such ratio by the spaced introduction of the original synthesis gas having a lower hydrogen to carbon monoxide ratio. In view of the foregoing it will be simple for anyone skilled in the art to so adjust the flow in the several lateral pipes 41 as to maintain a reasonable approximation of the desired predetermined feed gas ratio throughout the reactor whereby such ratio in the effluent reactant gas can be held within limits readily adjustable by the additional increment of low ratio, reformer synthesis gas introduced just prior to the second stage.

A similar arrangement may advantageously be provided in connection with the second stage reactor and may comprise a branch pipe 43 provided with laterally extending inlet pipes 44 with valves 45 projecting into the catalyst mass at spaced vertical points. Many other subsidiary modifications of the foregoing are also available. Thus, for example, a portion of the reformer synthesis gas from the line 31 may be introduced into the lines 40 and/or 43 for the purpose of adjusting the side feed make-up to any desired hydrogen to carbon monoxide ratio.

Attention is directed to the fact that the present invention is not limited to two stage operation but contemplates division of the process into any number of stages. While the drawing is limited to two-stage operation in the interest of clarity of the exemplification, as many as six or more reactors may be employed by so conducting the reaction in each as to complete a proportionate part of the reaction and conducting the effluent after separation of the liquid fractions as previously indicated to the next succeeding stage. In such an arrangement the synthesis gas reformer 30 may be supplied with tail gas from the last or later stages to supply a reformed synthesis gas to any or all of the previous stages subsequent to the first.

Attention is also directed to the fact that, for the purposes of this invention, multiple stage operation does not necessitate multiple reactors but can be carried out in a single reactor. Thus, for example, pipe 46 with valve 47 could be used to convey reformer synthesis gas from reformer 30 to manifold line 40 and thence through the several branches 41 and valves 42 to several portions or zones, disposed consecutively along the vertical dimension, of reactor 5. In this way, the spaced injection of reformer synthesis gas of low hydrogen to carbon monoxide ratio, say 1:1, serves to adjust downwardly the ratio of hydrogen to carbon monoxide, say 2:1, of the reactant gases entering through feed inlet 4 since this ratio tends to increase as the reactant gases flow up through reactor 5. If the system had only one reactor, then the gaseous effluent from separator 13 would pass directly to reformer 30 by connecting pipe 15 with pipe 29. If desired, the spaced injection of reformer synthesis gas

through branch pipes 41 could be supplemented by some fresh synthesis gas from line 2, admitted into manifold line 40 by opening valve 40a.

By way of illustrating one feasible method of operation in accordance with the present invention, the reactors are supplied with catalyst comprising an iron powder which passes through a 200 mesh screen, about 85% of which passes a 325 mesh screen. The powder is substantially pure iron containing about 1% of potassium oxide (K_2O) and about 2% alumina (Al_2O_3) incorporated as promoters. Synthesis gas having a hydrogen to carbon monoxide ratio of about 2:1 and a temperature of about $550^{\circ}F.$, is fed into a reactor having a mass of fluidized catalyst approximately 12 feet in depth. The reactor operates throughout with a temperature of about $600^{\circ}F.$ and a pressure of 200 pounds per square inch gauge under a condition of dense phase fluidization. The gases passing through the reactor have a linear velocity of about 1 foot per second. The liquid products in the gaseous effluent are condensed and separated and the residual gases continue through a second stage reactor reacting under substantially the same conditions as in the first stage reactor. The effluent from the second stage separator, consisting largely of carbon dioxide, hydrogen and methane with smaller amounts of 2, 3 and 4 carbon atom hydrocarbons, and substantially no carbon monoxide, is passed to the synthesis gas reformer where carbon dioxide and lower hydrocarbons react with the formation of a synthesis gas stream of slightly above but closely approximating a hydrogen to carbon monoxide ratio of 1:1. This stream is mixed with an effluent gas stream from the first stage separator having a hydrogen to carbon monoxide ratio of approximately 3:1 to bring the resulting mixture to a ratio of substantially 2:1.

