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Canadian Patents Database

(12) Patent:		001 - 09:08:34 CA 638139
(54) PRODUCTION OF SYNTE	HESIS GAS	
(54)		
(72) (Country):	NICK P. PEET (Not Available)	produces and the second
(73) (Country):	ESSO RESEARCH AND ENGINEERING COMPANY (United Star	tes)
(71) (Country):		
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(45)	Mar. 13, 1962	
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1	The present invention is directed to the production
2	of synthesis gas. More particularly, the invention is
3⊦	concerned with the production of synthesis gas from methane.
14	In its more specific aspects, the invention is concerned
5	with a method of producing synthesis gas for use in the
6	production of methanol or hydrocarbons.
7	The present invention may be briefly described as
8	a method for producing synthesis gas from methane in which
9	a methane feed stream is divided into a first portion and
10	and a second portion. The first portion is contacted in
11	admixture with steam and carbon dioxide obtained in a later
12	step of the invention at an elevated temperature in a
13	conversion zone with a catalyst to produce synthesis gas.
14	The second portion of the methane feed stream is burned
15	in the conversion zone to provide the elevated temperature
16	and to form a combustion gas containing substantial amounts
17	of carbon dioxide. The combustion gas is cooled with water
18	to generate steam and reduce the temperature of the
19	combustion gas. Carbon dioxide is recovered from the
20	cooled combustion gas, and the steam and recovered carbon
21	dioxide are admixed with the first portion.
55	The synthesis gas comprising carbon monoxide
2 3	and hydrogen is recovered from the contacted mixture and
24	may then be used in the production of methanol or in the
25	production of hydrocarbons.
26	The temperature at which the first portion is
27	contacted with the catalyst to produce snythesis gas may
28	suitably range between about 1100° and 1850°F, with

satisfactory operations obtained at a temperature of about 1 1500 F. Pressures for the production of synthesis gas may 2 3 range from about 0 to about 300 pounds per square inch 4 gauge, with suitable operations conducted at a pressure of 5 about 150 pounds per square inch gauge. 6 The catalyst employed in the production of the 7 synthesis gas is suitably a nickel catalyst, such as reduced 8 nickel oxide, nickel-thoria-magnesia, nickel-alumina-9 magnesia, nickel-magnesia, nickel on carbon, or nickel on 10 alumina; other suitable catalysts may include cobalt 11 molybdate supported on alumina, a Group VIII metal on 12 metal oxide on a suitable support, nickel and iron on a 13 support or carrier, and the like. 14 The present invention is suitably conducted to 15 produce a synthesis gas containing approximately two parts 16 of hydrogen and one part of carbon monoxide, with about 50 to about 75 per cent of the combustion gas being cooled 17 18 with water to generate steam and reduce the temperature of the gas. 19 20 The present invention will be further illustrated 21 by reference to the drawing in which the single figure is in the form of a flow sheet of a preferred mode. 22 23 Referring now to the drawing, numeral 11 designates 24 a charge line by way of which a methane-containing feed 25 stream such as natural gas is introduced into the system from a source, not shown. The methane feed stream is 26 divided into two portions, with one portion being introduced 27 28 into a conversion zone 12 arranged in a furnace 13, while

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1	the second portion is fed by way of line 14 into line 15
2	for admixture with air for charging to furnace 13 to be
3	burned in burners 16 to raise the temperature of the
4	methane introduced into reaction zone 12, which is in the
5	form of a coil containing a suitable synthesis gas catalyst
6	of the type illustrated. By virtue of the burning or
7	combustion operation in zone 13, a synthesis gas having
8	a composition as shown in Table I may be formed.
9	TABLE I
10	Synthesis Gas
11 12 13 14 15	25.3% CO 5.7% CO ₂ 67.5% H ₂ 1.3% H ₂ O 0.1% CH ₄ 0.1% N ₂
17	This synthesis gas is recovered from zone 12 by line 17
18	and cooled in cooler 18 for introduction as may be desired
19	into a methanol synthesis or a hydrocarbon synthesis
50	operation by way of line 19.
21	The flue gas issues from zone 13 by way of
22	line 20 with from about 50 to 75 per cent of the flue
23	gas being recovered by way of line 21 while the remainder
24	is discharged by way of line 22 into a suitable stack
25	for venting to the atmosphere, the stack not being shown.
26	The flue gas then passes through a suitable
27	boiler 23 into which water is admitted by way of line 24

