

(21) Application No: **1603252.6**
(22) Date of Filing: **25.02.2016**
(30) Priority Data:
(31) **1503606.4** (32) **03.03.2015** (33) **GB**

(51) INT CL:
C10L 3/08 (2006.01)

(56) Documents Cited:
GB 2060686 A **EP 3018190 A1**
EP 2843031 A1 **WO 2012/001401 A1**
CN 103865600 A **US 20090264542 A1**

(71) Applicant(s):
Johnson Matthey Davy Technologies Limited
5th Floor, 25 Farringdon Street, LONDON, EC4A 4AB,
United Kingdom

(58) Field of Search:
INT CL **C10K, C10L**
Other: **EPODOC, WPI**

(72) Inventor(s):
Madhanakrishanan Janardhanan
Riyaz Ezzuddin Khambati

(74) Agent and/or Address for Service:
Johnson Matthey Catalysts
Intellectual Property Department, PO Box 1,
Belasis Avenue, BILLINGHAM, Cleveland, TS23 1LB,
United Kingdom

(54) Title of the Invention: **Process**
Abstract Title: **Method of producing substitute natural gas**

(57) A process is described for producing a substitute natural gas (SNG) comprising the steps of: feeding a feed gas comprising hydrogen, carbon monoxide and/or carbon dioxide in parallel to a first bulk methanator, a second bulk methanator and one or more subsequent bulk methanators, each bulk methanator containing a methanation catalyst such that the feed gas is at least partially methanated to form a methanated gas stream, wherein the first, second and at least one subsequent methanators are connected in series so that the feed gas to the second and each of the one or more subsequent bulk methanators is diluted with a methanated gas stream recovered from the previous bulk methanator, wherein all of the methanated gas stream recovered from the first bulk methanator is used to dilute the feed gas to the second bulk methanator, a portion of the methanated gas stream recovered from the second or one or more subsequent bulk methanators is recirculated in a recirculation loop to the first bulk methanator and used to dilute the feed gas fed to said first bulk methanator, and wherein at least one bulk methanator is located outside the recirculation loop.