The liquid product of this reaction comprises about 80% hydrocarbons boiling in the gasoline range, i.e. a fraction starting with hydrocarbons of four carbon atoms and terminating at an end point of 400°F. About 20% of the hydrocarbons formed boil above this range and the overall conversion on the basis of carbon monoxide supplied is approximately 95% of the theoretical yield. While the foregoing example does not contemplate recycle of unreformed tail gas, in accordance with another example, the tail gas from the final stage is split into equal parts, 50% being recycled to the first stage reactor and the remainder passing to the reformer as before. This results in an increase of the hydrogen to carbon monoxide ratio of the feed to the first stage reactor, substantially above the fresh feed gas ratio of 2:1 and in this embodiment the proportion of reformer synthesis gas mixed with the gaseous product of the first stage for feed to the second stage is advantageously so proportioned as to meet the same ratio.

It will be apparent from the foregoing that the present invention provides an effective means for maintaining the reaction in close conformance with a predetermined relation of the two reactant gases and in addition accomplishes an extremely high utilization efficiency of synthesis gas. In short, by operation of the process under desired hydrogen to carbon monoxide ratios and by recycling otherwise waste gaseous products in the manner taught, it is possible to utilize substantially all of the reactant feed in the production of hydrocarbons.

It is desirable to employ a fresh feed gas which is free from nitrogen or other inert diluents in order to prevent excessive build-up of these materials in the recycle stream. Where, however, such impurities are necessarily

present in the fresh feed they may be removed and separated from the recycle stream by any conventional means. Branch line 33 with valve 33a may be used for venting a portion of the recycle stream and thus avoiding build-up of inert diluents in the system. This venting of recycle gas is also important in balancing the operation of the entire process.

As indicated above I prefer to use an iron catalyst although the advantages of the present invention are available to a lesser extent when using equivalent catalysts such as iron and nickel. It is, of course, understood that various promoters such as the alkali and alkaline earth metals mentioned above, the oxides of titanium and silicon, and the salts of molybdenum and chromium as well as many others, may be employed preferably in minor proportions up to, for example 5%. The catalyst may be employed in either supported or unsupported condition and the supports, where employed, may be any of those conventional, such as diatomaceous earth and silica gel.

While the foregoing invention has been described more specifically in connection with certain preferred embodiments, it is to be understood that these are by way of illustration and not by way of limitation and the invention should not be limited thereto except as determined by the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The process for the synthesis of compounds of the class consisting of hydrocarbons and oxygenated hydrocarbons by the catalytic reaction of hydrogen and carbon monoxide, which comprises passing a gaseous mixture comprising hydrogen and carbon monoxide under reaction conditions through a first reaction zone containing a mass of catalyst comprising a metal of the iron group, withdrawing from said first reaction zone a gaseous reaction effluent containing unreacted hydrogen and carbon monoxide, passing said effluent under reaction conditions through a subsequent reaction zone containing a mass of catalyst comprising a metal of the iron group, withdrawing a gaseous reaction effluent from said subsequent reaction zone, separating from the second said effluent desired reaction products and a normally gaseous fraction containing carbon dioxide and gaseous hydrocarbons, subjecting said normally gaseous fraction to reforming conditions whereby the contained carbon dioxide and gaseous hydrocarbons react to produce a synthesis gas having a relatively low hydrogen to carbon monoxide ratio, and supplementing the first said effluent flowing to said subsequent reaction zone with said reformed synthesis gas to adjust the hydrogen to carbon monoxide ratio thereof downwardly.

2. The process for the synthesis of compounds of the class consisting of hydrocarbons and oxygenated hydrocarbons by the catalytic reaction of hydrogen and carbon monoxide, which comprises passing a gaseous mixture comprising

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hydrogen and carbon monoxide through a plurality of successive reaction zones each containing a mass of catalyst comprising a metal of the iron group maintained under reaction conditions to effect only partial reaction in each zone, separating a normally gaseous fraction containing carbon dioxide and gaseous hydrocarbons from the gaseous reaction effluent from a zone subsequent to the first zone, subjecting said normally gaseous fraction to reforming conditions whereby the contained carbon dioxide and gaseous hydrocarbons react to produce a synthesis gas having a hydrogen to carbon monoxide ratio approximating 1:1, supplementing the gaseous reaction effluent flowing from one of said zones to a successive zone with said reformed synthesis gas to adjust the hydrogen to carbon monoxide ratio thereof downwardly, and recovering desired reaction products from the gaseous reaction effluent from at least the last of said zones.