for generation of steam which is withdrawn by line 25

1	and which is recycled to line if for charging with the
2	first portion of the methane to reaction zone 12.
3	The cooled flue gas is then introduced by line
4	26 into a recovery unit 27 which suitably may be an
5	absorber for carbon dioxide such as a tower with internal
6	baffling equipment or other suitable gas-liquid contacting
7	means such as bell cap trays and the like. Introduced
8	into the top of absorption zone 27 is a suitable absorbent,
9	such as monoethanolamine, by way of line 28, but which
10	may be any other suitable absorbents for carbon dioxide.
11	The unabsorbed flue gas is discharged from
12	absorption zone 27 by line 29, while the enriched solution
13	containing absorbed carbon dioxide is withdrawn from zone
14	27 by line 30 into a stripping zone 31, where heat is
15	applied to drive the absorbed carbon dioxide from the
16	monoethanolamine. The carbon dioxide is recovered by
17	line 32 and discharged into line 11 to form the feed
18	admixture to the reaction zone 12.
19	By virtue of an operation such as described
20	in the drawing, the synthesis gas is generated solely
21	from methane and air in a suitable combined furnace-
22	conversion zone.
23	The operation described in the drawing produces
24	a synthesis gas containing approximately 2 parts of
25	hydrogen to 1 part of carbon monoxide. Approximately
26	1/2 to $3/4$ of the flue gas from the combustion operation
27	is cooled, compressed and processed to extract carbon
28	dioxide which is then used to supply the carbon dioxide

requirements for the synthesis gas operation. 1 EXAMPLE I 2 A stream of natural gas amounting to 12.2 3 4 million cubic feet/day is divided into a first portion 5 of 7.5 million cubic feet/day which is charged to a conversion reactor and a second portion of 4.7 million 6 cubic feet/day which is burned in a furnace providing 7 heat for conversion of the aforementioned first portion. 8 The heat released from combustion of the 4.7 million 9 cubic feet/day portion is in balance with that required 10 for conversion of the 7.5 million cubic feet/day in 11 the reactor. 12 Natural gas suitable for this operation may 13 14 have a typical analysis as follows: mol per cent 15 16 17 18 19 20 0.3 parts per million by weight 21 A portion of the flue gas from the reactor 22 furnace is passed through a steam generating system from 23 which is produced 800,000 lbs./day of steam. The cooled 24 flue gas from the steam generating plant is passed to 25 a CO2 recovery system from which 2.5 million cubic feet/day 26 of CO2 is recovered from the flue gas. 27 The total feed gas mixture to the reactor 28 comprises 7.5 million cubic feet/day of natural gas, 29 2.5 million cubic feet/day of CO2, and 639,000 lbs/day 30

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of steam (the steam comprising approximately 80% of that
1
      generated by the flue gases cooled for recovery of COo).
2
      This admixture is passed at 1000 V/V/Hr. (based on outlet
3
      Ho + CO) through furnace tubes packed with a nickel
4
      catalyst such as the Girdler Corp. type G-29 catalyst
5
      which contains 27% nickel on a suitable support. The
6
      effluent from the reactor at 20 psig and 1550°F., amounting
7
      to 38.8 million cubic feet/day, comprises a mixture having
8
      the following approximate composition:
9
10
                          Hydrogen
                          CŌ
11
12
13
      The above mixture is passed through a scrubber-cooler
14
      whereupon it is cooled to a temperature of approximately
15
      100°F. A gaseous mixture is recovered from the scrubber-
16
      cooler having the following composition:
17
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18	Ha	67.5%
19	rg cg	25.3%
20		5.7%
21	00 ₂ ყვი	67.5% 25.3% 5.7% 1.3%

The above mixture, which is at 15 psig, is then compressed and may be used for conversion to methanol.

While the invention has been described and illustrated by reference to use of methane as the feed, it will be preferred to employ natural gas as the feed. Natural gas as produced usually comprises a major amount of methane and minor amounts of ethane, propane and butane. Accordingly, it is contemplated that mixtures of these several hydrocarbons having 1 to 4 carbon atoms in the molecule may be used or the hydrocarbons in a substantially purified form may comprise the feed stock.