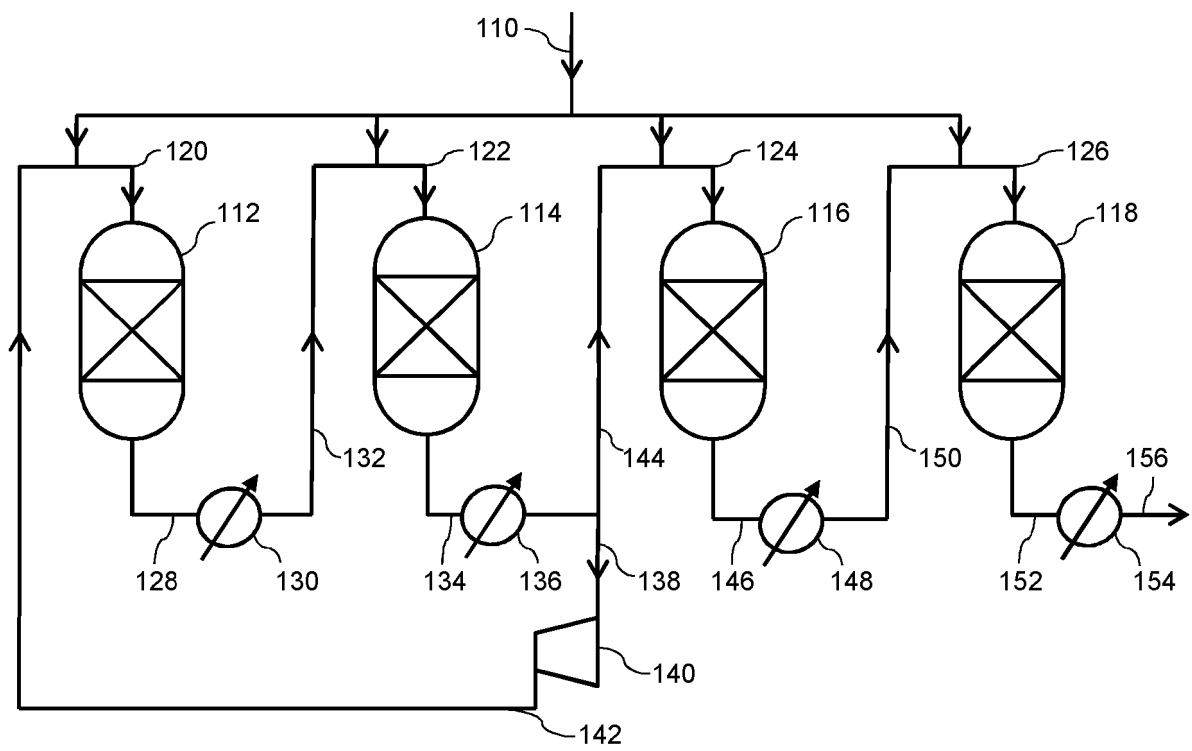


Figure 1

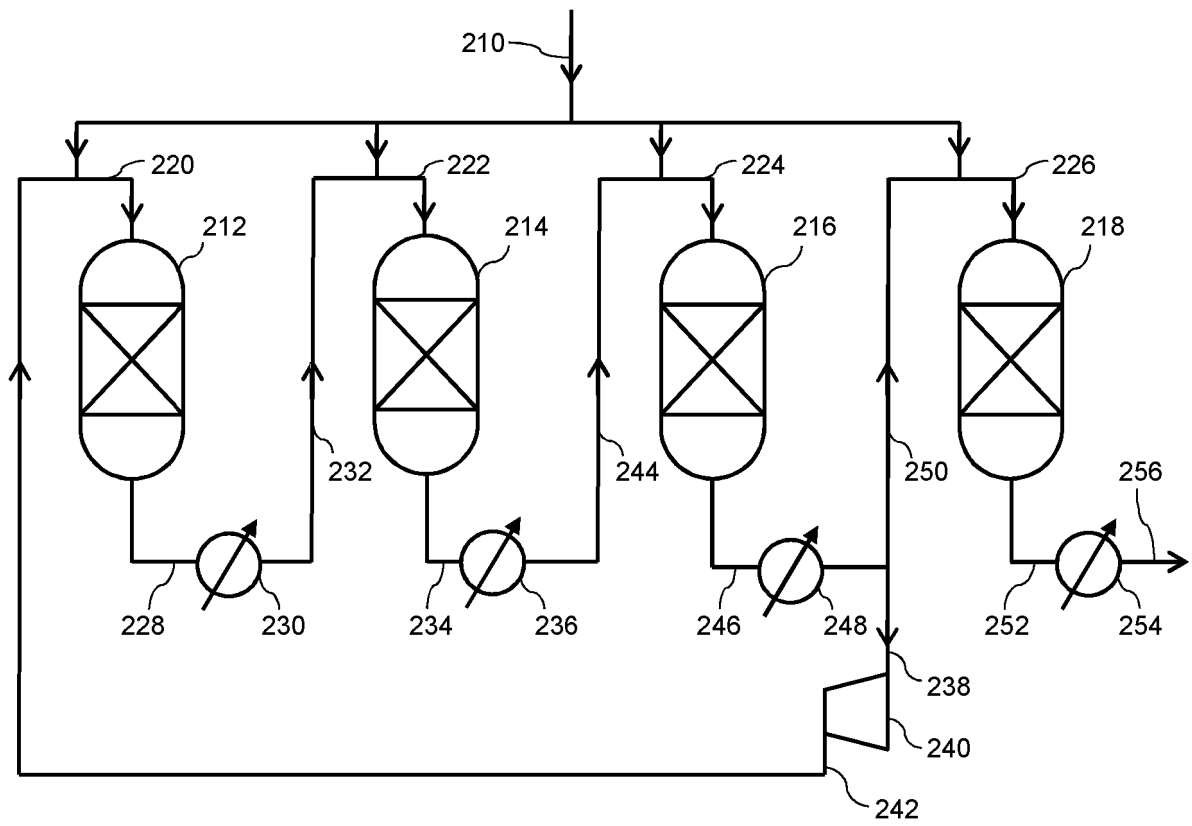


Figure 2

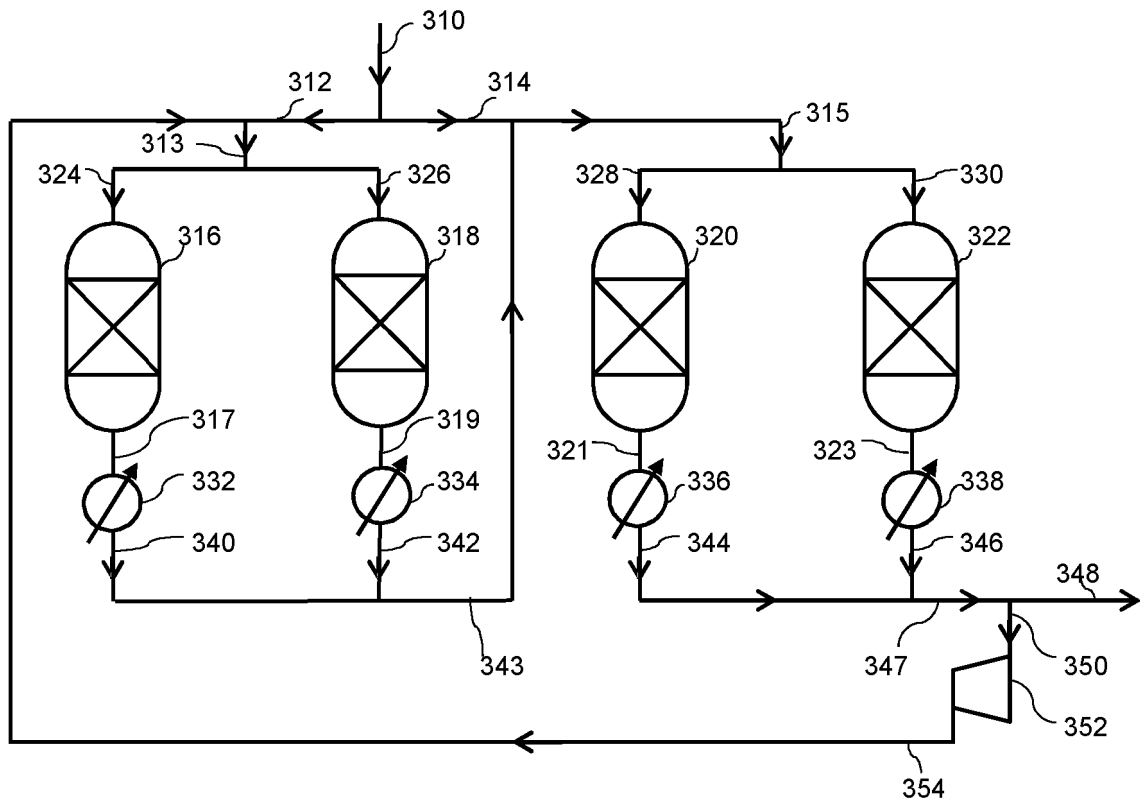


Figure 3

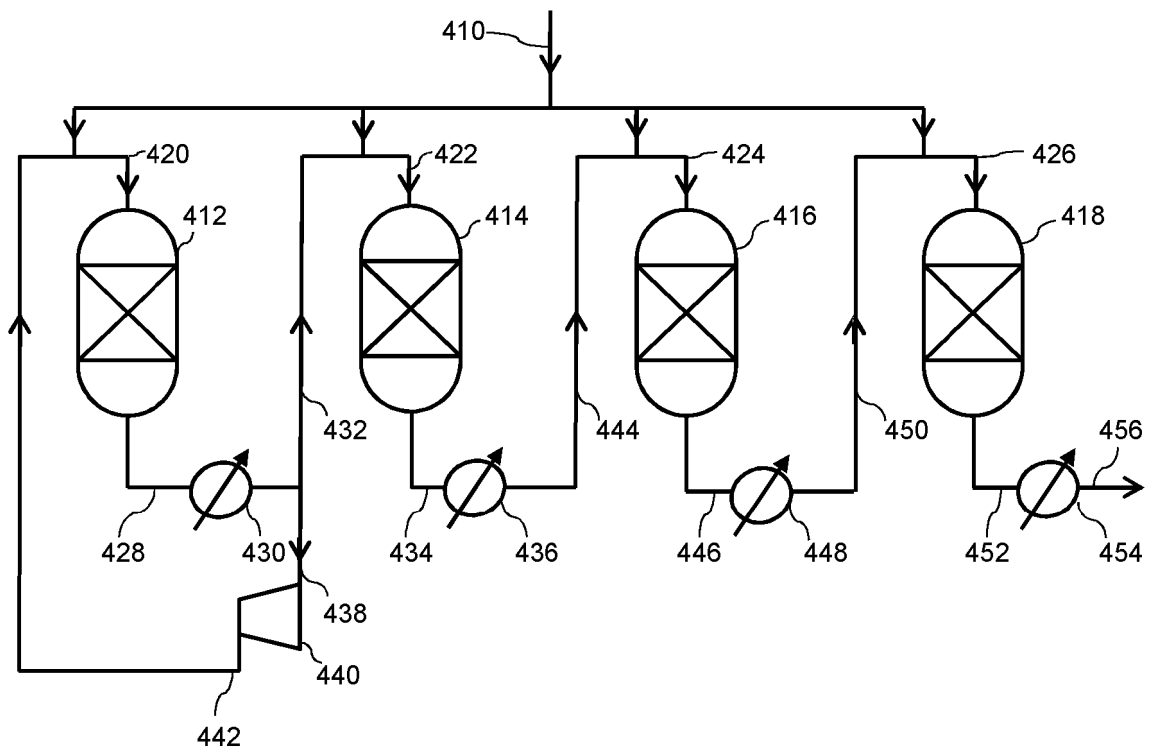


Figure 4

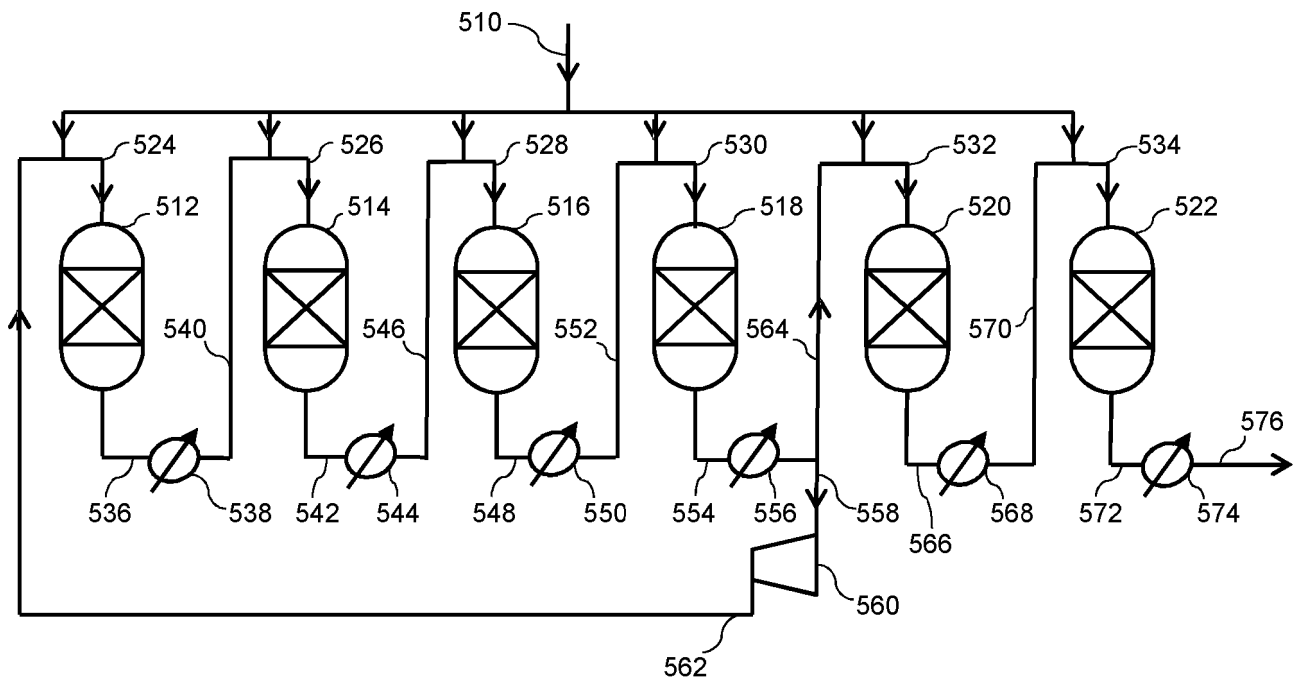


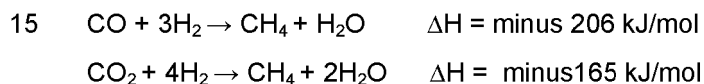
Figure 5

Process

This invention relates to a process for the production of fuel gases suitable for use as a substitute natural gas (SNG) from a synthesis gas.

- 5 SNG is a clean fuel which can be distributed with existing natural gas pipelines and facilities, and can be used as a substitute for natural gas in a wide range of applications.

The process to produce substitute natural gas (SNG) involves catalytic methanation of a synthesis gas comprising hydrogen and carbon oxides. By the reaction of methanation, the
 10 synthesis gas is converted to a product consisting of 95% or more of methane (CH₄) with small amounts of carbon dioxide, hydrogen and inerts. The synthesis gas may be obtained from coal or biomass gasification. The methanation of the syngas involves the following, highly exothermic reactions:



