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PRESSURE HYDROGASIFICATION OF NATURAL GAS LIQUIDS
AND PETROLEUM DISTILLATES

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2 Sheets-Sheet 2

Fig. 2

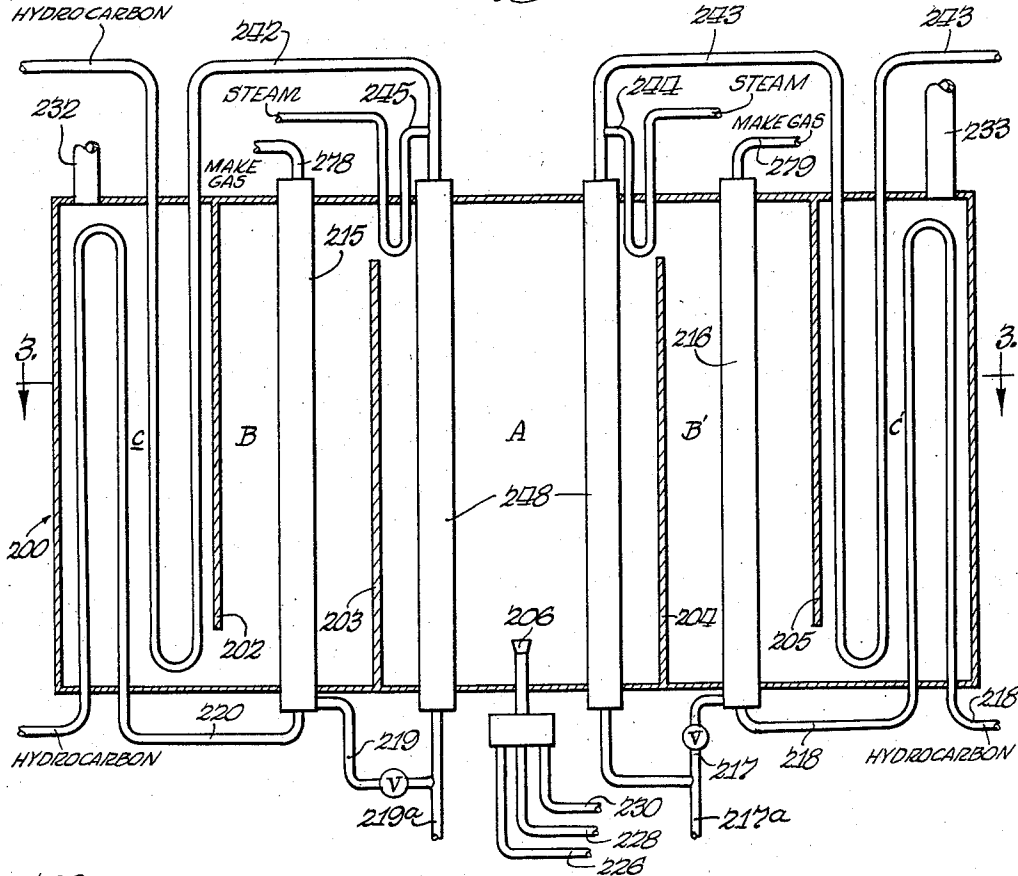
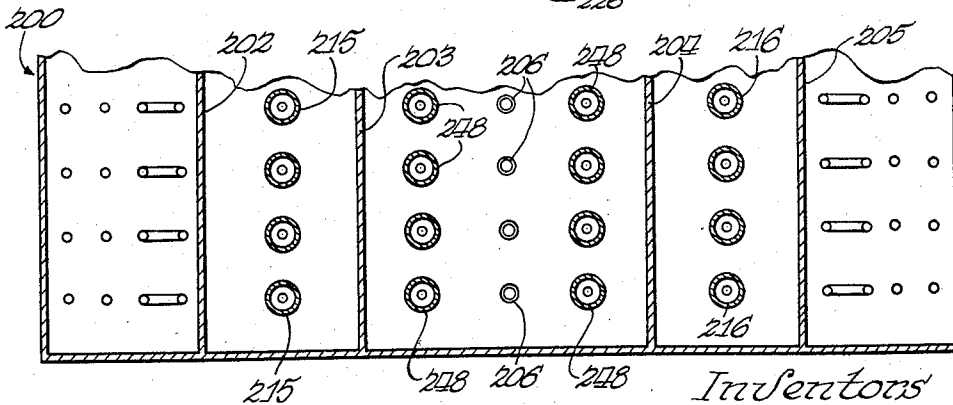


