

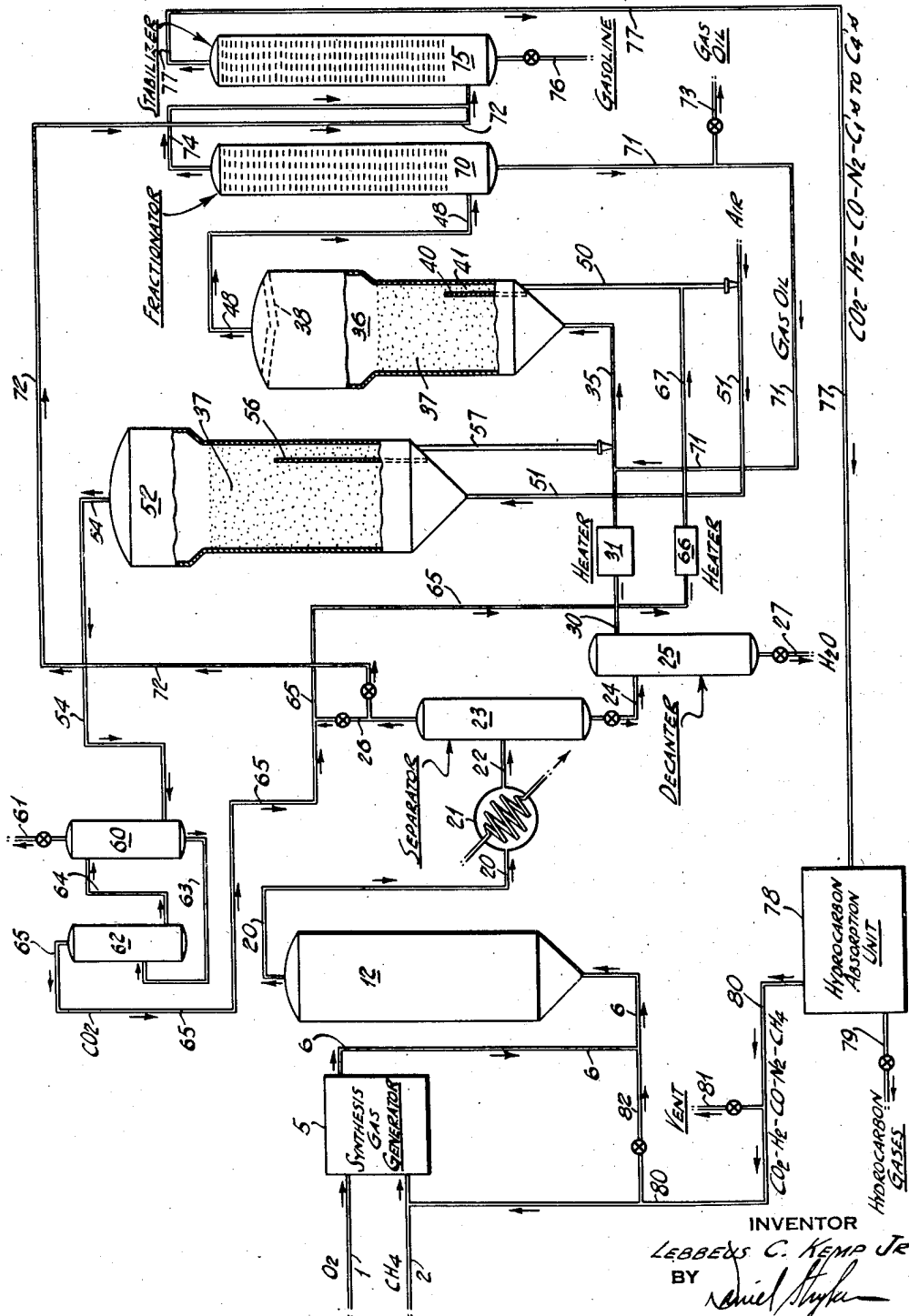
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METHOD OF MANUFACTURING MOTOR FUEL

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## METHOD OF MANUFACTURING MOTOR FUEL

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**1** This invention relates to a process for preparing gasoline hydrocarbons of high octane rating.

The invention involves catalytic conversion of synthesis gas, i. e., a mixture of carbon monoxide and hydrogen, into hydrocarbons and hydrocarbon derivatives under suitable conditions of temperature and pressure. The resulting hydrocarbons and hydrocarbon derivatives are converted into liquid hydrocarbons of high octane rating by treatment with a cracking catalyst at elevated temperatures, as will be described.