Typically the reactions are carried out in a methanation section comprising a plurality of adiabatic reactors operated in series with heat recovery and gas recirculation. Heat recovery
 20 and gas recirculation are used to keep the exothermic reactions under control and avoid an excessive temperature inside reactors, that may damage the reactor itself and/or the catalyst. Heat recovery may be provided by heat exchangers cooling the hot gas stream at the outlet of each reactor e.g. by producing high pressure steam. Recirculation is a further measure to control the reaction rate and the temperature inside the reactors, by dilution of the fresh
 25 synthesis gas fed to the first reactor with a portion of the reacted gas. The gas recirculation requires the provision of an appropriate compressor.

Various processes are known for producing SNG. One such process is described in US 4016189. Here the feed gas is treated in a single high temperature bulk methanator
 30 followed by treatment in a single low temperature trim methanator. In this process all of the fresh feed is fed to the bulk methanator where a large proportion of the carbon oxides are methanated to methane. Since the reaction is highly exothermic, a thermal mass is required to limit the temperature rise across the bulk methanator to an acceptable level. This thermal mass is supplied in the form of a recycle gas which is taken from downstream of the bulk
 35 methanator but prior to the trim methanator. The recycle stream is compressed prior to being fed upstream of the bulk methanator. The single stage of trim methanation described in US 4016189 is adequate to produce a low calorific gas with a methane content of 60%. This is below the required methane level for current SNG product specifications.

In general it should be noted that a bulk methanator is one which receives part or all of the synthesis gas feed, i.e. fresh synthesis gas feed to the plant. Thus a "bulk methanator" is a reactor in which a reactant gas comprising at least a portion of fresh synthesis gas is catalytically methanated. A trim methanator is one that does not receive any fresh synthesis gas feed and carries out trim methanation on a partially methanated gas stream, usually at lower temperature than in the bulk methanator, to produce a SNG product. Thus a "trim methanator" is a reactor in which a reactant gas, consisting of a partially methanated gas recovered from either a bulk methanator or a trim methanator, is catalytically methanated.

