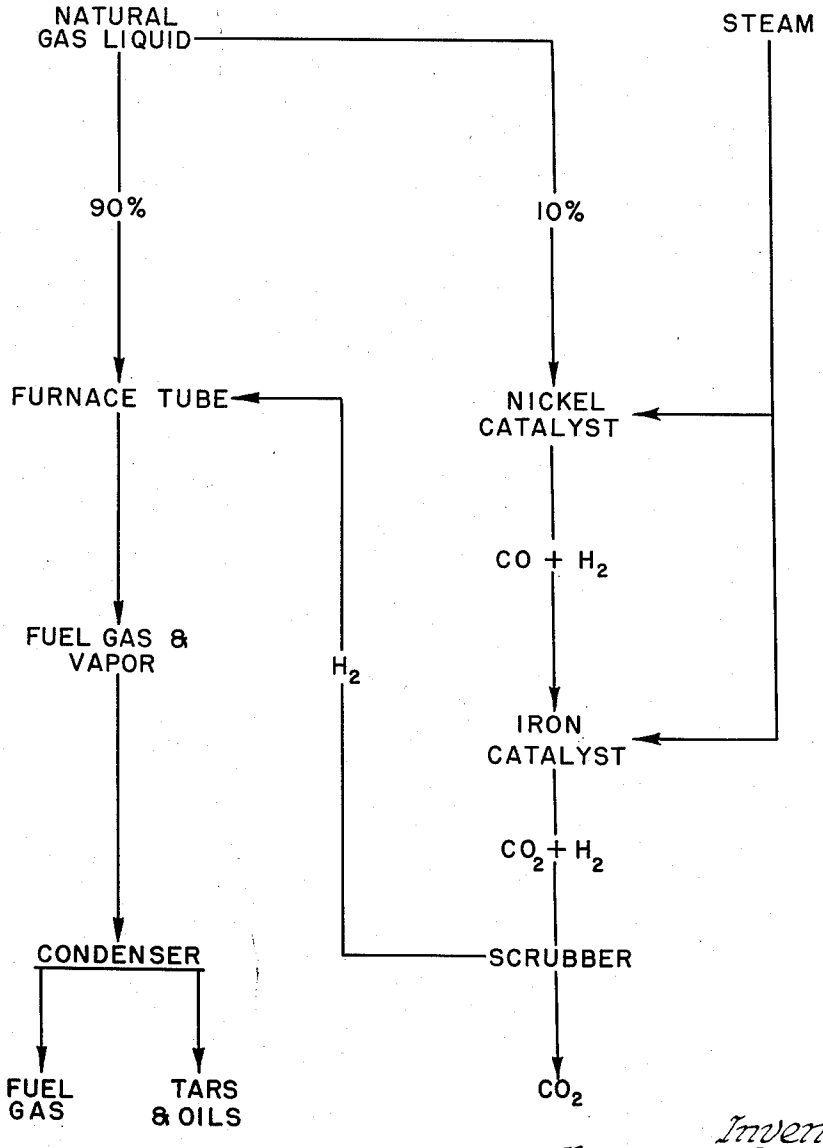
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METHOD OF MAKING A FUEL GAS

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METHOD OF MAKING A FUEL GAS

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5 Claims. (Cl. 48—197)

This invention relates to a thermal cracking method for converting natural gas liquids and petroleum oils into fuel gases.

An important object of the present invention is to provide a method of the nature indicated capable of converting all, or at least a much greater portion than has heretofore been possible, of the cracked natural gas liquids or petroleum oils into a fuel gas absolutely interchangeable with natural gas when burned in a burner adjusted for natural gas.

Other and further objects and features of the present invention will become apparent from the following description and appended claims as illustrated by the accompanying flowsheet showing, by way of an example, a process according to the present invention.

The starting materials employed in the method of this invention include the natural gas liquids such as propane, butane and natural gasoline. Distillate petroleum oils may also be used.

According to the present invention, the starting material (in vapor form) is thermally cracked (in absence of catalyst) under conditions disclosed as follows: The temperature ranges from 1400° to 1600° F., and preferably is kept at from 1450° to 1550° F. The contact time ranges from 2 to 10 seconds, and preferably is kept at from 4 to 5 seconds. The pressure ranges from 2.5 to 7 or 8 or more atmospheres absolute, and preferably is maintained at from 3 to 5 atmospheres absolute. The cracking is carried out in the presence of hydrogen in

amounts ranging from 20 to 60 or more s. c. f./gallon of starting material.