Fig. 3

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PRESSURE HYDROGASIFICATION OF NATURAL GAS LIQUIDS AND PETROLEUM DISTILLATES

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Application June 14, 1954, Serial No. 436,406

1 Claim. (Cl. 48—197)

This invention relates to an improved method and apparatus for manufacturing a high heating value oil gas which is completely interchangeable with natural gas. One of the major problems facing the utility gas industry is the supply of peak load gas in areas where gas house heating is widely used and where the cost of gas is predicated on the major portion being supplied by pipe line. Since long distance transmission lines can be operated economically only under near capacity steady loads, methods for computing natural gas prices on the basis of demand, commodity and minimum charges have been generally accepted. It is, therefore, not economically advantageous to meet peak gas load demands above a certain level set by local conditions through the purchase of flowing pipe line gas. Consequently, there is a need for an efficient, economical method for producing artificially a gas that can be used interchangeably for all or part of the natural gas normally supplied, in all varieties of gas burners.

In our copending application Serial No. 337,078, filed February 16, 1953, now Patent No. 2,759,806, we disclose a method for making completely interchangeable gases which involves high temperature vapor phase cracking of light liquid hydrocarbons under pressure in the presence of hydrogen gas. The advantages of employing an atmosphere of hydrogen in addition to pressure in converting vaporized hydrocarbons into B. t. u. gases are several. The gaseous product contains a relatively high proportion of paraffins and a relatively low proportion of olefins, thus approximating more closely the actual composition of natural gas and its heating value and burning properties. Furthermore, the process permits substantially complete conversion of hydrocarbon feed stocks having a boiling point up to about 500° F. (natural gasoline, naphthas, and kerosene) without objectionable carbon and pitch deposition in the take-off system of the cracking apparatus. Also, large volumes of feed stocks may be processed in a relatively small reactor space. This process, therefore, offers a number of important advantages over conventional oil cracking methods. The present invention constitutes an improvement over the method described in said copending application Serial No. 337,078 and has as an object the provision of an improved process for cracking light liquid hydrocarbon fractions under pressure and in the presence of an atmosphere of hydrogen gas in which the hydrogen utilized as the cracking atmosphere is manufactured as an integral part of the gas manufacturing process, and which process is further characterized by the efficient utilization of heat required for producing the hydrogen, cracking the hydrocarbon and preheating raw materials used in the process. The term "hydrocarbon" used throughout this specification with reference to feed stock for cracking is intended to cover the light liquid hydrocarbons referred to in the art as natural gas liquids and petroleum distillates.

A further object is to provide an efficient continuous process for simultaneously manufacturing hydrogen and cracking hydrocarbons, in which the cracking tempera-

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ture is lower than the temperature required to produce the hydrogen so that the hot gases supplied for furnishing heat to the production of hydrogen, or hydrogen-rich gas, may be utilized thereafter to supply heat for cracking the hydrocarbons in the presence of hydrogen.

Another object is to provide a process of the type described in which the hydrogen, or hydrogen-rich gas, is made under pressure greater than the pressure in the hydrogasification or cracking reactor, thus maintaining a driving force to move the gases through the apparatus and eliminating the necessity for compressing the gas before introduction into said reactor.

Another object is the provision of a simple apparatus in which the process of the invention may be economically carried out. These and other objects will become apparent from the following description when read in conjunction with the accompanying drawing, in which:

Figure 1 is a sectional semi-diagrammatic view illustrating the process and apparatus of the invention;

Figure 2 is a similar view of a modified furnace for the apparatus of Figure 1; and

Figure 3 is a sectional view taken along line 3—3 of Figure 2.