In the operation of a fluid catalytic cracking unit, there exists the problem of removing the higher boiling hydrocarbons which are adsorbed on the cracking catalyst before the catalyst is reactivated in the regenerator section of the cracking unit. As this reactivation comprises removal by oxidative combustion of carbonaceous material which has accumulated on the catalyst during the cracking of the hydrocarbons, considerable loss of valuable higher boiling hydrocarbons, which are adsorbed on the catalyst, would ensue if provision were not made for their removal prior to the reactivation of the catalyst in the cyclic operation of fluid cracking units. Moreover, the presence of adsorbed hydrocarbons in the regenerator during the reactivation of the catalyst would result in the overloading of the regenerator and of the equipment for the supply of air needed for combustion. In conventional fluid catalytic cracking operation, desorption of the adsorbed higher boiling hydrocarbons from the catalyst prior to its reactivation, is effected by the use of steam in a stripping section of the cracking reactor. There is an inherent disadvantage in the use of steam for this purpose, namely, a resulting gradual deactivation of the cracking catalyst.

In the method of this invention, wherein a carbon monoxide hydrogenation process is employed in conjunction with a fluid catalytic cracking operation, the removal of the adsorbed hydrocarbons from the cracking catalyst prior to its reactivation is effected by treating the catalyst with carbon dioxide, which is recovered from the flue gas formed in the regenerator section of the cracking unit by the oxidative removal of the coke from the catalyst and with a portion of the gaseous components of the effluent from the hydrogenation of carbon monoxide. The gaseous components of the effluent stream from the Fischer-Tropsch reactor comprise carbon dioxide, nitrogen, low molecular weight hydrocarbons up to about C<sub>10</sub>'s and unreacted carbon monoxide and hydrogen, with carbon di-

**2** oxide usually constituting from 40 to 60% of the whole. Thus, the gas which is used to effect the desorption of the adsorbed hydrocarbons from the cracking catalyst contains mostly inert carbon dioxide, as is a composite of carbon dioxide, separated from the flue gas formed in the regenerator, and a portion of the gaseous components of the effluent stream from the hydrogenation of carbon monoxide.

Numerous advantages accrue from the use of a gas which comprises mainly inert carbon dioxide for stripping the adsorbed higher boiling hydrocarbons from a fluidized cracking catalyst prior to its reactivation.

First, there is materially reduced the gradual deactivation of the cracking catalyst which results from the conventional use of steam to accomplish the stripping of adsorbed hydrocarbons from the catalyst in fluid cracking operations.

Secondly, the partial pressure of the liquid hydrocarbons in the fluid catalytic cracker is lowered substantially by the use of a gas comprising mainly inert carbon dioxide to strip the adsorbed hydrocarbons from the catalyst since the stripping gas issues from the stripping section into the reactor of the cracking unit. The reduction of the partial pressure of the hydrocarbons that are to be cracked results in decreased coke accumulation on the catalyst with consequent improvement in the efficiency of the cracking operation.

Thirdly, whatever portion of the stripping gas is carried over to the regenerator section modulates the temperature of the combustion taking place therein because of the inert character of the main constituent of the stripping gas. This modulation of the temperature of the combustion taking place in the regenerator zone is advantageous in order to minimize the deactivation of the catalyst at elevated temperatures.

The invention can be better described and more fully understood by reference to the accompanying drawing wherein the method of flow of the whole operation is diagrammatically presented. Many other advantages and features of the invention will be apparent from the detailed description of the mode of operation which ensues.

The drawing shows only those operations which are essential for a complete understanding of the process of the invention; conventional heat exchangers and pumps are omitted in the interest of simplification.

Oxygen or an oxygen-rich gas, which is obtained from a source not shown, is introduced into

a synthesis gas generator 5 through a feed pipe 1. This gas ordinarily contains at least 50% molecular oxygen, but it is feasible to use air for the combustion. However, in most operations, the oxidizing gas used for preparing synthesis gas contains at least 50% molecular oxygen and preferably over 75% molecular oxygen.