3. The process for the synthesis of compounds of the class consisting of hydrocarbons and oxygenated hydrocarbons by the catalytic reaction of hydrogen and carbon monoxide, which comprises passing a gaseous mixture comprising hydrogen and carbon monoxide through a plurality of successive reaction zones each containing a mass of catalyst comprising a metal of the iron group maintained under reaction conditions to effect only partial reaction in each zone with a consequent substantial increase of the hydrogen to carbon monoxide ratio of the gaseous reaction effluent from each zone as compared with the hydrogen to carbon monoxide ratio of the gaseous feed thereto, separating desired reaction products and a normally gaseous fraction containing carbon dioxide and gaseous hydrocarbons from the gaseous reaction effluent from the final zone, subjecting said normally gaseous fraction to reforming conditions whereby the contained carbon dioxide

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and gaseous hydrocarbons react to produce a synthesis gas having a hydrogen to carbon monoxide ratio approximating 1:1, and supplementing the gaseous feed to a zone subsequent to the first zone with said reformed synthesis gas to adjust the hydrogen to carbon monoxide ratio thereof downwardly.

4. The process for the synthesis of compounds of the class consisting of hydrocarbons and oxygenated hydrocarbons by the catalytic reaction of hydrogen and carbon monoxide, which comprises passing a gaseous mixture comprising hydrogen and carbon monoxide in predetermined molar ratio through a plurality of successive reaction zones each containing a mass of catalyst comprising a metal of the iron group maintained under reaction conditions to effect only partial reaction in each zone with a consequent substantial increase of the hydrogen to carbon monoxide ratio of the gaseous reaction effluent from each zone as compared with the hydrogen to carbon monoxide ratio of the gaseous feed thereto, separating normally liquid reaction products from the gaseous reaction effluent from each zone, separating a normally gaseous fraction containing carbon dioxide and gaseous hydrocarbons from the gaseous reaction effluent from a zone subsequent to the first zone, subjecting said normally gaseous fraction to reforming conditions whereby the contained carbon dioxide and gaseous hydrocarbons react to produce a synthesis gas having a hydrogen to carbon monoxide ratio substantially lower than that of the gaseous feed to a zone subsequent to the first zone, and supplementing the gaseous feed to said zone subsequent to the first zone with said reformed synthesis gas to adjust the hydrogen to carbon monoxide ratio thereof downwardly.

5. The process of Claim 4 wherein the step of supplementing the gaseous feed to said zone subsequent to the first zone with said reformed synthesis gas is conducted so as to adjust the hydrogen to carbon monoxide ratio of said gaseous feed to substantially the predetermined molar ratio of the gaseous mixture fed to the first zone.

6. The process for the synthesis of compounds of the class consisting of hydrocarbons and oxygenated hydrocarbons by the catalytic reaction of hydrogen and carbon monoxide which comprises passing a gaseous mixture comprising hydrogen and carbon monoxide in predetermined molar ratio under reaction conditions through a first reaction zone containing a mass of catalyst comprising a metal of the iron group, withdrawing from said first reaction zone a gaseous reaction effluent containing unreacted hydrogen and carbon monoxide in a ratio substantially greater than said predetermined ratio, separating normally liquid reaction products from said gaseous effluent, passing the residual gaseous effluent under reaction conditions through a subsequent reaction zone containing a mass of catalyst comprising a metal of the iron group, withdrawing a gaseous reaction effluent from said subsequent reaction zone, separating from the second said effluent desired reaction products and a normally gaseous fraction containing carbon dioxide and gaseous hydrocarbons, subjecting said normally gaseous fraction to reforming conditions whereby the contained carbon dioxide and gaseous hydrocarbons react to produce a synthesis gas having a hydrogen to carbon monoxide ratio substantially smaller than said ratio of the gaseous effluent from said first reaction zone, and supplementing said residual gaseous effluent flowing to said subsequent reaction zone with said reformed synthesis gas to adjust the hydrogen to carbon monoxide ratio

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thereof downwardly to approximate said predetermined ratio.