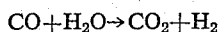
The objects of our invention are achieved by taking advantage of the fact that the cracking of light liquid hydrocarbons in the presence of hydrogen requires surprisingly less heat than cracking without hydrogen, and that the temperature at which this reaction proceeds is lower than the optimum temperature for reforming hydrocarbons with steam in the first step of production of hydrogen gas. For example, the amount of heat at reaction temperature required to convert 26# RVP natural gasoline in the presence of hydrogen is about 25% of the heat required to convert the same quantity of the same gasoline in the absence of hydrogen. The waste heat from the catalytic reforming reaction, therefore, will meet the heat requirements for hydrogasification, in spite of the additional sensible heat requirements for preheating the hydrogen. By employing a furnace divided into three interconnected zones, the heat supplied to the process may be utilized in the first zone for reforming a hydrocarbon gas or light liquid hydrocarbon to produce hydrogen. The remainder is transferred to the second zone in which the cracking of the hydrocarbon takes place in the presence of hydrogen at a substantially lower temperature to produce a gas interchangeable with natural gas. The balance of the original heat flows into the third zone for preheating the feed stocks for the reactions proceeding in zones 1 and 2. The temperature in the first combustion zone normally will be above 1800° F., while that in the second zone will be between 1350 and 1700° F. Preferably, the temperature in the furnace is maintained several hundred degrees higher than the maximum temperature desired in the reaction tube housed within the furnace. A high temperature gradient permits a high rate of conversion and, therefore, a high through-put. The hot flue gases, which may be generated in the first zone of the furnace by means of oil burners or gas burners, lose a portion of their heat to the reactor tubes within said zone for catalytically reforming hydrocarbons, but still contain sufficient heat to effect cracking of the light hydrocarbon fraction in zone 2, which reaction in the presence of hydrogen requires substantially less heat. The balance of the heat in the gases is utilized to preheat the raw materials in zone 3 of the furnace, as indicated. Efficient utilization of heat in this manner minimizes the heat requirements per cubic foot of gas produced, hence making the process of the invention very economical as compared with a similar process in which hydrogen is produced in a separate apparatus.

Referring now to the drawing, a furnace indicated generally at 10 is divided into three zones, designated

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as 1, 2 and 3, by means of bulkheads or dividers 12 and 14. The interior walls of the furnace and the dividers are made from any suitable ceramic refractory material, such as fire brick. It will be noted that the divider 12 does not run completely to the top of the furnace, thus permitting zones 1 and 2 to be interconnected through the opening 16. In like manner, divider 14 extends downwardly short of the bottom of the furnace, leaving an opening 18 for interconnecting zones 2 and 3. Heat is generated within zone 1 by means of a bank of conventional burners 20, 22 and 24, which are capable of burning either oil or gas. Several banks of burners are provided depending upon the length of the furnace. Gas is supplied to the burners through the line 26, oil through line 28, and air required for combustion of these hydrocarbons through line 30. Throughout the drawing the letter V indicates a valve, M a flow meter, and P a pump or blower. The hot flue gases generated within zone 1 flow through opening 16 into zone 2, downwardly through zone 2, out the opening 18 into zone 3, upwardly through zone 3 and are discharged through the flue 32.

Hydrocarbon feed stock for preparing hydrogen is fed from line 34 through the tube 36 mounted within zone 3 of the furnace for preheating the hydrocarbon. The feed stock may be a liquid hydrocarbon such as natural gasoline, naphtha or kerosene, supplied to line 34 through supply line 40; or the feed stock may comprise a recycled make gas supplied from the discharge conduit 90, natural gas, propane or the like, which is supplied to line 34 through supply line 42. Steam required in the reforming reaction for converting the hydrocarbon feed stock into hydrogen gas is supplied from line 44 and passes through a coil 46 within zone 1 of the furnace for superheating. The superheated steam joins the hydrocarbon feed stock in line 38, which connects to the top of the catalytic reactors 48 within zone 1. The reactors 48 are arranged longitudinally within the furnace in banks. Each reactor is an elongated chamber of any suitable cross section, preferably circular. The temperature of the walls of the reactor tubes is maintained at 1600-1800° F. and the pressure within the tubes above 50, and preferably at 70-100 pounds per square inch absolute. The catalytic reactors 48 contain a suitable catalyst, such as nickel, for converting the hydrocarbon feed stock and steam into hydrogen plus some carbon dioxide and carbon monoxide. This hydrogen-rich gas may then be fed to tubes 13 and 15 for reaction with the hydrocarbon feed stock in making fuel gas through valved conduit 52. Preferably, however, the valve in conduit 52 is closed and the carbon monoxide in the gas is converted by reaction with steam into carbon dioxide and additional hydrogen gas, and the carbon dioxide subsequently removed. This may be accomplished by passing the carbon oxides and hydrogen from the catalytic reactors 48 through conduit 50 into the catalytic water gas shift reactor 54, containing a conventional water gas shift catalyst. The carbon monoxide generated within the reactors 48 is converted to carbon dioxide plus additional hydrogen in the reactor 54 in accordance with the well known reaction:



Additional steam required for the reaction is introduced into the line 50 from feed line 52. Preferably, sufficient water is introduced into the line 50 so that the temperature within the reactor 54 is maintained at 600 to 800° F., preferably at 750° F. The pressure within the reactor 54 will be equal to the pressure maintained within reforming tube 48, less any pressure drop in conduit 50. The magnitude of the pressure in reactor 54 and tube 48 is controlled by downstream pressure control valve 69.

