

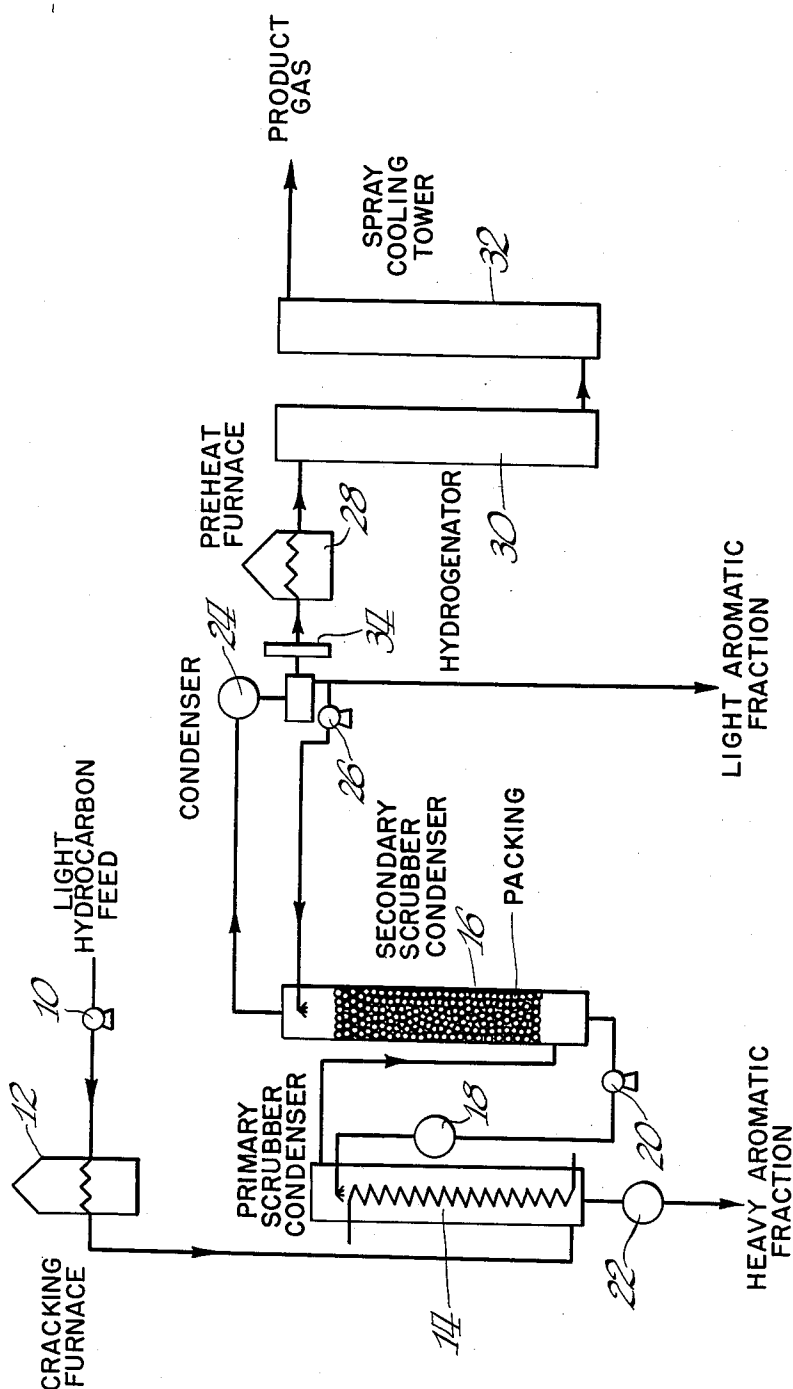
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METHOD OF MAKING A FUEL GAS INTERCHANGEABLE WITH NATURAL GAS

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METHOD OF MAKING A FUEL GAS INTER- CHANGEABLE WITH NATURAL GAS

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This invention relates to a method of converting a hydrocarbon mixture, and preferably a normally liquid hydrocarbon mixture, into a fuel gas absolutely interchangeable with natural gas.