A hydrocarbon gas preferably consisting mainly of methane is introduced through a feed pipe 2 into the synthesis gas generator 5. In the diagram the oxygen-containing gas and the hydrocarbons gas are shown entering the generator 5 through separate feed lines in which there are usually inserted heaters which are not shown. The oxygen and hydrocarbon gas advantageously may be premixed before introduction into the synthesis gas generator 5 so that the whole charge to the generator may be heated at once.

In the synthesis gas generator 5, combustion occurs between oxygen and gaseous hydrocarbon to produce a mixture comprising mainly carbon monoxide and hydrogen. This generator 5 may be of the furnace type which contains either refractory material on which simple surface combustion occurs or a catalyst such as nickel deposited on a suitable carrier to catalyze the combustion. Other types of synthesis gas generators may be used, such as one employing the principle of a gas turbine to convert the heat liberated in the combustion into available mechanical energy. The power obtained from the use of a gas turbine as a synthesis gas generator may advantageously be employed to compress and liquefy air in the preparation of oxygen.

Carbon dioxide, which is obtained from a source which will be described in detail later, is also introduced into the synthesis gas generator 5. Thereby the temperature of the highly exothermic combustion of methane with oxygen is tempered by the endothermic reaction of carbon dioxide with methane and means are provided for varying the molecular ratio of carbon monoxide to hydrogen in the synthesis gas.

The quantities of methane, oxygen and carbon dioxide introduced into the synthesis gas generator 5 are regulated so as to produce a synthesis gas containing carbon monoxide and hydrogen in the desired ratio. Usually a molecular ratio of carbon monoxide to hydrogen of 1:2 is the most advantageous. However, there are circumstances when molecular ratios of carbon monoxide to hydrogen varying from 1:1 to 1:3 are desired. In some cases it may be desirable or expedient to operate with carbon monoxide to hydrogen ratios even higher than 1:3.

It is possible to effect tempering of the highly exothermic combustion of methane with oxygen by the introduction of steam into the synthesis gas generator 5 for steam also undergoes an endothermic reaction with methane. Moreover, the introduction of steam provides means of adjusting the carbon monoxide to hydrogen ratio in the synthesis gas. The introduction of steam, as an alternative for, or in conjunction with carbon dioxide, is not shown in the diagram, but such operation is included within the concept of the invention.

Synthesis gas, containing the desired molecular ratio of carbon monoxide to hydrogen leaves the generator 5 through a pipe 6. The synthesis gas contains varying minor proportions of carbon dioxide and steam which may be removed, if desired, by conventional means, not shown, before introduction of synthesis gas into a reactor suit-

able for the hydrogenation of carbon monoxide. Thus steam can be removed by conventional condensation and carbon dioxide can be removed by passage of the gases through an absorber which contains a solution of an alkaline agent such as triethanolamine.

The synthesis gas is brought to the desired temperature in a heat exchanger, also not shown, before introduction through the pipe 6 into a hydrogenation reactor 12. The temperature at which the synthesis gas is introduced into the reactor 12 depends upon the catalyst and the type of operation that is employed. For example, a fixed bed operation employing a cobalt catalyst supported on a carrier at atmospheric pressure operates most effectively at a temperature of about 375° to 400° F. to produce liquid hydrocarbons in the gasoline range. A fluidized catalyst operation employing an unsupported iron catalyst at about 200 to 250 pounds pressure operates most effectively in the range of 550 to 650° F. to produce liquid hydrocarbons in the gasoline range.

The reactor 12 can be of the fixed bed type or one of the various modifications of fluidized catalyst systems.

An iron, cobalt, nickel, ruthenium or rhenium catalyst, either supported or unsupported, may be used in the reactor 12 to effect the catalytic conversion of synthesis gas into hydrocarbons. As indicated previously, the type of catalyst employed determines the temperature at which the reactor 12 is maintained.

If a fluidized system of catalytic conversion is employed, means such as cyclone separators are provided to remove entrained catalyst dust from the effluent stream from the reactor 12.

If the reactor 12, synthesis gas is converted into hydrocarbons by contact with the catalytic material contained therein and then issues from the reactor through the pipe 20. The effluent stream from the reactor contains unreacted carbon monoxide and hydrogen, diluent nitrogen, gaseous hydrocarbons, liquid hydrocarbons, carbon dioxide and steam, which latter two are by-products of the catalytic conversion. The effluent stream is cooled from the high temperature at which it issues from the reactor 12 in a heat exchanger 21. In the heat exchanger 21 there is effected condensation of the steam and normally liquid constituents contained in the effluent from the reactor 12.