When natural gas liquids are cracked under the conditions described hereinabove, carbon is formed in such small amounts (less than 2% of the starting material) that the cracking may conveniently be carried out continuously (for periods such as 24 hours) in a suitable furnace tube. Further, the yield of fuel gas in increased more than 20% over that obtained in conventional cracking methods, and the fuel gas is completely or absolutely interchangeable with natural gas in gas burners adjusted for natural gas. For instance, in the case of propane, 97% of the starting material is gasified to form a fuel gas of 1031 B. t. u./s. c. f. diluent free heating value and a specific gravity of 0.55 (air=1.000). In the case of 12 lb. R. V. P. natural gasoline, 77% of the starting material is gasified to form a fuel gas of 971 B. t. u./s. c. f. diluent free heating value and a specific gravity of 0.53 (air=1.000). Both of these two fuel gases are absolutely interchangeable with natural gas. The character of the liquid by-products (tars and light oils) is essentially the same as that of the liquid by-products of conventional thermal cracking of the same starting materials, although the amounts of such liquid by-products formed are greatly reduced, as compared with conventional processes.

The procedural steps of carrying out the methods of the present invention need not differ from conventional cracking methods, apart from the steps required to maintain the above disclosed conditions. Thus, the starting material and the hydrogen are passed through a heated stainless steel tube. The resulting oil gas is passed through conventional cooling and condensing equipment to remove and recover any tar and light oils formed. Any remaining tar fog may next be removed with an electrostatic precipitator.

By way of illustrative example, the conditions and results of a number of cracking runs are tabulated hereinbelow. These runs were carried out using no hydrogen, as well as with various amounts of hydrogen, to afford a comparison. Runs Nos. 225, 384, 385, 387 and 388 were carried out with 12 lb. Reid vapor pressure natural gasoline. Runs Nos. 243 and 389 were carried out with propane.

TABLE I

Operating and burner test data for pressure hydrogasification of natural gas liquids

Run No.	225	384	385	387	388	243	389
Operating Conditions:							
Carrier Gas H_2, S. C. F./Gal. Hydrocarbon	0	27.17	20.49	47.45	57.94	0	40.83
Total Pressure, Atm.	3.11	3.05	5.12	2.96	5.10	3.05	5.01
Gauge Pressure, P. s. i. g.	31.4	30.4	60.9	29.1	60.5	30.3	59.2
Cracking Temp., °F.	1,500	1,420	1,470	1,480	1,480	1,500	1,470
Residence Time, Secs.	4.91	4.72	4.92	4.95	5.01	4.23	4.42
Operating results:							
B. t. u. Recovery, M B. t. u./Gal.	74.70	86.48	82.70	89.68	87.32	76.18	87.47
Oil Gas Yield,[1] S. C. F./Gal.	70.2	71.22	67.69	75.36	81.86	73.82	69.77
H_2 Absorbed, S. C. F./Gal.	−13.83	6.39	5.76	18.83	30.80	−13.36	13.13
Tar yield, Wt. percent	[2] 39.6	22.6	27.6	19.8	20.3	[2] 22.2	0
Light Oil Yield, Wt. percent		1,549	0.420	1,691	0.417		0.599
Carbon Yield, Wt. percent	2.47	1.0	1.1	1.2	1.2	0.55	1.9
Material Balance, percent	99.7	98.7	97.0	99.2	98.2	102.9	99.1
Gas Properties:							
Gas Composition, Inert-Free, Vol. percent—							
H_2	20.1	22.6	17.9	27.5	24.9	18.1	28.4
CH_4	57.4	53.2	59.3	50.6	55.6	58.5	43.5
C_2H_6	5.2	6.6	8.1	7.8	8.7	5.1	12.0
C_3H_8	0.1	0.2	0.1	0.1		0.3	1.4
Butanes	0.1						0.1
Pentanes	0.2						
C_2H_4	14.6	14.7	12.7	12.7	9.5	16.0	11.8
C_3H_6	1.2	0.7	0.9	0.4	0.3	0.9	1.6
Butenes	0.1	0.2	0.2	0.1	0.2	0.1	0.2
Pentenes							

TABLE I.—Continued

Run No.	225	384	385	387	388	243	389
Acetylene		0.2		0.1	0.1		0.1
Butadienes	0.2	0.2	0.2	0.2	0.1	0.2	0.2
Pentadienes	0.1	0.1	0.1			0.1	0.1
Benzene	0.7	1.2	0.5	0.5	0.6	0.7	0.5
Toluene		0.1					0.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Inert-Free Heating Value, B. t. u./ S. C. F.	1,068	1,034	1,083	1,008	971	1,033	1,031
Spec. Grav., Inert-Free, Air=1.00	0.610	0.588	0.604	0.551	0.526	0.601	0.550
Light Oil Properties:							
Specific Gravity, 60° F./60° F.		0.857	0.840	0.864	0.850		
Index of Refraction, N_D 25° C.		1.4840	1.4751	1.4917	1.4841		
Substitutability Data:							
Adjustment Natural Gas	High Inert	High Methane	High Methane		High Methane	High Inert	High Methane
Test Gas Heating Value, B. t. u./ S. C. F.	1,051	1,030	1,058		986	1,032	991
Test Gas Spec. Grav., Air=1.00	0.617	0.590	0.607		0.552	0.602	0.574
Relative Input, percent	107.5	101.8	103.1		100.8	106.9	99.3
Substitutability, percent—							
−2	Less than 100	[3] 85	78		78	100	[3] 95
0	Less than 100	100	100		100	100	100
+2	100	100	100		100	100	100