With the increasing demand for gas as a premium fuel for domestic house heating, seasonal variation in gas sendout has been growing from year to year. To meet the resulting peak demands, it is desirable to produce and feed a substitute gas into the mains or pipelines. For this purpose, a method for making a substitute gas that is absolutely interchangeable with the normal sendout gas has long been desired but has heretofore not been available.

It is therefore an important object of the present invention to provide a method of preparing a fuel gas absolutely interchangeable with natural gas as prepared or, at the most, after admixture with the fuel gas of a small amount of an inert or diluent gas such as air, nitrogen, carbon dioxide, combustion gas or the like.

Another object of this invention is to provide a method of the nature indicated which can be operated continuously in simple relatively inexpensive apparatus.

Other and further objects and features of this invention will become apparent from the following description and appended claims as illustrated by the accompanying drawing showing, diagrammatically and by way of example, apparatus for carrying out the method of this invention and the flow of material therethrough.

The starting materials of the method of this invention are the gaseous and liquid paraffinic light petroleum fractions having a final boiling point up to about 500° F. These materials may also be characterized as having an average molecular carbon content ranging up to and including nine carbon atoms per molecule. Examples of such materials are propane, butane, hexane, heptane, octane, mixtures of aliphatic hydrocarbons up to and including pentadecane, natural gasoline, straight run gasoline and straight run naphtha. From the standpoint of economical storage, the preferred starting materials are those requiring no pressure or only a slight pressure, say, from five to ten pounds per square inch, on storage in liquid condition, for instance, natural gasoline.

Referring now to the flow sheet of the drawing, a light hydrocarbon material is fed, as by means of a pump 10, into a tube maintained at an elevated temperature within a cracking furnace 12. The tube may be empty or may be filled with suitable refractory packing material. Steam may be added to control cracking conditions. In this tube the hydrocarbon material is vaporized and cracked thermally to form a gaseous fraction and a vapor fraction made up predominantly of aromatic products which are separated from the gaseous products of the cracking step, for instance, in the manner illustrated in the flow sheet and described as follows:

The total products of the cracking step may be passed into the bottom portion of a first scrubber-condenser 14 made up of a vertical tube traversed longitudinally by a coil through which a cooling medium is circulated. The

first scrubber-condenser is otherwise empty. Intermediate aromatic material in liquid form separated in a second scrubber-condenser 16 and cooled in a cooler 18 is sprayed into the top of the first scrubber-condenser 14, as by means of a pump 20. In this first scrubber-condenser 14, an aromatic fraction (made up of heavy and intermediate aromatics such as tars, naphthalene and its derivatives, higher alkyl benzenes and the like) is separated in liquid form from the other products of the cracking step. This heavy aromatic fraction may be passed through a cooler 22 and thereafter recovered.

After separation of the heavy aromatic fraction (as described), the remaining products of the cracking step (which remain in gaseous or vapor form) are passed into the bottom portion of the second scrubber-condenser 16 filled with suitable packing material. A light aromatic fraction separated in liquid form in a condenser 24 is sprayed into the top of the second scrubber-condenser 16, as by means of a pump 26. An intermediate aromatic fraction is separated in liquid form in the second condenser-scrubber 16 which, as disclosed, is sprayed into the first scrubber-condenser 14. The cracking products left after the separation of the intermediate aromatic fraction pass into the condenser 24 and are there separated into a gas fraction and a liquid light aromatic fraction including benzene, toluene, xylenes and the like, which is recovered separately.

The separated gaseous fraction may be passed through a preheating furnace 28 and a vessel 30 filled with a hydrogenation catalyst.

After cooling in a spray tower 32, the product gas is recovered.

In the event the gaseous cracking products contain objectionable concentrations of sulfur compounds, the latter are preferably removed ahead of the catalyst chamber 30, as by passing the gases through an iron oxide purifier 34. But ordinarily the starting materials can be secured in a form sufficiently free from sulfur compounds to be used as obtained.