From the heat exchanger 21, the effluent flows along a pipe 22 into a gas-liquid separator 23. Therein the effluent is separated into normally gaseous constituents and normally liquid ones. The water and normally liquid hydrocarbons leave the separator through a pipe 24 which leads to a decanter 25. The gaseous components of the effluent issue from the separator 23 through a pipe 26. The disposal of these gaseous components will be described in detail later.

In the decanter 25, water is separated from the normally liquid hydrocarbons and is removed through an exit pipe 27. The normally liquid hydrocarbons leave the decanter 25 through a pipe 30 and therethrough are introduced into a pre-heater 31.

In the pre-heater 31, the normally liquid hydrocarbons which are now at a low temperature are raised to about 650° F. before being charged to the fluid catalytic cracking unit. As described later, the so pre-heated hydrocarbons are further heated by contact with hot regenerated

catalyst which is being returned to the cracking reaction zone.

The hydrocarbons leave the heater 31 at the desired elevated temperature through a pipe 35 and then are introduced to a cracking unit employing a fluidized catalytic operation. In a reactor 36 of this fluidized catalytic cracking unit, the hydrocarbons contact a catalyst which is in the fluidized state, such as disclosed in U. S. Patent No. 2,361,978, for example. The numeral 37 designates the catalyst whose average particle size varies from 40 to 60 microns depending upon the type of a fluid system that is employed.

The catalyst 37 may be of the synthetic type such as silica-alumina, alumina-boria, etc., or it may be of a natural type such as natural or acid activated clays of the bentonite type; moreover, it may be promoted or unpromoted. The type of catalyst employed will determine the operating conditions that will be maintained in the reactor 36. In general, a temperature between 850 to 1050° F. is maintained and the reactor may be designed to withstand operating pressures up to and above 150 pounds per square inch.

By contact under the conditions outlined above, the hydrocarbon material which has been introduced into the reactor 36 through the pipe 35 and which contains high boiling naphthas, gas oil, Diesel oil and other hydrocarbon material of low octane rating, is cracked to give a greater portion of hydrocarbons boiling in the gasoline range of high octane rating. During this cracking operation, some oil is adsorbed and converted into carbon which accumulates on the catalytic material thereby coating the active catalytic centers and decreasing the activity of the catalyst. Therefore a portion of the fluidized catalyst is continuously removed from the reactor 36 for reactivation by removal of carbonaceous material in the regenerator section of the fluid catalytic cracking unit.

Thus, a portion of the fluidized catalyst flows continuously over a baffle 40 into a stripping section 41 in the lower portion of the cracking reactor 36. Herein there is introduced through a pipe 67 a stripping gas comprising mainly carbon dioxide which is obtained from sources which will be described in detail later. This stripping gas enters the stripping section 41 at a temperature in the range of about 300 to 500° F., which is suitable for stripping the adsorbed hydrocarbons from the catalyst.

The catalyst particles which enter the stripping section 41 contain a considerable amount of higher boiling hydrocarbons adsorbed on their surface and condensed in the capillaries and interstices of the catalyst. In conventional operation, steam is employed to strip these hydrocarbons from the catalyst in a stripping section of the fluid reactor. The cracking catalyst suffers gradual deactivation through the use of steam to effect removal of the adsorbed hydrocarbons from the catalyst.

In the method of this invention, desorption of the higher boiling hydrocarbons from the catalyst, prior to its reactivation, is effected by treating the catalyst with a gas comprising mainly carbon dioxide in the stripping section 41 at an elevated temperature. The use of this gas substantially reduces the deactivation of the catalyst which results from the use of steam for this purpose, and at the same time efficiently accomplishes the stripping of the hydrocarbons from the catalyst.

After the gas, comprising mainly inert carbon dioxide, has effected the desorption of the higher boiling hydrocarbons from the catalyst, it passes through and around the baffle 40 and into the cracking section proper of the reactor 36. The presence of this inert gas in the reactor 36 reduces the partial pressure of the hydrocarbons that are cracked therein. This reduction in partial pressure of crackable hydrocarbons effects decreased coke formation on the catalyst thereby increasing the efficiency of the cracking operation.