- 2 -

1	The present invention is directed to the production
2	of synthesis gas. More particularly, the invention is
3-	concerned with the production of synthesis gas from methane.
1‡	In its more specific aspects, the invention is concerned
5	with a method of producing synthesis gas for use in the
6	production of methanol or hydrocarbons.
7	The present invention may be briefly described as
8	a method for producing synthesis gas from methane in which
9	a methane feed stream is divided into a first portion and
10	and a second portion. The first portion is contacted in
11	admixture with steam and carbon dioxide obtained in a later
12	step of the invention at an elevated temperature in a
13	conversion zone with a catalyst to produce synthesis gas.
14	The second portion of the methane feed stream is burned
15	in the conversion zone to provide the elevated temperature
16	and to form a combustion gas containing substantial amounts
17	of carbon dioxide. The combustion gas is cooled with water
18	to generate steam and reduce the temperature of the
19	combustion gas. Carbon dioxide is recovered from the
20	cooled combustion gas, and the steam and recovered carbon
21	dioxide are admixed with the first portion.
52	The synthesis gas comprising carbon monoxide
23	and hydrogen is recovered from the contacted mixture and
24	may then be used in the production of methanol or in the
25	production of hydrocarbons.
26	The temperature at which the first portion is
27	contacted with the catalyst to produce snythesis gas may
28	suitably range between about 1100° and 1850°F. with

satisfactory operations obtained at a temperature of about 1 1500 F. Pressures for the production of synthesis gas may 2 range from about 0 to about 300 pounds per square inch 3 gauge, with suitable operations conducted at a pressure of 4 about 150 pounds per square inch gauge. 5 The catalyst employed in the production of the 6 synthesis gas is suitably a nickel catalyst, such as reduced 7 nickel oxide, nickel-thoria-magnesia, nickel-alumina-8 magnesia, nickel-magnesia, nickel on carbon, or nickel on 9 alumina; other suitable catalysts may include cobalt 10 molybdate supported on alumina, a Group VIII metal on 11 metal oxide on a suitable support, nickel and iron on a 12 support or carrier, and the like. 13 The present invention is suitably conducted to 14 produce a synthesis gas containing approximately two parts 15 of hydrogen and one part of carbon monoxide, with about 50 16 to about 75 per cent of the combustion gas being cooled 17 with water to generate steam and reduce the temperature of 18 19 the gas. The present invention will be further illustrated 20 by reference to the drawing in which the single figure is 21 in the form of a flow sheet of a preferred mode. 22 Referring now to the drawing, numeral 11 designates 23 a charge line by way of which a methane-containing feed 24 stream such as natural gas is introduced into the system 25 from a source, not shown. The methane feed stream is 26 divided into two portions, with one portion being introduced 27 into a conversion zone 12 arranged in a furnace 13, while 28

- 4 **-**

ı	the second portion is fed by way of line 14 into line 15
2	for admixture with air for charging to furnace 13 to be
3	burned in burners 16 to raise the temperature of the
4	methane introduced into reaction zone 12, which is in the
5	form of a coil containing a suitable synthesis gas catalyst
6	of the type illustrated. By virtue of the burning or
7	combustion operation in zone 13, a synthesis gas having
8	a composition as shown in Table I may be formed.
9	TABLE I
10	Synthesis Gas
11 12 13 14 15 16	25.3% CO 5.7% CO ₂ 67.5% H ₂ 1.3% H ₂ O 0.1% CH ₄ 0.1% N ₂
17	This synthesis gas is recovered from zone 12 by line 17
18	and cooled in cooler 18 for introduction as may be desired
19	into a methanol synthesis or a hydrocarbon synthesis
20	operation by way of line 19.
21	The flue gas issues from zone 13 by way of
22	line 20 with from about 50 to 75 per cent of the flue
23	gas being recovered by way of line 21 while the remainder
24	is discharged by way of line 22 into a suitable stack
25	for venting to the atmosphere, the stack not being shown.
26	The flue gas then passes through a suitable
27	boiler 23 into which water is admitted by way of line 24
28	for generation of steam which is withdrawn by line 25