Modern SNG plants typically have two or more bulk methanators in series. For example, an alternative process is described in WO2012/001401 (A1), which discloses providing a feed gas to a first and/or second and/or subsequent bulk methanator; subjecting that feed gas to methanation in the presence of a suitable catalyst; removing an at least partially reacted stream from the first bulk methanator and supplying it to the second and/or subsequent bulk methanator where it is subjected to further methanation; passing a product stream from the final bulk methanator to a trim methanator train where it is subjected to further methanation; removing a recycle stream downstream of the first, second or subsequent bulk methanator, and, in any order, passing it through a compressor, subjecting it to cooling and then supplying to a trim and/or recycle methanator for further methanation before being recycled to the first and/or second and/or subsequent methanator. A recycle methanator is one which is contained within the recycle loop returning a methanated gas stream to an upstream methanator and which does not receive any fresh synthesis gas feed.

Whereas having two bulk methanators in series is useful for minimising the pressure drop over the plant, the process requires a higher product gas recycle and places a limitation on capacity due to the maximum size of the methanator vessels that may be fabricated. Therefore, currently for large-scale plants with higher capacities, reactors and equipment items inside the bulk methanation recycle gas loop have to be twinned, i.e. parallel sets of reactors and ancillary equipment have to be used. A large-scale SNG Plant may be considered to be one with a capacity that requires installation of at-least two bulk methanators in series with one or both of the bulk methanators also having parallel vessels due to the transportation and/or shop floor manufacturing limitations.

We have now surprisingly found that by increasing the number of bulk methanators both inside and outside the recycle gas loop, higher capacities can be achieved without the need for parallel reactors and ancillary equipment items.

Accordingly, the invention provides a process for producing a substitute natural gas comprising the steps of: feeding a feed gas comprising hydrogen, carbon monoxide and/or carbon dioxide

in parallel to a first bulk methanator, a second bulk methanator and one or more subsequent bulk methanators, each bulk methanator containing a methanation catalyst such that the feed gas is at least partially methanated to form a methanated gas stream, wherein the first, second and at least one subsequent methanators are connected in series so that the feed gas to the

5 second and each of the one or more subsequent bulk methanators is diluted with a methanated gas stream recovered from the previous bulk methanator, wherein all of the methanated gas stream recovered from the first bulk methanator is used to dilute the feed gas to the second bulk methanator, a portion of the methanated gas stream recovered from the second or one or more subsequent bulk methanators is recirculated in a recirculation loop to the first bulk

10 methanator and used to dilute the feed gas fed to said first bulk methanator, and wherein at least one bulk methanator is located outside the recirculation loop.

The invention further comprises a methanation system for converting a feed gas comprising hydrogen, carbon monoxide and/or carbon dioxide into substitute natural gas, said methanation

15 system being adapted to operate according to the claimed process. Accordingly the invention includes a methanation system comprising a feed gas supply configured to supply a feed gas in parallel to a first bulk methanator, a second bulk methanator and one or more subsequent bulk methanators, each bulk methanator containing a methanation catalyst, wherein the first, second and at least one subsequent methanators are connected in series so that the feed gas

20 to the second and each of the one or more subsequent bulk methanators may be diluted with a methanated gas stream recovered from the previous bulk methanator, wherein the feed gas supply to the second bulk methanator is configured such that all of the methanated gas stream recovered from the first bulk methanator may be used to dilute the feed gas to the second bulk methanator and a recirculation loop is connected to the second or one or more subsequent

25 bulk methanators so that a portion of a methanated gas stream may be recovered from the second or one or more subsequent bulk methanators and recirculated in the recirculation loop to the first bulk methanator and used to dilute the feed gas fed to said first bulk methanator and wherein at least one bulk methanator is located outside the recirculation loop.

30 The methanation system can be a subsection of a plant for producing substitute natural gas, said plant including further subsections like a gasifier, air separation unit (ASU), CO shift converter to provide appropriate ratio between hydrogen and CO content of the syngas, acid gas removal, and so on.

35 US 2009/0264542 discloses a process in which a carbon oxide rich feed is split and fed to a series of bulk methanators wherein the product gas is recycled from the exit of the first bulk methanator back to the inlet of the first bulk methanator. Unlike the aforesaid US 2009/0264542 in which only one methanator is placed inside the recycle gas loop and second, third and subsequent trim methanators are placed outside the recycle gas loop, the

present invention by having at least 2 bulk methanators inside the recycle gas loop provides a saving on recycle flow and shaft power.

Similar methanation processes are disclosed in US2013/0165535, US2013/0047509,
 5 US2013/0055637, WO2013/159662, GB2060686, CA1088311, CN103865600, CN102329671
 and CN101649233.