The products of the catalytic cracking and the gas which has been used to effect the desorption of the hydrocarbons from the cracking catalyst prior to its reactivation, issue from the reactor 36 through a pipe 48. The baffles 38 remove entrained catalytic material from the gaseous stream before it issues from the reactor 36. Cyclone separators may be used instead of the baffles 38 to effect the removal of the entrained catalytic particles from the gaseous stream. The treatment of the effluent which leaves the reactor 36 through the pipe 48 will be described in detail later.

After the catalyst has been stripped of adsorbed hydrocarbons in the stripping section 41 of the reactor 36 through the action of a gas comprising mainly carbon dioxide, but also containing a minor fraction of carbon monoxide and hydrogen, nitrogen, and low molecular weight hydrocarbons, it is continuously withdrawn from the reactor 36 through the conduit 50, and proceeds therethrough to a pipe 51. Air or oxygen, which is obtained from a source not shown, is pumped under pressure through the pipe 51, thereby providing means for transporting the catalyst from the reactor 36 to the regenerator 52 through the pipe 51. In the regenerator 52, the catalyst is reactivated by removal of the accumulated coke by combustion with the air or oxygen which has been introduced therein in the manner just described. Air is ordinarily used to effect this combustion. It is desirable to keep the combustion temperature in the regenerator 52 in the range of 1,000 to 1,200° F. in order to avoid deactivation of the cracking catalyst.

In normal operation, a small percentage of stripping medium is carried over to the regenerator 52. Since the stripping medium used in accordance with the method of this invention comprises mainly inert carbon dioxide, the stripping gas, which is carried over to the regenerator 52, moderates the intensity of the oxidative combustion taking place therein.

The numeral 37 also designates the catalytic material which is undergoing reactivation by removal of the coke in the regenerator 52. Cyclone separators plus electrical precipitators or similar devices, not shown, are provided to remove entrained catalyst from the effluent stream from the regenerator 52.

A portion of the reactivated catalyst continuously flows over a baffle 56 into the lower portion of the regenerator 52 whence it is continuously returned to the reactor 36. The reactivated catalyst leaves the regenerator 52 through a conduit 57 which flows into the feed line 35 through which the hydrocarbons that are to be cracked are introduced into the reactor 36. The flow of these hydrocarbons along the pipe 35 provides means of returning the reactivated catalyst to the reactor 36. The catalyst, which is at an elevated temperature as a result of the combustion, im-

parts its heat to the stream of hydrocarbons that are introduced into the reactor 36 through the pipe 35.

The effluent from the regenerator 52 contains mostly carbon dioxide, carbon monoxide, nitrogen and oxygen which has not been used in the combustion. The effluent passes along the pipe 54 to a carbon dioxide adsorbing tower 60. Therein the carbon dioxide portion of this effluent is adsorbed in a suitable medium, such as a solution of triethanolamine. The unabsorbed components of the gas stream are vented through the vent 61. The absorbing medium is continuously passed to a carbon dioxide-stripping section 62 through a pipe 63. In the stripping section 62, the carbon dioxide is stripped from the absorbing medium and leaves the stripping section 62 through a pipe 65. The regenerated absorbing medium returns to the absorbing section 62 through a pipe 64.

The carbon dioxide which has been stripped from the flue gas formed in the combustion taking place in the regenerator 52 is used in its entirety as stripping gas whose function in the stripping section 41 has been described in detail heretofore. The carbon dioxide proceeds along the pipe 65 to a heater 66 wherein it is raised to a temperature suitable for the stripping of adsorbed hydrocarbons from the catalyst prior to its reactivation. A temperature in the range of about 300 to 600° F. is suitable for this purpose.

The carbon dioxide obtained from the flue gas is augmented by a portion of the gaseous components of the effluent stream from the hydrogenation of carbon monoxide. Ordinarily this gaseous fraction of the effluent from the hydrogenation of carbon monoxide comprises about 40 to 60% carbon dioxide, about 5 to 20% nitrogen and varying smaller quantities of carbon monoxide, hydrogen and hydrocarbons, which are mainly normally gaseous ones but some of which are of higher molecular weight up to about the C<sub>10</sub>'s. This gaseous fraction of the effluent from the hydrogenation of carbon monoxide is separated from the normally liquid components in the separator 23 and issues therefrom through the pipe 26. The pipe 26 connects with the pipe 65 through which the carbon dioxide separated from the flue gas flows. It is possible to supplement the carbon dioxide from the flue gas with any portion of the gaseous fraction of the effluent from the hydrogenation of carbon monoxide that is considered necessary to accomplish efficient desorption in the stripping section 41. The portion of the gaseous fraction of the effluent from the hydrogenation of carbon monoxide which is used to augment carbon dioxide flows through the pipe 26 into the pipe 65 and there-through enters the heater 66 in which the total stripping gas is raised to a temperature suitable for stripping. The stripping gas leaves the heater 66 through a pipe 67 and therethrough is introduced into the stripping section 41 of the reactor 36 at the desired temperature. In the stripping section 41, the stripping gas effects the desorption of the adsorbed hydrocarbons in a manner which has been described in detail previously.

