



Industry
Canada

Industrie
Canada

Canada

strategis.gc.ca

Strategis Index:



Canadian Patents Database

12/19/2001 - 09:03:54

(11) CA 421168

(12) Patent:

(54) HYDROCARBON SYNTHESIS

(54) SYNTHESE D'HYDROCARBURES

(72) Inventor (Country):	LEBBEUS COURTRIGHT KEMP (Not Available)
(73) Assignee (Country):	Texaco Development Corporation (United States)
(71) Applicant (Country):	
(74) Agent:	
(45) Filing Date:	June 27, 1944
(22) Priority:	
(43) Publication:	
(52) IPC Class.:	260/678.6
(51) Int. Class.:	N/A

(36) International Publication No. **No**

(30) Foreign Application No. **None**

(71) Inventor Name **N/A**

(72) Inventor Address **Unknown**

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

View or Download Images :

- Cover Page Image
- Abstract Image
- Claims Image
- Disclosures Image
- Drawings Image

421168

X
421168

This invention relates to the synthesis of hydrocarbons, and has to do particularly with the production of higher boiling hydrocarbons, including gasoline, from a light hydrocarbon gas, such as methane.

In accordance with the invention, methane or a gas rich in methane, such as natural gas, is decomposed to carbon and hydrogen, the carbon oxidized to carbon monoxide, and the carbon monoxide and hydrogen then converted into hydrocarbons.

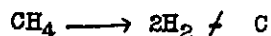
The invention will be fully disclosed by the following description thereof taken in connection with the accompanying drawing, which shows a diagrammatical sketch of one form of apparatus for carrying out the process of the invention.

Referring to the drawing, methane or natural gas, which usually consists of about 95% or higher of methane, is charged through the line 1 to a desulfurizer 2. The Desulfurizer is in the form of a vertical tower filled with a suitable contact material 3, such as quartz, or other inert material. The charge enters the lower portion of the tower and in passing upwardly through the contact material, is intimately contacted with a desulfurizing reagent such as sodium phenolate, triethanolamine or tripotassium phosphate, introduced into the upper portion of the tower through the line 5. The treatment is preferably conducted at temperatures of the order of 80° to 100°F. and pressures from about 100 to 5000 pounds per square inch. High pressures are beneficial in that the effectiveness of the desulfurizing solution is increased and the equipment sizes are less. The desulfurizing solution, containing the dissolved sulfur com-

h
pounds, is removed from the bottom of the desulfurizing tower through the line 6.

The purified gas is withdrawn from the upper portion of the desulfurizer through the line 7 and the pressure thereon reduced by the valve 8 to about 25 pounds per square inch or less. It is usually necessary to maintain only sufficient pressure to effect a flow of the gas through the subsequent steps of the process. If desired, instead of the valve 8, advantage may be taken at this point of the power available in the gas by effecting a reduction in pressure through an expansion engine of suitable design, not shown. After reduction in pressure, the gas is preheated preferably by heat exchange, not shown, with the hot products, referred to hereinafter, leaving the converters.

The preheated gas is introduced into either of two converters 10 and 12, through the lines 13 and 14 respectively, which are in communication with the line 7. The converters are large cylindrical vessels suitably lined with refractory material and packed with pieces of refractory material 14 capable of ready absorption and liberation of heat. Any well known materials which are employed in regenerative furnaces may be used for this purpose. Prior to the introduction of the natural gas into the converters, sufficient heat, as will be described hereinafter, has been added to the refractory packing to effect conversion of the gas. The conversion effected according to the following reaction



is dependent on the temperature, as indicated by the following data taken for convenience from the American Chemical

Society Monograph No. 60 by Parks and Huffman, "Some Free Energies of Organic Compounds."

<u>Temp. °C.</u>	<u>Temp. °F.</u>	<u>*% H₂ in Gas</u>
527	982	50.6
627	1162	73.7
727	1342	87.6
827	1522	94.2
927	1702	97.0
1127	2062	99.0

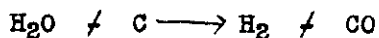
*Remainder of gas is unconverted methane.

It is possible by the use of suitable cracking catalysts, such as aluminum oxide, for example, to reduce substantially the temperatures indicated above.

During the conversion the refractory material in the converter will be coated with carbon. The hydrogen remaining after the methane conversion is swept out and the carbon then oxidized to carbon monoxide either by controlled combustion or water gas reaction. Oxygen or water for this purpose is introduced through the line 15 and branch lines 16 and 18, communicating with the converters 10 and 12 respectively. The exothermic heat from the conversion of carbon to carbon monoxide is taken up by the refractory material so that at the conclusion of this stage of the operation the bed may again be used for methane conversion. By providing two converters 10 and 12 and alternating them in methane conversion and carbon oxidation, a continuous process is obtained. It is possible that the heat required for the methane conversion and to make up for the radiation losses will be greater than that available for the oxidation

7
reaction. In this event, an outside combustion chamber burning either natural gas or waste gas from the synthesis step, referred to hereinafter, may be employed to add heat to the refractory materials following the carbon removal operation.