To remove the carbon dioxide from hydrogen produced in both reactions, the effluent gases are first passed

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from the lower end of the reactor 54 into the contact cooler 56 for cooling. The gases flow upwardly in the cooler countercurrent to water spray introduced at the top of the cooler through the line 58, out the discharge conduit 60 and into the scrubber 62 near the lower end thereof. The water that falls to the bottom of the cooler 56 flows out through pipe 64 and is used again for cooling the product gas, as described hereinbelow. A material capable of absorbing carbon dioxide, such as an ethanolamine solution, is introduced into the scrubber through the top countercurrent to the mixture of carbon dioxide and hydrogen which flows upwardly through the scrubber. The carbon dioxide is absorbed by the ethanolamine solution which is removed through discharge line 66 in the bottom of the scrubber. The hydrogen gas, essentially free of carbon oxides, passes out through line 68, back pressure control valve 69, coil 19 in zone 3 of the furnace, for preheating, and into the first pressure hydrogasification tube 13 within zone 2 of the furnace. The hydrogen produced will contain some impurities such as carbon dioxide, carbon monoxide and methane. Total quantities as high as 5 to 10 percent can be tolerated.

Hydrocarbon feed stock to be converted into a gas interchangeable or substitutable for natural gas is fed from the supply line 11 through coil 17 in zone 3 for vaporization, and then into the first tube 13 of pairs of pressure gasification tubes extending along the length of the furnace in zone 2. Although reaction tubes 13 and 15 are shown in pairs in the drawing, it will be understood that a bank of single tubes having an equivalent volume will serve the same purpose. The hydrocarbon employed for cracking may range in volatility up to that of kerosene, and includes what are generally known as the light liquid petroleum fractions and the natural gas liquids, such as propane, butane and natural gasolines.

The vaporized hydrocarbons from coil 17 and the preheated hydrogen from the coil 19 flow under pressure into the lower ends of the pressurized gas tubes 13 where the vapors and gas are thoroughly intermixed and the cracking begins. Because the hydrogen gas is generated under pressure it is not necessary to compress it as would be the case where hydrogen is provided from some external source. Partially cracked gases flow upwardly through the tubes 13 back down into the tubes 15 through the U-shaped connections at the top. Cracking is completed within the tubes 15 at a maximum temperature ranging from 1300 to 1500° F. and a pressure of about 50-80 pounds per square inch absolute.

The amount of hydrogen introduced into the reactors may range from 50 to 110 cubic feet per gallon of liquid hydrocarbon feed stock, depending upon the properties of the feed stock. The hydrogen must be increased in proportion to the carbon content and molecular weight of the feed stock. The residence time in the reactors ranges from 2 to 10 seconds, preferably from 3 to 5 seconds, and may be varied at will by changing the rate of flow through the reactors. The product gas discharged from the tubes 15 is rich in methane and ethane and also contains some ethylene and light oils in vapor form. The amount of carbon, tar and pitch formed during this reaction is nil. The amount of light normally liquid hydrocarbons formed is usually less than 20%.

The cracking products issuing from the reactors pass through large quench tubes 78 connected to the bottom of the tubes 15 and through conduits 70 into a quench water separator 72. Water for cooling the product gas flows from the cooler 56 through the line 64 into the separator 72 and is pumped therefrom through the line 74 into the quench tube 78, as indicated at 76. Preferably, the water is introduced in a spray so that the temperature of the effluent product gas is effectively reduced. A constant level device 80 of conventional construction

is connected with the separator 72 to maintain the water level within the separator at a predetermined level, the waste being discharged through the line 82. The partially-cooled product gas, which may contain some light oils in vapor form, flows from the separator 72 through the conduit 84, through the condenser 86, and into the phase separator 88. The light oils, which are condensed in the condenser 86, are permitted to separate from the gas in the phase separator 88. The light oils are recovered. The make gas flows out of the separator 88, through the line 90 to storage or to the location where it is to be used. An automatic pressure regulating valve 92 maintains the pressure upstream thereof at a predetermined level, preferably from 50–80 pounds per square inch absolute. The make gas will have a heating value of from 930 to 1100 B. t. u.'s per standard cubic foot. It generally will contain from 45–55% methane and ethane, from 30–40% hydrogen, and about 8–11% ethylene, plus minor proportions of benzene, carbon dioxide and the higher paraffins and olefins. The specific gravity will range from about 0.5 to 0.65.