7. The process for the synthesis of compounds of the class consisting of hydrocarbons and oxygenated hydrocarbons by the catalytic reaction of hydrogen and carbon monoxide, which comprises passing a gaseous mixture comprising hydrogen and carbon monoxide under reaction conditions through a reaction zone containing a mass of catalyst comprising a metal of the iron group, withdrawing a gaseous reaction effluent from said reaction zone, separating from said effluent desired reaction products and a normally gaseous fraction containing carbon dioxide and gaseous hydrocarbons, subjecting said normally gaseous fraction to reforming conditions whereby the contained carbon dioxide and gaseous hydrocarbon react to produce a synthesis gas having a relatively low hydrogen to carbon monoxide ratio, and supplementing said gaseous mixture passing through said reaction zone by introducing said reformed synthesis gas into said reaction zone at not less than one spaced point along the length of said reaction zone beyond the point of entrance of said gaseous mixture to adjust the hydrogen to carbon monoxide ratio thereof downwardly.

8. The process of Claim 7 wherein the catalyst comprising a metal of the iron group is predominantly an iron-type catalyst.

9. In the synthesis of compounds of the class consisting of hydrocarbons and oxygenated hydrocarbons, by the catalytic interaction of hydrogen and carbon monoxide, wherein a synthesis gas comprising essentially hydrogen and carbon monoxide is successively passed through a plurality of successive reaction zones in contact with catalyst comprising a metal of the iron group maintained under reaction conditions

such that substantial conversion of the reactants occurs in each reaction zone with progressive increase of the molar ratio of hydrogen to carbon monoxide in the residual effluent from each successive reaction zone, the improvement which comprises continuously readjusting the molar ratio of hydrogen to carbon monoxide downwardly in a subsequent zone to a value approximating that being supplied to an earlier zone by steps including withdrawing the effluent product stream from the final reaction zone, recovering desired products of reaction therefrom, subjecting a residual portion of the said effluent product stream containing essentially carbon dioxide and undesired hydrocarbons to reforming conditions including an elevated temperature at which said carbon dioxide and hydrocarbons react to produce a synthesis gas of characteristically low hydrogen to carbon monoxide molar ratio and continuously supplementing the gaseous feed to said subsequent zone with reformed synthesis gas in a regulated amount sufficient to effect said readjustment of the relative proportions of hydrogen and carbon monoxide contained in the feed thereto, to a value approximating that of the earlier zone.

10. The method according to Claim 9, wherein the catalyst comprises essentially iron.

11. The method according to Claim 10, wherein the molar ratio of hydrogen to carbon monoxide in the fresh feed synthesis gas is of the order of 2:1.

12. In the synthesis of compounds consisting of hydrocarbons and oxygenated hydrocarbons by the catalytic interaction of hydrogen and carbon monoxide wherein a synthesis gas comprising essentially hydrogen and carbon monoxide in relative molar ratio in the range of about 2:1 to 3:1 is passed in series through a plurality of successive reaction

zones, each containing a mass of catalyst comprising a metal of the iron group, maintained under reaction conditions such that a substantial proportion of the reactants is converted in each reaction zone into said desired products of reaction with the formation of substantial quantities of by-product carbon dioxide and the progressive increase of the molar ratio of hydrogen to carbon monoxide in the effluent from each successive reaction zone, the improvement which comprises continuously effecting downward readjustment of the molar ratio of hydrogen to carbon monoxide of the gas stream being supplied to a subsequent zone of said successive reaction zones to a value substantially equal to the molar ratio of hydrogen to carbon monoxide of the synthesis gas entering the first reaction zone of said series, by steps including withdrawing the effluent product stream from the final reaction zone, recovering desired products of reaction therefrom, subjecting a residual portion of said effluent product stream comprising essentially said by-product carbon dioxide and gaseous hydrocarbons to reforming conditions, including an elevated temperature at which said carbon dioxide and gaseous hydrocarbons react to produce a reformer gas of characteristically low hydrogen to carbon monoxide molar ratio, not above about 1:1, and continuously injecting said reformer gas into the gas feed to said subsequent reaction zone in a relative amount such that the ratio of hydrogen to carbon monoxide in the resulting mixture supplied to said subsequent reaction zone approximates that of the synthesis gas supplied to said first reaction zone.

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13. The method according to Claim 12, wherein the catalyst comprises essentially iron and the temperature within said reaction zones is in the range of from about 500-700°K.

14. The method according to Claim 12, wherein normally liquid reaction products are separated from the reaction stream passing between successive reaction zones.