The effluent from the reactor 36, comprising the products of the cracking operation and the gas, mainly inert carbon dioxide, which was used to effect the stripping of the adsorbed hydrocarbons, passes along the pipe 48 to a fractionator 70. Herein the higher boiling hydrocarbons such as gas oil, which have not been converted into

gasoline hydrocarbons in the cracking operation, are condensed and thereafter are recycled through a pipe 71 to the reactor 36 for further treatment, or are discharged through an exit pipe 73. The pipe 71 leads into the feed line 35 whence the recycle gas oil is returned to the reactor 36. The recycle gas oil is raised to cracking temperature by contact with the hot regenerated catalyst which flows through the conduit 57 into the feed line 35.

Gasoline, normally gaseous hydrocarbons and the stripping gas leave the fractionator 70 through a pipe 74 and therethrough are introduced into a stabilizer 75. Herein the gaseous components of the effluent from the cracking, such as carbon dioxide, hydrogen, carbon monoxide, nitrogen and C<sub>1</sub> to C<sub>4</sub> hydrocarbons, are separated from the gasoline hydrocarbons. The gasoline fraction is removed through the pipe 76 and is piped to storage, not shown.

The portion of the gaseous components of the effluent from the hydrogenation of carbon monoxide which is not used as part of the medium employed to strip the adsorbed hydrocarbons from the cracking catalyst in the stripping section 41, passes along a pipe 72 which leads from the pipe 26 through which the gaseous effluent leaves the separator 23. Through the pipe 72, this portion of the gaseous effluent from the hydrogenation of carbon monoxide enters the stabilizer 75, wherein any gasoline hydrocarbons contained therein are separated. The gasoline separated therefrom merges with the gasoline resulting from the catalytic cracking and is removed from the stabilizer through the pipe 76. The gaseous components comprising carbon dioxide, nitrogen, unreacted carbon monoxide and hydrogen, and C<sub>1</sub> to C<sub>4</sub> hydrocarbons combine with the gaseous fraction of the effluent from the cracking reactor 36.

The gas which leaves the stabilizer 75 through a pipe 77 comprises a major portion of carbon dioxide and minor portions of nitrogen, carbon monoxide, hydrogen and C<sub>1</sub> to C<sub>4</sub> hydrocarbons. This gas passes along the pipe 77 to a hydrocarbon absorption unit 78 which is of the conventional type adapted to effect absorption of hydrocarbon gases. A major portion of the C<sub>2</sub> to C<sub>4</sub> hydrocarbons, together with some methane, is absorbed in the absorption unit 78 wherein an absorbing medium, such as charcoal or gas oil, is employed. The hydrocarbons which are adsorbed in the absorbing medium are stripped from the absorbent in a separate section of the absorption unit 78 and are removed therefrom through a pipe 79 through which they are piped to storage, not shown.

The gas which leaves the hydrocarbon absorption unit 78 through the pipe 80 comprises a major portion of carbon dioxide and minor quantities of nitrogen, hydrogen, carbon monoxide and methane. This gas at least in part is advantageously returned to the synthesis gas generator 5 wherein its content of methane and carbon dioxide may be utilized in the preparation of synthesis gas. The hydrogen and carbon monoxide present in this gaseous fraction may serve as diluents to moderate the highly exothermic oxidation taking place in the synthesis gas generator 5. A portion of the gas must first be vented, however, to prevent an accumulation of nitrogen in the system. This may be accomplished through a vent 81. The unvented portion of this tail gas proceeds along the pipe 80 until it is introduced

into the hydrocarbon feed line 2 whence it is introduced into the generator 5.

Alternately or simultaneously a portion of this gas comprising carbon monoxide, hydrogen, carbon dioxide, methane and nitrogen may be introduced into the synthesis reactor 12 through a pipe 82 which leads from the pipe 80 to the feed pipe 6.