Prior art processes have not used an arrangement of multiple bulk methanators wherein (i) all
 of the methanated gas stream recovered from the first bulk methanator is used to dilute the
 10 feed gas to the second bulk methanator, (ii) a portion of the methanated gas stream recovered
 from the second or one or more subsequent bulk methanators is recirculated in a recirculation
 loop to the first bulk methanator and used to dilute the feed gas fed to the first bulk methanator,
 and (iii) at least one bulk methanator is located outside the recirculation loop.

15 Accordingly, compared to prior art processes, the present invention offers lower recycle gas
 flow and power consumption, an easier plot layout, smaller line sizes and equipment sizes, and
 higher capacities can be achieved without installing parallel equipment items.

The feed gas mixture may be a synthesis gas comprising hydrogen, carbon dioxide and carbon
 20 monoxide. Other gases such as nitrogen and/or methane and/or higher hydrocarbons may
 also be present in the feed gas. The feed gas may be formed from the gasification of
 carbonaceous feedstocks, such as coal or petcoke or biomass using conventional techniques.
 Alternatively, the feed gas mixture may be prepared by mixing a hydrogen-containing gas
 mixture with a carbon dioxide-containing gas mixture. The hydrogen containing gas mixture
 25 may be a synthesis gas or may be a gas stream containing hydrogen.

In the methanation process it is desirable that for a feed gas containing carbon monoxide,
 carbon dioxide and hydrogen for x mols/hr of carbon monoxide and y mols/hr carbon dioxide,
 and z mols/hr hydrogen; z is about $(3x + 4y)$. The upstream adjustment of the feed gas
 30 composition may be achieved using known methods, such as by employing one or more water-
 gas shift stages and/or a stage of acid gas removal (AGR).

It may be desirable, in order to prevent catalyst poisoning, to subject the feed gas mixture to a
 desulphurisation step prior to the methanation process. For example the feed gas mixture may
 35 be passed over a bed of a particulate zinc oxide desulphurisation material. Suitable inlet
 temperatures for desulphurisation are in the range 100-300°C. A particularly effective zinc
 oxide desulphurisation material is Puraspec_{JM}TM 2020, available from Johnson Matthey PLC. In
 addition, should the feed gas mixture contain unsaturated compounds (e.g. dienes or
 acetylenes) that might present coking problems on the methanation catalyst, these may be

removed by hydrogenation over a suitable hydrogenation catalyst, such as a copper catalyst, upstream of the first bulk methanator. Oxygen and organic sulphur compounds may also be removed using a suitable catalyst or sorbent, such as a copper catalyst, upstream of the first bulk methanator.

5

The methanation catalyst used in the first, second and subsequent bulk methanators is desirably a nickel- or ruthenium-methanation catalyst, preferably a particulate nickel-containing methanation catalyst, more preferably a precipitated Ni catalyst with a Ni content in the range 35 to $\geq 50\%$ by weight. Particularly suitable methanation catalysts are Katalco™ CRG-S2R, and Katalco™ CRG-S2CR available from Johnson Matthey PLC. The same or different methanation catalyst may be present in the first, second and/or subsequent methanation reactors. The methanation catalyst may be in the form of pellets or extrudates, but may also be a foam, monolith or coating on an inert support. Particulate methanation catalysts are preferred such that the feed gas is preferably passed over a fixed bed of particulate methanation catalyst disposed within each methanator. Suitable particulate catalysts are pellets or extrudates with a diameter or width in the range 2-10 mm and an aspect ratio, i.e. length /diameter or width in the range 0.5 to 4. The flow through the catalyst in the first, second and one or more subsequent bulk methanators may be axial-flow, radial flow or axial-radial flow.

20

The first, second or one or more subsequent bulk methanators may contain another type of catalyst in addition to the methanation catalyst. For example, a water-gas shift catalyst and/or a methanol synthesis catalyst may be included upstream of the first bed of methanation catalyst in the first, second or one or more subsequent bulk methanators. Suitable water-gas shift catalysts include those based on iron, copper and cobalt/molybdenum. Suitable methanol synthesis catalysts include those based on copper/zinc oxide/alumina.

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The methanation catalyst may be operated at an inlet temperature in the range 200-450°C, preferably 200-350°C, more preferably 300-350°C. The inlet temperature may be achieved by heat exchange with a suitable heating medium. In one embodiment the feed gas heating may be done using hot product gas recovered from the final bulk methanator or the final trim methanator using a suitable gas-gas interchanger. Where the methanators are operated adiabatically, the exit temperatures may be in the range 450-750°C, preferably 500-650°C and more preferably 550-650°C. The process pressure may be in the range 5-80 bar abs. The gas hourly space velocity (GHSV) of the feed gas mixtures through the catalyst beds may be in the range 2000 to 20000 hr⁻¹.