If desired, the olefins in the make gas may be converted into paraffins by autohydrogenation. This improvement can be effected by passing the gas over a nickel-on-kieselguhr catalyst at a temperature of from 200 to 500° F., and a space velocity up to 1000 standard cubic feet per cubic foot of catalyst per hour. Under these conditions a high conversion of olefins and diolefins to the equivalent paraffins, and comparable reduction of hydrogen content were obtained.

It is desirable to recover the ethanolamine employed as a scrubbing agent so that it may be recycled through the scrubber continuously. Any suitable means may be employed for this purpose. An example of suitable apparatus is shown in Figure 1 to the right of the scrubber 62. The ethanolamine, saturated with carbon dioxide, flows through the pipe 66 and the heat exchanger 102 into the regenerator 100. The ethanolamine is preferably sprayed into the regenerator through a nozzle 104. The temperature of the regenerator is maintained at about 300° F. and about 40 pounds per square inch pressure. Under these condition the carbon dioxide is driven off and passes upwardly to the conduit 106 connecting to the regenerator near the top and is discharged therethrough. Water cooled coils 108 disposed within the top of regenerator 100 serve to condense any ethanolamine and much of the steam that is volatilized. The ethanolamine solution, free of carbon dioxide, drains to the bottom of the regenerator and is recirculated to the scrubber 62 through line 110. To cool the ethanolamine as it passes to the scrubber, heat exchangers 102 and 112 are provided in the line 110, the heat exchanger 102 employing saturated ethanolamine from the scrubber as a coolant. The temperature within the regenerator is maintained by means of a heating coil 114 submerged below the level of the ethanolamine in the bottom of the regenerator.

The modification of the apparatus shown in Figures 2 and 3 involves changes only in the construction of the furnace and its contents, the other parts being essentially as shown in Figure 1. The furnace 200 shown in Figures 2 and 3 is designed to generate approximately twice the volume of gas produced in the apparatus of Figure 1. Furnace 200 is divided in five different zones, designated as zones A, B, B₁, C and C₁, by baffles 202, 203, 204 and 205. Heat for operating the process is generated in zone A by means of a bank of burners 206, extending the length of the furnace between the catalytic reactors 248. The burners are fed with gas or oil and air through lines 226, 228, and 230, respectively. Hydrocarbon feed stock for reforming into a hydrogen-rich gas is fed to catalytic reactor tubes 248 through lines 242 and 243. Steam required for the reaction is introduced through lines 244 and 245. It will be noted that lines 244 and 245 pass through zone A for purposes of superheating the steam,

and lines 242 and 243 pass through zones C and C₁ to preheat the hydrocarbon feed stock.

Cracking tubes 215 and 216 are disposed within zones B and B₁. Hydrogen-rich gas generated in reactors 248 may flow directly into tubes 215 and 216 through valved conduits 217 and 219 connecting to the lower ends thereof. Preferably, the carbon monoxide in the gas is converted to hydrogen and carbon dioxide by passing the gas through conduits 217a and 219a to the catalytic water gas shift reactor 54, and the carbon dioxide removed in the scrubber, as shown in Figure 1, prior to delivery to the cracking tubes 215 and 216. Hydrocarbon feed stock is supplied to reactors 215 and 216 through lines 220 and 218 which pass through zones C and C₁, respectively, for preheating the feed stock. Make gas produced in tubes 215 and 216 is discharged to the condensing portion of the apparatus through conduits 278 and 279.