[1] Net yield of gaseous hydrocarbons and hydrogen (if any).
[2] Includes light oil.
[3] Estimated from Rochester Test Burner Yellow Tip Number.

TABLE II

Liquid product analyses for pressure hydro-gasification of natural gas liquids

Run No.	225	384	385	387	388	243
Pressure, Atm.	3.11	3.05	5.12	2.96	5.10	3.05
Cracking, Temp., °F.	1,500	1,470	1,470	1,480	1,480	1,500
Residence Time, Secs.	4.91	4.72	4.92	4.95	5.01	4.23
Specific Gravity:						
60° F./60° F.	0.9916	1.011	1.016	1.002	0.988	1.0158
°API	11.2	8.5	7.8	9.7	10.2	7.8
Distillation:						
Wt. Percent Distilled, °C.—						
I.B.P.	69.0		67.0		65.0	59.0
0–70	0.2	0.0	0.2	0.5	0.5	0.1
70–100	11.1	18.2	31.2	23.4	33.0	11.5
100–120	16.0	7.5	1.7	10.4	6.2	19.3
120–140	7.0	1.8	2.6	0.5	1.1	6.0
140–160	4.4	3.5	3.2	0.7	0.0	1.3
160–180	2.3	3.3	1.4	2.6	0.6	2.0
180–200	2.4	3.1	1.0	3.5	2.1	4.9
200–220	1.6	4.8	7.0	4.6	4.7	7.4
220–240	8.2	8.5	8.9	10.5	10.3	6.0
240–260	4.4	6.7	5.7	5.4	5.2	2.8
260–280	1.7	3.6	0.7	2.9	1.8	1.5
280–300	2.7	2.8	2.5	2.2	1.9	3.8
300–355	6.3	7.9	6.4	7.5	8.9	8.7
Pitch	31.9	26.8	26.8	24.7	21.6	23.2
Percent Distillate to 200° C.	43.4	37.4	41.3	41.6	48.2	45.1
Percent Distillate to 300° C.	62.0	63.8	66.1	67.2	67.4	66.6
Percent Distillate 300–355° C.	6.3	7.9	6.4	7.5	8.9	8.7
Percent Pitch	31.9	26.8	26.8	24.7	21.6	23.2
Percent Recovery	100.2	98.5	99.3	99.4	97.9	98.5
Composition of 0–200° C—						
Distillate, Percent by wt.:						
Paraffins	25.0					1.0
Olefins	12.6					16.8
Aromatics	62.4					82.2
Refractive Index, N_D^{25}—						
Cut Fractions, °C.:						
0–70			1.4900		1.5033	
70–100	1.4781	1.5002	1.4998	1.4996	1.5024	1.4960
100–120	1.4832	1.5032	1.5091	1.5073	1.4905	1.5021
120–140	1.4909	1.5104	1.5174	1.4890	1.4906	1.5193
140–160	1.5053	1.5196	1.5302	1.4899	No Sample	1.5450
160–180	1.5249		1.5450	1.4907	1.4905	1.5667
180–200	1.5462			1.4908	Solid	Solid

The method of this invention, when applied to natural gas liquids as a continuous furnace tube operation, may include a hydrogen generating step in which a part of the feed stream is utilized as a source of hydrogen. For this purpose, a part of the hydrocarbon feed stream is passed over a nickel catalyst with an amount of steam and at a temperature sufficient to bring nearly to completion the reaction:

$$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2$$

The product gas is then cooled to 700° to 1000° F. by water injection and the resultant steam-gas mixture (with such added steam as may be required to force the next following reaction to go nearly to completion) is passed over an iron catalyst for the water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Next, to raise the hydrogen concentration, the carbon dioxide-hydrogen gas mixture is scrubbed to remove the carbon dioxide, by any suitable conventional method.

Reference is made to the accompanying flowsheet for the combined cracking—hydrogen generating steps which may be carried out continuously as one form of the present invention. This flowsheet is believed self-explanatory. Each of the above indicated reactions being known per se, a person skilled in the art will know how to carry

out the combined process in the light of the disclosure given herein.