- 5 -

1	and which is recycled to line II for charging with the
2	first portion of the methane to reaction zone 12.
3	The cooled flue gas is then introduced by line
4	26 into a recovery unit 27 which suitably may be an
5	absorber for carbon dioxide such as a tower with internal
6	baffling equipment or other suitable gas-liquid contacting
7	means such as bell cap trays and the like. Introduced
8	into the top of absorption zone 27 is a suitable absorbent,
9	such as monoethanolamine, by way of line 28, but which
10	may be any other suitable absorbents for carbon dioxide.
11	The unabsorbed flue gas is discharged from
12	absorption zone 27 by line 29, while the enriched solution
13	containing absorbed carbon dioxide is withdrawn from zone
14	27 by line 30 into a stripping zone 31, where heat is
15	applied to drive the absorbed carbondioxide from the
16	monoethanolamine. The carbon dioxide is recovered by
17	line 32 and discharged into line ll to form the feed
18	admixture to the reaction zone 12.
19	By virtue of an operation such as described
20	in the drawing, the synthesis gas is generated solely
21	from methane and air in a suitable combined furnace-
22	conversion zone.
23	The operation described in the drawing produces
24	a synthesis gas containing approximately 2 parts of
25	hydrogen to 1 part of carbon monoxide. Approximately
26	1/2 to $3/4$ of the flue gas from the combustion operation
27	is cooled, compressed and processed to extract carbon
28	dioxide which is then used to supply the carbon dioxide

requirements for the synthesis gas operation. 1 2 EXAMPLE I A stream of natural gas amounting to 12.2 3 million cubic feet/day is divided into a first portion 4 of 7.5 million cubic feet/day which is charged to a 5 conversion reactor and a second portion of 4.7 million 6 cubic feet/day which is burned in a furnace providing 7 heat for conversion of the aforementioned first portion. 8 The heat released from combustion of the 4.7 million 9 cubic feet/day portion is in balance with that required 10 for conversion of the 7.5 million cubic feet/day in 11 12 the reactor. Natural gas suitable for this operation may 13 have a typical analysis as follows: 14 mol per cent 15 16 17 18 CH₄ 19 20 0.3 parts per million by weight H₂S 21 A portion of the flue gas from the reactor 22 furnace is passed through a steam generating system from 23 which is produced 800,000 lbs./day of steam. The cooled 24 flue gas from the steam generating plant is passed to 25 a CO2 recovery system from which 2.5 million cubic feet/day 26 of CO2 is recovered from the flue gas. 27 The total feed gas mixture to the reactor 28 comprises 7.5 million cubic feet/day of natural gas, 29 2.5 million cubic feet/day of CO2, and 639,000 lbs/day 30

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of steam (the steam comprising approximately 80% of that
1
      generated by the flue gases cooled for recovery of CO2).
2
      This admixture is passed at 1000 V/V/Hr. (based on outlet
3
      H<sub>2</sub> + CO) through furnace tubes packed with a nickel
4
      catalyst such as the Girdler Corp. type G-29 catalyst
5
      which contains 27% nickel on a suitable support. The
6
      effluent from the reactor at 20 psig and 1550 F., amounting
7
      to 38.8 million cubic feet/day, comprises a mixture having
8
      the following approximate composition:
9
                           Hydrogen
10
                           CŌ
11
12
13
      The above mixture is passed through a scrubber-cooler
14
      whereupon it is cooled to a temperature of approximately
15
      100°F. A gaseous mixture is recovered from the scrubber-
16
      cooler having the following composition:
17
                           H<sub>2</sub>
CO
CO<sub>2</sub>
H<sub>2</sub>O
18
19
20
21
                 The above mixture, which is at 15 psig, is then
22
      compressed and may be used for conversion to methanol.
23
                 While the invention has been described and
24
      illustrated by reference to use of methane as the feed,
25
      it will be preferred to employ natural gas as the feed.
26
      Natural gas as produced usually comprises a major amount
27
      of methane and minor amounts of ethane, propane and butane.
28
      Accordingly, it is contemplated that mixtures of these
29
      several hydrocarbons having 1 to 4 carbon atoms in the
30
      molecule may be used or the hydrocarbons in a substantially
31
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purified form may comprise the feed stock.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