The gases generated in the converters are conducted from the upper portion thereof through the lines 19 and 20 and may be mixed in either of the lines 21 or 22, by suitable regulation of the by-pass lines 23 and 24, connecting with the line 19, and the by-pass lines 25 and 26, connecting with the line 20, with suitable regulation of the valves therein. It is desirable that the ratio of hydrogen to carbon monoxide in the mixture be about 2:1 or slightly lower. From the equation given above, it is apparent that if all of the carbon is converted to carbon monoxide by combustion, the ratio of hydrogen to carbon monoxide will be exactly 2:1. If the water gas reaction is used, the following equation is applicable:



The use of the water gas reaction would result in a ratio of hydrogen to carbon monoxide of 3:1. It is intended that, if necessary, some hydrogen may be diverted from the system by exhausting from the system a portion of the stream leaving the methane converter through the lines 19 or 20, as the case may be. The excess hydrogen exhausted from the system may be used in the revivification of the catalyst used in the synthesis step, described hereinafter.

The mixture of gases in the lines 21 or 22 may be adjusted automatically for the maintenance of the desired carbon monoxide ratio, for example, by means of a recording calorimeter acting through suitable control

mechanisms to maintain a mixture of constant heating value. The mixture is then passed through the line 28 to a heat exchanger or cooler 30, wherein the hot gases pass in indirect heat exchange with a cool material which is to be preheated. Such a material may conveniently be a charge to the converters, for example the material leaving the desulfurizer 2 through the line 7. The cooled mixture is then passed through the line 31 to a final desulfurizer 32. In the latter a desulfurizing solution may be employed which will not remove the carbon monoxide, for example sodium carbonate solution, which may be introduced into the top of the desulfurizer through the line 34 and withdrawn from the bottom thereof through line 35. In case it is unnecessary to further desulfurize the gas, the final desulfurizer may be by-passed, or eliminated. For this purpose there is shown a by-pass line 36.

The gas is discharged from the top of the final desulfurizer 32 through the line 38 or through the by-pass line 36, as the case may be, and conducted through the line 40 to a heater 42, wherein the gas is preheated, and thereafter transferred through the line 32 to a converter 44. In the heater the gases are raised to a sufficiently high temperature to maintain a temperature of about 350° to 375°F. in the converter.

The converter is shown as a tower type although it is to be understood that other types of converters may be used; for example one similar to converters 10 and 12. In the tower type of converter as shown, a number of catalyst beds 45 containing a suitable catalyst, preferably cobalt, iron and/or nickel, to which other materials and/or metallic

9
oxides may be added as promoters, are used. These catalysts are well known in the art for the conversion of hydrogen and carbon monoxide to hydrocarbons, and it is contemplated that any of the prior art catalysts may be used. Inasmuch as the reaction temperature is critical, the temperature of the catalyst bed must be very carefully controlled. This may be done by equipping each bed with a thermo-syphon cooling system, comprising a coil submerged in the catalyst, through which water circulates, connected with a boiler, wherein steam is generated at a constant pressure, as required to maintain the proper temperature in the catalyst bed.

In order to prolong the catalyst life, by removing the heavy materials formed in the reaction, a gas oil wash may be used. The highly saturated nature of the gas oil produced in the system renders it highly satisfactory for this purpose. By preheating the gas oil to the temperature maintained in the converter, loss of efficiency due to any cooling effect may be avoided. Such a gas oil wash may be introduced into the upper portion of the converter and withdrawn from the lower portion thereof, by means not shown. In case it is undesirable to contact the catalyst beds with the gas oil wash, it is contemplated that bubble trays spaced between each catalyst bed may be used. Heated gas oil may be introduced separately to each bubble tray or a system of downflow pipes may be used, whereby the same gas oil is used on a number of the trays. Means for using in such way an indirect gas oil wash is not shown in the drawing.

The tower type converter has certain advantages over the ordinary chamber type converter. For example, progressively higher or lower temperatures may be carried as

10
desired to obtain the highest conversion efficiency. The tower type, furthermore, is considerably cheaper for a given plant capacity.