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The present invention comprises a first bulk methanator, a second bulk methanator and one or more further bulk methanators in a bulk methanator train. Hence three, four or more bulk

- methanators may be employed, i.e. N may be in the range 3-10, preferably 3-6, where N is the number of bulk methanators. The number of bulk methanators in the recycle loop may be $N-1$, or $N-2$ when $N \geq 4$. In one preferred arrangement four bulk methanators are used, with recycle of the partially methanated gas stream from the second or third bulk methanators to the first
- 5 bulk methanator such that there are one or two bulk methanators outside the recycle loop. In an alternative preferred arrangement, six bulk methanators are used, with recycle of the partially methanated gas stream from the fourth bulk methanator to the first bulk methanator such that there are two bulk methanators outside the recycle loop.
- 10 The portion of the feed gas fed to the first bulk methanator and the second and/or subsequent bulk methanator may be the same or different. Each of the feed gas streams fed to the first, second and one or more subsequent bulk methanators may be in the range 10vol% to 60vol% of the total feed gas feedstock, the exact value being adjusted to control the methanator isotherm. In one arrangement with three bulk methanators about 15-20vol%, especially about
- 15 18vol% of the fresh feed gas is fed to the first bulk methanator, with the remainder being fed to the second and third bulk methanators. However, it will be understood that the split of feed between the methanators will depend on the number of bulk methanators, the operating conditions and the feed composition.
- 20 In each bulk methanator, the hydrogen reacts with carbon dioxide and carbon monoxide to form methane. A portion of the hydrogen in the feed gas typically remains unreacted because there is an equilibrium limitation on the extent of conversion
- Whereas the present process is particularly suited for adiabatic operation of the bulk
- 25 methanators, if desired cooling may be applied to one or more methanation catalyst beds by passing a coolant, such as a portion of the feed gas mixture, through one or more heat exchange devices disposed within the catalyst. The coolant flow may be arranged co-current or counter-current to the flow of reacting gases passing through the methanators.
- 30 In order to prevent overheating of the catalyst and unwanted side reactions in the second and subsequent bulk methanators it is desirable to adjust the temperature of the partially methanated gas mixture recovered from the first, second and subsequent bulk methanators before mixing it with the feed gas. This may be performed by passing the partially methanated gas mixture through one or more heat exchangers, such as a shell and tube heat exchanger
- 35 fed with water under pressure as the cooling medium.

The re-circulation loop may be configured using known methods such as using a recycle compressor or by using a steam ejector. A steam ejector may also add steam to the process to dilute the feed gas or provide steam for water-gas shift. Where steam is added, a single stage

of steam addition is preferred. Preferably the recycle loop comprises a compressor for the re-circulated gas stream and a pre-heater for heating the diluted gas stream before entering the first bulk methanator. This preheater may be a gas-gas interchanger fed with a hot methanated gas stream, e.g. a product gas stream from a final bulk or trim methanator. Preferably the

5 temperature of the recycled portion is adjusted, to a temperature in the range 100-200°C, preferably 120-180°C.

The proportion of the methanated gas stream recycled to the first bulk methanator may be 40-60% vol, preferably 45-55% vol of the methanated gas recovered from the second or one or

10 more subsequent bulk methanators.

The volume ratio between the total diluted gas flow entering the first bulk methanator, and the feed gas stream fed to said first bulk methanator may be between 1.5 and 7, with the exact value depending on the feed gas composition and pressure.

15 Steam may be added at the inlet of at least the first bulk methanator to further dilute the inlet gas. Hence, if desired steam may be used to further dilute the feed gas to the first, second, and one or more further bulk methanators.

A methane-containing substitute natural gas product may be recovered from the final bulk

20 methanator. If desired, the methane-containing substitute natural gas product may be subjected to further processing including subjecting it to one or more further stages of methanation in a trim methanator train. Trim methanators may be used to produce high-specification substitute natural gases. The trim methanator train may comprise one or more,

25 e.g. 1 to 4, particularly 1 or 2, trim methanators. Where more than one trim methanator is present, they will generally be located in series and be fed with a gas mixture consisting of a methanated gas stream and optionally steam. The inlet temperature for trim methanators may be in the range 200-300°C, preferably 230-280°C. Where more than one trim methanator is used, they may be operated at the same temperature or the temperature may be lower in the second and any subsequent trim methanator(s) than in the first trim methanator. Otherwise the

30 trim methanation train may be operated using the same catalysts and catalyst arrangements as the bulk methanation train.

A fully-methanated substitute natural gas product may be recovered from the final trim methanator, if used. The fully methanated gas may be subjected to one or more further SNG

35 preparation stages such as drying to remove water and/or carbon dioxide removal. The drying may be performed by cooling the product gas stream to below the dew point and collecting the liquid condensate, optionally with polishing over a suitable desiccant such as molecular sieves. CO₂-removal, if required, may be accomplished using solvent- or amine-wash techniques known in the art.

The invention is further illustrated by reference to the accompanying drawings in which;
 Figure 1 is a depiction of a flow sheet of one embodiment according to the present invention,
 Figure 2 is a depiction of a flow sheet of a further embodiment according to the present invention,

5 Figure 3 is a depiction of a comparative process with twinned pairs of bulk methanators,
 Figure 4 is a depiction of a comparative process as described in US 2009/0264542, and
 Figure 5 is a depiction of a flow sheet of a further embodiment according to the present invention.