While mention is specifically made of the use of methane for the preparation of synthesis gas, other hydrocarbon gases may also be utilized in the preparation of carbon monoxide and hydrogen. As a matter of fact, synthesis gas from any source may be used.

In the description of the invention, the hydrogenation of carbon monoxide is described as employed in conjunction with a fluidized system of catalytic cracking. However, the invention contemplates the use of a carbon monoxide hydrogenation process in conjunction with any type of catalytic cracking operation, wherein a portion of the catalyst is continuously regenerated and wherein stripping of the adsorbed hydrocarbons prior to regeneration is necessary in order to avoid the loss of a considerable portion of hydrocarbons in the combustion which takes place in the regenerator zone.

In accordance with the invention, the hydrogenation of carbon monoxide can be employed in conjunction with a hydroforming operation. The hydrogen resulting from the hydroforming process may be used to supplement the synthesis gas in which there may be at times a deficiency of hydrogen depending on the source of the synthesis gas.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. In the catalytic conversion of a mixture of carbon monoxide and hydrogen into liquid hydrocarbons of high octane rating, the steps which comprise preparing synthesis gas comprising hydrogen and carbon monoxide in a synthesis gas generation zone by the oxidation of carbonaceous material, converting said synthesis gas into hydrocarbons and hydrocarbon derivatives by contact with a synthesis catalyst under conversion conditions of temperature and pressure, separating the reaction products into a normally liquid fraction and a normally gaseous fraction, continuously passing the liquid fraction in contact with a mass of finely divided solid, hydrocarbon-conversion catalyst maintained at a temperature effective for catalytically cracking hydrocarbons, continuously discharging products of cracking from the cracking zone, continuously removing from the cracking zone used catalyst, subjecting removed catalyst to contact with an oxidizing gas in a zone of reactivation to effect combustion of carbonaceous material contained in the catalyst, thereby forming a flue gas containing carbon dioxide, separating carbon dioxide from said flue gas, subjecting said used catalyst prior to said combustion to contact with a stripping gas comprising a mixture of said separated carbon dioxide and a portion at least of the gaseous effluent from the catalytic conversion of carbon monoxide and hydrogen, in a stripping zone under conditions effective to strip adsorbed hydrocarbons from said catalyst, passing said stripping gas and resulting desorbed hydrocarbons from the stripping zone to said

cracking zone, subjecting the combined products from the cracking zone to a separation process effective to recover normally liquid hydrocarbon products of reaction and deliver a normally gaseous stream containing the normally gaseous products from said cracking zone, supplying a substantial portion of said normally gaseous stream to said gas generation zone for the production of additional synthesis gas by the oxidation of carbonaceous materials therein, utilizing said additional synthesis gas in the production of additional hydrocarbons, and adding a second portion of said normally gaseous stream to the synthesis gas subjected to contact with said synthesis catalyst.

2. In a catalytic conversion of a mixture of carbon monoxide and hydrogen into liquid hydrocarbons of high octane rating the steps which comprise preparing synthesis gas comprising hydrogen and carbon monoxide in a gas generation zone by the oxidation of carbonaceous material, converting said synthesis gas into hydrocarbons and hydrocarbon derivatives by contact with a synthesis catalyst under conversion conditions of temperature and pressure, separating the reaction products into a normally liquid fraction and a normally gaseous fraction, continuously passing the liquid fraction in contact with a mass of finely divided solid, hydrocarbon-conversion catalyst maintained at a temperature effective for catalytically cracking hydrocarbons, continuously removing from the cracking zone used catalyst, subjecting removed catalyst to contact with an oxidizing gas in a zone of reactivation to effect combustion of carbonaceous material contained in the catalyst, thereby forming a flue gas containing carbon dioxide, separating carbon dioxide from said flue gas, subjecting said used catalyst, prior to said combustion, to contact with a stripping gas comprising a mixture of said separated carbon dioxide and a portion at least of the gaseous effluent from the catalytic conversion of carbon monoxide and hydrogen, in a stripping zone under conditions effective to strip adsorbed hydrocarbons from said catalyst, passing said stripping gas and resulting desorbed hydrocarbons from the stripping zone to said cracking zone, recovering the combined reaction effluent from said cracking zone, subjecting said effluent, including both products of reaction and products of stripping, to a separating step effective to recover normally liquid hydrocarbons and delivering a stream of normally gaseous products including gaseous hydrocarbons and carbon dioxide, recycling a portion of said last named stream to said synthesis gas generation zone for formation of additional synthesis gas, including said additional synthesis gas in the mixture converted to hydrocarbons and hydrocarbon derivatives, as aforesaid, and continuously admixing a second portion of said normally gaseous product stream with the synthesis gas subjected to contact with the synthesis catalyst for the preparation of hydrocarbons and hydrocarbon derivatives.