The flue gases generated within zone A flow upwardly and divide, part passing over the baffle 203 into zone B and the remainder passing over the baffle 204 into zone B₁. It will be noted that the flow of feed stock and hydrogen is counter to the flow of heat in zone B since the hot combustion gases enter zone B at the top and exit at the bottom. Thus, the temperature of the feed stock is gradually increased as it passes upwardly through reaction tubes 215, 216. After giving up a portion of their heat to the reactors in zones B and B₁ the gases flow beneath baffles 202 and 205 in zones C and C₁, where they give up heat to the hydrocarbon feed stocks for both the catalytic and cracking reactors. The gases then pass out stacks 232 and 233.

Other modifications in the arrangement of the furnace and its contents will become apparent from the foregoing description.

Examples 1 and 2, set forth below, illustrate typical operating conditions employed in the pressure hydrogasification of 26 pound RVP natural gasoline and kerosene, respectively, in accordance with the invention, and the compositions of the make gases produced.

Example No.-----	1	2
Operating Conditions:		
Reactor Tube, Temp., ° F.—		
East Tube:		
avg.-----	1,320	1,316
max.-----	1,412	1,367
West Tube:		
avg.-----	1,324	1,316
max.-----	1,411	1,358
Reactor Pressure, p. s. i. a.-----	70.3	71.3
Residence Time, sec.-----	4.73	3.75
Feed Rate, Feed Stock, lb./hr.-----	264	304
Feed Rate, Feed Stock, gal./hr.-----	49.6	45.1
Feed Rate, hydrogen, s. c. f./gal.-----	60.0	104.3
Fuel Consumption, M B. t. u./hr.-----	1,032	998
Operating Results:		
H ₂ Reacted, s. c. f./gal. Feed-----	25.5	39.1
H ₂ Reacted, Percent-----	42.5	37.5
Gas Make, s. c. f./hr.-----	5,770	6,920
Gas Yield, s. c. f./gal.-----	116.4	153.4
B. t. u. Recovery, B. t. u./gal. Feed (gross)-----	124,490	143,280
B. t. u. Recovery, B. t. u./gal. Feed (net)-----	105,340	109,970
Light Oil Yield, wt. percent-----	None	18.5
Residual Oil Yield, wt. percent-----	None	None
Material Balance, percent-----	101.4	100.3
Composition, mole percent:		
N ₂ -----	0.6	1.0
CO ₂ -----	0.2	0.1
H ₂ -----	29.3	42.5
CH ₄ -----	43.0	30.2
C ₂ H ₆ -----	10.7	12.4
Higher Paraffins-----	0.8	0.9
C ₂ H ₄ -----	10.6	7.9
Higher Olefins-----	3.3	3.8
Benzene-----	1.2	1.0
Toluene-----	0.3	0.2
Total-----	100.0	100.0
Heating Value, as made, B. t. u./s. c. f.-----	1,070	934
Specific Gravity, as made, air=1.00-----	0.64	0.51

Particular attention is called to the operating results of Example 1 wherein gasoline is the hydrocarbon feed stock. The conversion to gas is 100% complete, no residue, liquid or solid, resulting. We have found that

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to completely eliminate by-products, the feed stock should be a natural gas liquid with the cracking conditions being controlled within the following limits:

Temperature----- 1300-1500° F.
 Pressure----- 50-80 pounds per square inch absolute.
 Residence time----- 2-5 seconds.
 Feed hydrogen----- 50-80 cubic feet per gallon of hydrocarbon.

With a high molecular weight material, such as kerosene of Example 2, a light oil will be formed and remain as a residue, even though the operating conditions are carefully controlled.

From the foregoing it will be seen that we have provided a continuous, efficient process for the manufacture of a gas which is completely interchangeable with natural gas, the process being particularly characterized by the utilization of waste heat from the hydrogen-forming step.

We claim:

A process for completely converting natural gas liquids into a fuel gas completely interchangeable with natural gas which comprises producing a hydrogen-rich gas by catalytically reforming a hydrocarbon in the presence of steam, removing oxides of carbon from said hydrogen-rich gas to a residual concentration of less than 10 volume percent,

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preheating said feedstock to vaporize it without cracking thoroughly intermixing said hydrogen-rich gas and said vaporized feed stock but below cracking temperature, gradually increasing the temperature of said mixture of hydrogen-rich gas and vaporized feedstock to 1300-1500° F. at a pressure of 50-80 pounds per square inch absolute to convert substantially all of said feedstock into said interchangeable fuel gas, the quantity of hydrogen ranging from 50-80 cubic feet per gallon of feedstock and the residence time at 1300-1500° F. ranging from 2-5 seconds.

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