The products are conducted from the top of the converter through the line 47 to partial condenser 48 in which the heavy waxy products are condensed. The products are passed from the partial condenser through the line 49 to a receiver or separator 50, wherein the condensate is collected. The uncondensed vapors are passed from the top of the receiver through the line 51 to a contact condenser 53 wherein the vapors are subjected to condensation by direct contact with water introduced through the line 54. In this condenser substantially all the products except predominantly gaseous materials are condensed. The uncondensed gases are conducted from the top of the contact condenser through the line 55, in which may be installed a compressor, not shown, and discharged into the lower portion of absorber 58 in which the desired fractions are extracted from the gas. The gas leaving the top of the tower through the line 60 may be recycled to the converter, used for fuel or discarded as waste.

The condensate from the contact condenser 53 is passed through the run-down line 61 to a separator 62, wherein the water is separated and withdrawn from the bottom thereof through the line 64. The hydrocarbons are passed overhead from the separator 62 through the line 65 and may be combined with the condensate which is withdrawn from the receiver 50 through the line 66. It is generally desirable to discharge the heavy waxy products from the receiver 50 through the line 67 for other uses, for example the manufac-

ture of high melting point wax or for use as a charging stock to a cracking unit. The condensate from the separator 62 and any materials mixed therewith from the receiver 50 are passed through the line 68 and line 70, wherein they are combined with the rich absorbent oil withdrawn from the bottom of the absorber through the line 72. The mixture is passed through the line 73 and pump 74 to a heater 75, wherein they are heated to a distillation temperature and then transferred through the line 76 to a fractionator 78.

In the fractionator the products are separated into gasoline, which is removed overhead through the line 80, a light gas oil, which is collected on the tray 81, and a heavy gas oil, which is withdrawn from the bottom of the fractionator through the line 82. Light gas oil is withdrawn from the tray 81 through a line 84 to a stripper 85 which is connected by a vapor line 86 to the fractionator. The light gas oil is withdrawn from the stripper through the line 88 and forced by the pump 89 through the branch line 90 into the upper portion of the absorber 58, or through the line 91 to partial condenser 48 and thence through the line 92 to the upper portion of the converter 44. Any proportion of the light gas oil which is not needed in the absorber 58 and the converter 44, may be passed through the branch line 95 and mixed with the heavy gas oil in the line 82 for discharging from the system or other disposal, such as manufacture of Diesel fuel or as a charging stock to a cracking unit.

The gasoline removed from the top of the fractionator 78 through the line 80 may require further stabilization which may be done in a suitable stabilizer. The

12

gases from the stabilization operation may be subjected, if desired, to either catalytic or thermal polymerization, to convert the unsaturated constituents into normally liquid hydrocarbons, including gasoline.

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.

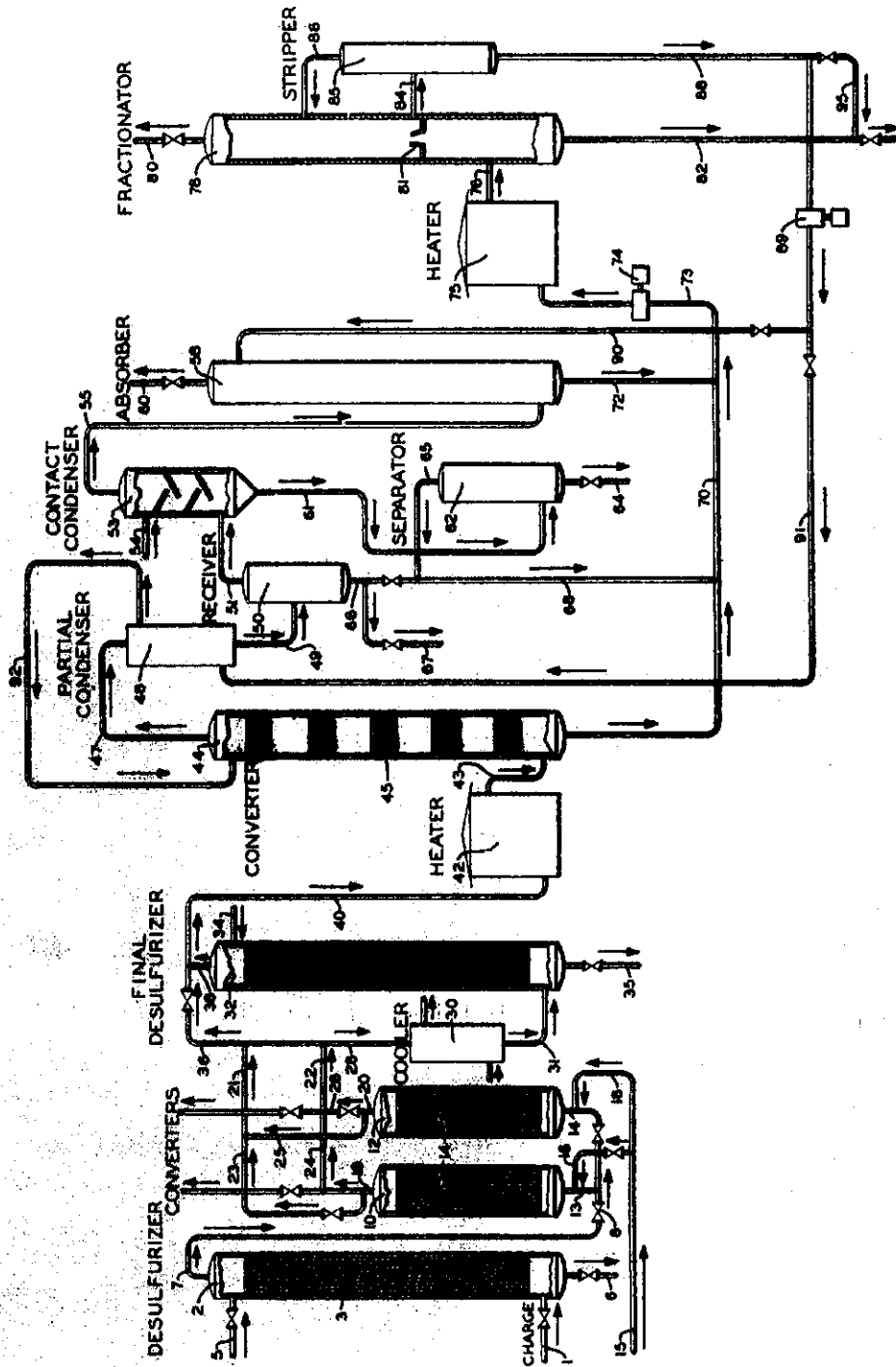
17
I CLAIM:

1. A process for the synthesis of higher boiling hydrocarbons from methane that comprises contacting a stream of methane with hot refractory material in a contact chamber at temperatures sufficiently high to decompose the methane into hydrogen and carbon, continuing the operation until a substantial amount of carbon is deposited on the contact material, then diverting said methane stream to another contact chamber and repeating the operation, simultaneously burning the carbon on the contact mass in said first mentioned contact chamber to carbon monoxide whereby exothermic heat of reaction is imparted to the contact material, alternating said chambers in methane decomposition and carbon burning, combining the hydrogen produced in the methane decomposition operation with the carbon monoxide formed during the carbon burning operation to form a mixture containing hydrogen and carbon monoxide in the ratio of about 2:1 and continuously passing said mixture to a chamber wherein conversion to normally liquid hydrocarbons in the presence of a catalyst is effected.

2. A process for the synthesis of normally liquid hydrocarbons from methane that comprises contacting a stream of methane with hot refractory material in a contact chamber at temperatures sufficiently high to decompose the methane into hydrogen and carbon, withdrawing the hydrogen from the contact chamber while depositing the carbon on the contact material, then diverting the methane stream to another contact chamber and carrying on the decomposition into hydrogen and carbon, simultaneously burning the carbon on the contact mass in said first mentioned contact chamber to form carbon monoxide and withdrawing the carbon monoxide therefrom, alternating said contact chambers in methane decomposition

14
and carbon burning, combining withdrawn hydrogen and carbon monoxide to form a mixture containing hydrogen and carbon monoxide in the ratio of about 2:1 and continuously passing said mixture to a catalytic reaction chamber wherein the mixture is subjected to reaction in the presence of a catalyst to form normally liquid hydrocarbons.

A
3. A process for the production of a reactive mixture of hydrogen and carbon monoxide adapted for catalytic synthesis to form normally liquid hydrocarbons that comprises contacting a stream of methane with hot refractory material in a contact chamber at temperatures sufficiently high to decompose the methane into hydrogen and carbon, withdrawing the hydrogen from the contact chamber while depositing the carbon on the contact material, then diverting the methane stream to another contact chamber and carrying on the decomposition into hydrogen and carbon, simultaneously burning the carbon on the contact mass in said first mentioned contact chamber to form carbon monoxide and withdrawing the carbon monoxide therefrom, alternating said contact chambers in methane decomposition and carbon burning, and continuously combining withdrawn hydrogen and carbon monoxide to form a mixture containing hydrogen and carbon monoxide in the ratio of about 2:1.



Lebbeus C. Kemp
INVENTOR

Certified to be the drawing referred to
in the specification hereunto annexed.

Ottawa, Ontario, Canada, September 13th, 19 40.

BY

Smart & Biggar