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1. A method for producing synthesis gas which comprises the steps of dividing a natural gas feed stream into a first portion and a second portion, 3 contacting the first portion in admixture with steam 4 and carbon dioxide obtained in a later step at an 5 elevated temperature in a conversion zone with a catalyst 6 to produce synthesis gas, burning the second portion to 7 provide said elevated temperature and to form a combustion 8 gas containing substantial amounts of carbon dioxide, 9 cooling the combustion gas with water to generate steam 10 and reduce the temperature of the combustion gas, recovering 11 carbon dioxide from the cooled combustion gas, admixing the 12 steam and recovered carbon dioxide with the first portion, 13 and recovering said synthesis gas comprising carbon 14 monoxide and hydrogen from the contacted admixture. 15

2. A method for producing synthesis gas which comprises the steps of dividing a natural gas feed stream into a first portion and a second portion, contacting the first portion in admixture with steam and carbon dioxide obtained in a later step at an elevated temperature within the range between about 1100° and 1850° F. in a conversion zone with a catalyst to produce synthesis gas, burning the second portion to provide said elevated temperature and to form a combustion gas containing substantial amounts of carbon dioxide, cooling the combustion gas with water to generate steam and reduce the temperature of the combustion gas, recovering carbon dioxide from the cooled combustion gas, admixing the steam and recovered carbon dioxide with the first portion and recovering said synthesis gas comprising carbon monoxide and hydrogen from the contacted admixture.

9 -

3. A method for producing synthesis gas which comprises the steps of dividing a methane-containing feed 2 stream into a first portion and a second portion, contacting 3 the first portion in admixture with steam and carbon dioxide 4 obtained in a later step at an elevated temperature in a 5 conversion zone with a nickel catalyst to produce synthesis 6 gas, burning the second portion to provide said elevated 7 temperature and to form a combustion gas containing substantial 8 amounts of carbon dioxide, cooling the combustion gas with 9 water to generate steam and reduce the temperature of the 10 combustion gas, recovering carbon dioxide from the cooled 11 combustion gas, admixing the steam and recovered carbon 12 dioxide with the first portion and recovering said synthesis 13 gas comprising carbon monoxide and hydrogen from the contacted 1.4 admixture. 15

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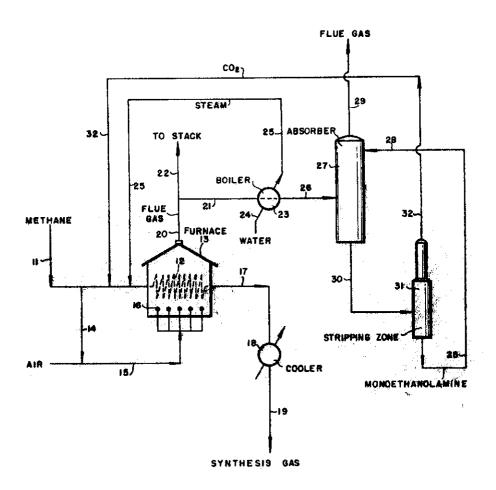
14

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4. A method for producing synthesis gas which comprises the steps of dividing a methane-containing feed stream into a first portion and a second portion, contacting the first portion in admixture with steam and carbon dioxide obtained in a later step at an elevated temperature in a conversion zone with a catalyst to produce synthesis gas containing approximately two parts of hydrogen to one part of carbon monoxide, burning the second portion to provide said elevated temperature and to form a combustion gas containing substantial amounts of carbon dioxide, cooling from about 50 per cent to about 75 per cent of the combustion gas with water to generate steam and reduce the temperature of the gas, recovering carbon dioxide from the cooled combustion gas, admixing the steam and recovered carbon dioxide with the first portion and recovering said synthesis gas from the contacted admixture.

1	5. A method for producing synthesis gas which
2	comprises the steps of dividing a hydrocarbon feed stream
3	having 1 to 4 carbon atoms in the molecule into a first
4	portion and a second portion, contacting the first portion
5	in admixture with steam and carbon dioxide obtained in
6	a later step at an elevated temperature in a conversion
7	zone with a nickel catalyst to produce synthesis gas,
8	burning the second portion in said conversion zone to
9	provide said elevated temperature and to form a combustion
.0	gas containing substantial amounts of carbon dioxide,
11	cooling the combustion gas with water to generate steam
12	and reduce the temperature of the combustion gas, recovering
13	carbon dioxide from the cooled combustion gas, admixing
14	the steam and recovered carbon dioxide with the first
15	portion, and recovering synthesis gas comprising carbon
16	monoxide and hydrogen from the contacted admixture.



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