Thus broadly speaking, our method can be sub-divided into three steps, viz., initial thermal cracking (without catalyst), removal of non-gaseous cracking products, and passing the gaseous cracking products over a hydrogenation catalyst. The gaseous cracking products contain both hydrogen and unsaturated hydrocarbons. In the catalyst chamber, the gaseous cracking products are autohydrogenated with formation of a product gas having reduced contents of hydrogen and unsaturated hydrocarbons and an increased paraffin content.

Merely subjecting a starting material such as those indicated to thermal cracking followed by removal of non-gaseous cracking products and autohydrogenation of gaseous cracking products does not necessarily yield a gas absolutely interchangeable with natural gas, as explained hereinbelow.

For such absolute interchangeability with natural gas, the substitute gas may have, but need not necessarily have, a chemical composition essentially similar to natural gas. The burning characteristics of the substitute gas must be similar to natural gas. To a limited extent, the specific gravity and the heating value may differ from those of natural gas, as long as the value obtained by dividing the heating value by the square root of the specific gravity equals the value obtained in similar fashion from the corresponding characteristics of natural gas. For a more complete discussion of the interchangeability of fuel gases with natural gas, reference is made to our copending application entitled "Method of Preparing Fuel Gas Interchangeable with Natural Gas," filed February 11, 1952, now Patent No. 2,707,675.

Natural gas may generally be characterized as free from hydrogen, from ethylene and from higher unsaturates; as

containing less than 15% of nitrogen and other incombustibles together with from 85% to 100% of paraffins having an average carbon number of from 1.0 to 1.3; as having a gross heating value ranging from 970 to 1200 B. t. u. per cubic foot and a specific gravity (air=1.000) ranging from 0.6 to 0.7; and as yielding a flame free from yellow tips or flash back.

According to the method of the present invention, the cracking is conducted under specific, critically important pressure, residence time and temperature conditions to yield continuously a gas which at least when catalytically autohydrogenated is absolutely interchangeable with natural gas.

In producing an oil gas having a high paraffins to olefins ratio (which makes the gas easily subject to autohydrogenation yielding a fuel gas absolutely interchangeable with natural gas), the pressure is maintained, whenever possible, at superatmospheric levels, say, at at least two atmospheres. Apart from the limitations specified in the next following paragraph, there is no upper limit for the pressure, although as the pressure is increased, the yield of liquid products is raised at the expense of the yield of gas. For this reason, we prefer to operate at 3 to 4 atmospheres pressure, whenever possible. The temperature is maintained at from 1300° to 1550° F. The residence time may range from 10 to 2 seconds except in the cases specified in the next succeeding paragraph.

To maintain the carbon deposition not above 2½ weight per cent of the material being cracked (whereby continuous cracking can be carried out for 24 hours or longer), the residence time and the pressure are limited as follows. In the case of a material of the volatility of natural gasoline, the maximum pressures and residence times are, respectively, at less than 1450° F.: 4 atmospheres and 10 seconds; and at 1450° to 1550° F.: 3 atmospheres and 5 seconds. In the case of material less volatile than natural gasoline and not less volatile than straight run naphtha, the maximum pressure and residence time at 1450° to 1550° F. are, respectively, 1 atmosphere and 3 to 4 seconds and at less than 1450° F., respectively, 2 or 3 atmospheres and 5 seconds.

For normal operating conditions within the indicated limits, the cracking step will yield a gas containing from 12 to 15% ethylene, from 1 to 5% higher unsaturated hydrocarbons, from 10 to 20% hydrogen, from 55 to 75% or more paraffins having an average carbon number ranging from 1.1 to 1.2 less than 2% nitrogen and other incombustibles and having a heating value of from 900 to 1250 B. t. u. per cubic foot as well as a specific gravity (air=1.000) ranging from 0.55 to 0.78. The liquid products are low viscosity oils of from 7° to 40° A. P. I. containing from 60 to 80% light aromatics and boiling below 300° C. The liquid products also include a heavy aromatic fraction. The amount of liquid products depends upon the starting material used and the pressure employed and may vary, for instance, from 4 to 40% of the total yield. Carbon deposition is negligible. Typical examples illustrating the nature of the gaseous and liquid products when cracking naphthas within the specified range of conditions are given hereinbelow.