3. In a catalytic synthesis of liquid hydrocarbons of high octane rating wherein a carbonaceous material is submitted to partial combustion in a synthesis gas generating zone in the presence of molecular oxygen under exothermic conditions for the production of a synthesis gas comprising hydrogen and carbon monoxide, the synthesis gas being converted into hydrocarbons and hydrocarbon derivatives in a reaction zone by contact with a hydrocarbon synthesis catalyst

under conversion conditions of temperature and pressure, the reaction products separated into a normally liquid fraction and a normally gaseous fraction, and the normally liquid fraction is continuously passed in contact with a mass of finely divided, solid particle, hydrocarbon-conversion catalyst maintained at a temperature effective for catalytically cracking said normally liquid fraction, the improvement which comprises continuously removing used catalyst from the cracking zone, subjecting said removed catalyst to contact with an oxidizing gas to effect combustion of carbonaceous material deposited on the catalyst, thereby forming a flue gas containing carbon dioxide, separating carbon dioxide from said flue gas, subjecting said used catalyst prior to combustion to contact with stripping gas comprising a mixture of said separated carbon dioxide and a portion at least of the said normally gaseous fraction derived from the catalytic reaction of carbon monoxide and hydrogen, in a stripping zone under conditions effective to strip adsorbed hydrocarbons from the catalyst, passing the said stripping gas and resulting desorbed hydrocarbons from the stripping zone to said cracking zone, recovering normally liquid hydrocarbons from the combined products of the cracking zone, thereby leaving a normally gaseous stream of products from the cracking zone, venting a portion of said normally gaseous stream, separating the remainder into at least two streams, continuously conveying one of said streams of gas into admixture with the synthesis catalyst, and continuously directing the other stream into said synthesis gas generation zone for the production of additional synthesis gas.

4. The method according to claim 1, wherein said carbonaceous material supplied to the gas generation zone comprises methane.

5. The method according to claim 1, wherein the oxidation of carbonaceous material in said gas generation zone comprises partial combustion of said carbonaceous material in the presence of free oxygen under exothermic conditions.

6. In the catalytic conversion of a mixture of carbon monoxide and hydrogen into liquid hydrocarbons of high octane rating, the steps which comprise preparing synthesis gas comprising hydrogen and carbon monoxide in a gas generation zone by the oxidation of carbonaceous material, converting said synthesis gas into hydro-

carbons and hydrocarbon derivatives by contact with a synthesis catalyst under conversion conditions of temperature and pressure, separating the reaction products into a normally liquid fraction and a normally gaseous fraction, continuously passing the liquid fraction in contact with a mass of finely divided, solid, hydrocarbon-conversion catalyst maintained at a temperature effective for catalytically cracking hydrocarbons, from the cracking zone, continuously removing from the cracking zone used catalyst, subjecting removed catalyst to contact with an oxidizing gas in a zone of reactivation to effect combustion of carbonaceous material contained in the catalyst, thereby forming a flue gas containing carbon dioxide, separating carbon dioxide from said flue gas, subjecting said used catalyst prior to said combustion to contact with a stripping gas comprising a mixture of said separated carbon dioxide and a portion at least of the gaseous effluent from the catalytic conversion of carbon monoxide and hydrogen, in a stripping zone under conditions effective to strip adsorbed hydrocarbons from said catalyst, passing said stripping gas and resulting desorbed hydrocarbons from the stripping zone to said cracking zone, subjecting the combined products from the cracking zone to a separation process effective to recover normally liquid hydrocarbon products of reaction and deliver a normally gaseous stream containing the normally gaseous products from said cracking zone, and continuously supplying a substantial portion at least of said normally gaseous stream to the synthesis gas subjected to contact with said synthesis catalyst for the preparation of hydrocarbon and hydrocarbon derivatives.

LEBBEUS C. KEMP, Jr.

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