In general, about 5 to 15% of the feed stream may be converted into hydrogen, as by the method disclosed above. About 10% will usually be satisfactory. The amounts of hydrogen thus obtainable are exemplified as follows: One gallon of propane is capable of yielding 40 s. c. f. hydrogen, and one gallon of 12 lb. R. V. P. natural gasoline is capable of yielding 52 s. c. f. hydrogen.

Thus, according to the present invention, natural gas liquids and petroleum oils may be converted into fuel gases with a fuel gas yield 20% higher than has heretofore been possible and with 20% less of liquid by-products, as compared with conventional oil gas processes. Further, the fuel gas obtained is absolutely interchangeable with natural gas. Reference is made to our copending application Serial Number 270,955 (filed February 11, 1952 and entitled "Fuel Gas Interchangeable with Natural Gas and Method of Preparing the Same"), now Patent No. 2,707,675, for a discussion of the interchangeability of fuel gases with each other.

The above noted features of the method of the present invention are of notable value. The demand for a fuel gas absolutely interchangeable with natural gas arises from the occurrence of a few days of peak gas requirement in the areas supplied with natural gas for domestic and/or industrial heating. On such days, the gas requirement rises above the delivery capacity of the pipe lines and must be met from other sources. The method of the present invention can supply large volumes of fuel gas interchangeable with natural gas without at the same time producing large amounts of liquid by-products, and the apparatus required to practice our methods can be relatively simple and inexpensive, which is important in view of the few days to which operation is confined.

Reference is made to our copending applications Serial Numbers 270,955 (filed February 11, 1952, and entitled Method of Making a Fuel Gas Interchangeable with Natural Gas, now Patent No. 2,707,675), 275,952 (filed March 11, 1952, and entitled Method of Making Oil Gas Interchangeable with Natural Gas), 287,122 (filed May 10, 1952 and entitled Method of Making Oil Gas Interchangeable with Natural Gas, now Patent No. 2,721,123) and 311,256 (filed September 24, 1952 and entitled Thermal Method of Making Oil Gas, now Patent No. 2,721,-122). These applications disclose cracking methods for making oil gas in which the fuel gas yield can be increased by adding hydrogen in amounts of from 20 to 60 s. c. f./gallon of liquid feed when the feed is cracked.

Many details may be varied without departing from the principles of this invention. Therefore, we do not intend to limit the scope of this patent otherwise than necessitated by the scope of the appended claims.

We claim:

1. A thermal cracking method (in absence of catalyst) of converting a hydrocarbon taken from the group consisting of propane, butane and natural gasoline into a fuel gas interchangeable with natural gas which comprises passing said hydrocarbon in vapor form through a heated reactor at a temperature from 1400° to 1600° F., a contact time of from 2 to 10 seconds and a pressure of at least 2.5 atmospheres absolute while simultaneously passing hydrogen from an external source through said reactor at a rate of from 20 to 60 s. c. f. per gallon of said hydrocarbon, and thereafter separating the fuel gas then formed from condensable by-products.

2. A method according to claim 1 comprising, as additional steps, converting a part of said hydrocarbon into hydrogen by initially reacting said part with steam to form a mixture of carbon monoxide and hydrogen, thereafter reacting said carbon monoxide with additional steam to form carbon dioxide and additional hydrogen, and thereafter separating said hydrogen from said carbon dioxide, the separated hydrogen being fed into said heated reactor as specified in claim 1.

3. A thermal cracking method (in absence of catalyst) of converting a hydrocarbon taken from the group consisting of propane, butane and natural gasoline into a fuel gas interchangeable with natural gas which comprises passing said hydrocarbon in vapor form through a heated reactor at a temperature of from 1450° to 1550° F., a contact time of from 2 to 10 seconds and a pressure of at least 2.5–8 atmospheres absolute while simultaneously passing hydrogen from an extended source through said reactor at a rate of from 20 to 60 s. c. f. per gallon of said hydrocarbon, and thereafter separating the fuel gas then formed from condensable by-products.

4. A method according to claim 3 comprising, as additional steps, converting a part of said hydrocarbon into hydrogen by initially reacting said part with steam to form a mixture of carbon monoxide and hydrogen, thereafter reacting said carbon monoxide with additional steam to form carbon dioxide and additional hydrogen, and thereafter separating said hydrogen from said carbon dioxide, the separated hydrogen being fed into said heated reactor as specified in claim 3.

5. A thermal cracking method (in absence of catalyst) of converting a hydrocarbon taken from the class consisting of propane, butane and natural gasoline which comprises passing said hydrocarbon through a heated reactor at a temperature of 1400–1600° F., a contact time of 2 to 10 seconds and a pressure of at least 2½ atmospheres absolute, while simultaneously passing hydrogen from an external source through said reactor at a rate of at least 20 s. c. f. per gallon of hydrocarbon, and thereafter separating the fuel gas then formed from condensable by-products.

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