The autohydrogenation must be carried out catalytically at a temperature below 1200° F. and preferably at from 400° to 800° F. Best results are obtained at 500° to 700° F. Super-atmospheric pressure is beneficial but not necessary. The space velocity is maintained below 1000 cubic feet per cubic foot of catalyst volume per hour and may range as low as 200 cubic feet or less. Any catalyst suitable for the hydrogenation of unsaturated hydrocarbons may be used; for instance, iron, nickel, cobalt, the oxides of these metals, platinum, palladium, vanadium and its oxide, the oxides of chromium and molybdenum.

The catalytic autohydrogenation, under the indicated conditions, of the gaseous products of the above described specific cracking step, yields a gas containing less than 5%

ethylene when the feed gas contains approximately equal percentages of hydrogen and ethylene. When there is a considerable excess of hydrogen (over the ethylene) in the feed gas, the ethylene concentration may be reduced to less than 1%. Conversely, in the instance of a higher concentration of ethylene than hydrogen in the feed gas, hydrogen concentration may be reduced to less than 1%. Normally, the combined hydrogen and ethylene concentration in the product gas will be below 15% while the concentration of paraffins will be above 80%, the paraffins having an average carbon number of from 1.1 to 1.3. The product gas will have a heating value ranging from 1050 to 1150 B. t. u. per cubic foot as well as a specific gravity (air=1.000) ranging from 0.6 to 0.7. This product gas has the same burning characteristics as natural gas and is therefore absolutely interchangeable therewith. In some instances, a small amount of air, nitrogen, combustion gas or the like diluent, incombustible or inert gas can be blended with the product gas to match a natural gas containing a considerable percentage of incombustible gas. If desired, an inert or incombustible diluent gas may be added ahead of the cracking step.

The following examples will illustrate the working of the method of this invention. In the three examples, naphthas were cracked at 3 atmospheres total pressure, a temperature of 1500° F. and residence times of 4.3 and 4.6 seconds.

The make gases were found to have the characteristics tabulated as follows:

	Residence Time	
	4.3 Sec.	4.6 Sec.
Gas Composition, Mol Percent:		
CO ₂	0.0	0.0
O ₂	0.0	0.0
CO.....	0.0	0.0
N ₂	1.8	0.2
H ₂	20.3	18.9
CH ₄	55.2	58.9
C ₂ H ₆	5.6	5.4
C ₃ H ₈	0.6	0.4
C ₄ H ₁₀	0.0	0.0
C ₅ H ₁₂	13.5	15.4
C ₆ H ₁₄	1.3	1.5
C ₇ H ₁₆	0.3	0.3
C ₈ H ₁₈	0.0	0.0
C ₉ H ₂₀	0.5	0.5
Diolefins and acetylene.....	0.9	0.5
Aromatics.....	1.023	1.080
Heating value, B. t. u./S. G. F.....	0.61	0.63
Specific gravity (air=1.000).....		

The above gases (identified hereinbelow as Gas A and Gas B) were autohydrogenated under different conditions. In both cases, we used a nickel oxide catalyst precipitated on kieselguhr containing 10% elemental nickel. The operating conditions and product gas compositions are tabulated as follows:

	Gas A	Gas B
Space velocity, S. O. F./C. F. catalyst/hour.....	300	250
Volume ratio, make gas/feed gas.....	0.851	0.915
Ethylene conversion, percent of ethylene.....	93	87
Carbon balance, percent.....	101	100
Hydrogen balance, percent.....	98	101
Catalyst Temperature, ° F.:		
Zone 1.....	595	670
Zone 2.....	565	705
Gas Composition, Mol Percent:		
CO ₂	0.1	0.2
O ₂	0.0	0.0
CO.....	0.0	0.0
N ₂	2.1	0.5
H ₂	5.4	11.4
CH ₄	65.7	64.9
C ₂ H ₆	22.0	16.6
C ₃ H ₈	1.4	1.0
C ₄ H ₁₀	0.1	0.2
C ₅ H ₁₂	1.1	2.2
C ₆ H ₁₄	0.7	1.2
C ₇ H ₁₆	0.0	0.5
C ₈ H ₁₈	0.1	0.1
C ₉ H ₂₀	0.0	0.1
Diolefins and Acetylene.....	1.1	1.1
Aromatics.....	1.175	1.143
Heating value, B. t. u./S. C. F.....	0.72	0.66
Specific Gravity (air=1.000).....		

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Both gases were found to be absolutely interchangeable with natural gas. Practically identical results were obtained by cracking and then catalytically autohydrogenating butane, propane, and straight run and natural gasoline.

The above disclosed process is characterized by a number of advantages. The investment in equipment for storage of starting material (when using gasoline and naphtha) is quite low. The product gas is absolutely interchangeable with natural gas. The light aromatic fraction obtained as a by-product is readily marketed for solvent and chemical manufacture and as a motor fuel. The heavy aromatic fraction obtained as another by-product can be burned to heat the cracking furnace and to generate steam.

Many details of construction may be varied within a wide range and it is therefore not our intention to limit the patent granted on this invention otherwise than necessitated by the scope of the appended claims.

This application is a continuation-in-part of application Serial No. 185,274, filed September 16, 1950, entitled "Method of Making a Calorific Gas Interchangeable with Natural Gas."

We claim:

1. A method for preparing a gas interchangeable with natural gas which comprises providing in vapor form a light paraffinic petroleum fraction having a final boiling point not in excess of 500° F., passing said vapor through a reactor maintained at a temperature of 1300 to 1550° F. and under a pressure of more than one atmosphere, the residence time in said reactor ranging from two to ten seconds, to thermally crack (without catalyst) said petroleum with the formation of a gas containing paraffins, olefins and hydrogen, separating the resulting product into a liquid fraction and a gaseous fraction and passing the gaseous fraction over a hydrogenation catalyst to effect autohydrogenation of said gas.

2. A continuous method for preparing a fuel gas interchangeable with natural gas characterized by minimum carbon deposition which comprises providing in vapor form an aliphatic hydrocarbon having a boiling point less than 500° F. and having the volatility of natural gasoline, passing said vapor through a reactor to thermally crack said vapor (without catalyst) while maintaining the temperature at from 1300 to 1550° F. and the residence time and pressure at values correlated with the temperature as tabulated:

Temperature	Time, Seconds	Pressure, Atmospheres
1,300 to 1,450° F.-----	2 to 10	2 to 4
1,450 to 1,550° F.-----	2 to 5	2 to 3

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to produce normally liquid products and a gas containing paraffins, olefins and hydrogen, separating the liquid fraction from the gas fraction and passing the gas fraction over a hydrogenation catalyst to effect autohydrogenation of said gas.

3. A continuous method of preparing a fuel gas interchangeable with natural gas characterized by a minimum carbon deposition which comprises providing in vapor form an aliphatic hydrocarbon having a final boiling point of less than 500° F. and a volatility less than that of natural gasoline, passing said vapor through a reactor to thermally crack said vapor (without catalyst) while maintaining the temperature at from 1300 to 1550° F. and the residence time and pressure at values correlated with the temperature as tabulated:

Temperature	Time, Seconds	Pressure, Atmospheres
1,300 to 1,450° F.-----	2 to 5	2 to 3
1,450 to 1,550° F.-----	2 to 4	

to produce normally liquid products and a gas containing paraffins, olefins and hydrogen, separating the liquid fraction from the gas fraction, and passing the gas fraction over a hydrogenation catalyst to effect autohydrogenation of said gas.

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