10 It will be understood by those skilled in the art that the drawings are diagrammatic and that
 further items of equipment such as feedstock drums, pumps, vacuum pumps, compressors,
 gas recycling compressors, temperature sensors, pressure sensors, pressure relief valves,
 control valves, flow controllers, level controllers, holding tanks, storage tanks and the like may
 15 be required in a commercial plant. Provision of such ancillary equipment forms no part of the
 present invention and is in accordance with conventional chemical engineering practice.

One embodiment of the present invention is illustrated in Figure 1. Desulphurised feed gas rich
 in carbon monoxide is fed in line 110 to the bulk methanation section which consists of four
 bulk methanators 112, 114, 116, 118, each containing a bed of particulate methanation
 20 catalyst. The first bulk methanator 112, the second bulk methanator 114, third bulk methanator
 116 and fourth bulk methanator 118 are each fed with a diluted portion of the feed gas 110 by
 lines 120, 122, 124 and 126 respectively. The feed gas is methanated in the bulk methanators
 112, 114, 116, 118. The methanated gas stream from the first bulk methanator 112 is passed
 in line 128 to heat exchanger 130 where it is cooled before being added via line 132 to the feed
 25 stream to the second bulk methanator 114. The methanated gas stream from the second bulk
 methanator 114 is passed in line 134 to a heat exchanger 136 where it is cooled. A portion of
 the stream from the heat exchanger 136 is passed in a recycle loop in line 138 to a compressor
 140. The compressed methanated gas from the compressor 140 is passed via line 142 to
 dilute the inlet feed gas fed to the first bulk methanator 112. If desired the compressed
 30 methanated gas may be heated to a suitable methanation inlet temperature in a heat
 exchanger (not shown). The remaining portion of the stream from heat exchanger 136 is
 passed via line 144 to dilute the inlet feed gas to the third bulk methanator 116. The
 methanated gas stream from the third bulk methanator 116 is passed in line 146 to a heat
 exchanger 148 where it is cooled. The methanated gas stream from heat exchanger 148 is
 35 passed via line 150 to dilute the inlet feed gas to the fourth bulk methanator 118. The product
 from the fourth bulk methanator 118 is removed in line 152 and passed through heat exchanger
 154 where it is cooled. It is then passed in line 156 to one or more subsequent trim
 methanators (not shown). The product SNG is withdrawn from the trim methanator and then is
 cooled and dried.

Depending on the feed composition and the operating conditions, it may be necessary or desirable to remove water from the methanated gas recovered from the second bulk methanator 114. This can be conveniently done before the compressor in line 138.

- 5 Steam may be added in line 120. This will only be required with some feed compositions and operating conditions.

In Figure 2, the arrangement of first 212, second 214, third 216 and fourth 218 bulk methanators is the same as depicted in Figure 1 except that the recycle loop of methanated gas 242 feed to the first bulk methanator 212 is recovered from the cooled methanated gas stream obtained from the third bulk methanator 216, rather than the second bulk methanator. Hence desulphurised feed gas rich in carbon monoxide is fed in line 210 to the bulk methanation section which consists of four bulk methanators 212, 214, 216, 218, each containing a bed of particulate methanation catalyst. The first bulk methanator 212, the second 15 bulk methanator 214, third bulk methanator 216 and fourth bulk methanator 218 are each fed with a diluted portion of the feed gas 210 by lines 220, 222, 224 and 226 respectively. The feed gas is methanated in the bulk methanators 212, 214, 216, 218. The methanated gas stream from the first bulk methanator 212 is passed in line 228 to heat exchanger 230 where it is cooled before being added via line 232 to the feed stream to the second bulk methanator 20 214. The methanated gas stream from the second bulk methanator 214 is passed in line 234 to a heat exchanger 236 where it is cooled before being added via line 244 to the feed stream to the third bulk methanator 216. The methanated gas stream from the third bulk methanator 216 is passed in line 246 to a heat exchanger 248 where it is cooled. A portion of the stream from the heat exchanger 248 is passed in a recycle loop in line 238 to a compressor 240. The 25 compressed methanated gas from the compressor 240 is passed via line 242 to dilute the inlet feed gas fed to the first bulk methanator 212. If desired the compressed methanated gas may be heated to a suitable methanation inlet temperature in a heat exchanger (not shown). The remaining portion of the stream from heat exchanger 248 is passed via line 250 to dilute the inlet feed gas to the fourth bulk methanator 218. A product stream 252 is recovered from the 30 fourth bulk methanator and cooled in heat exchanger 254. It is then passed in line 256 to one or more subsequent trim methanators (not shown). The product SNG is withdrawn from the trim methanator and then is cooled and dried.

In Figure 3 a comparative flow sheet is depicted in which the four bulk methanators are 35 arranged as twinned pairs. Hence a desulphurised feed gas 310 is divided and fed in parallel via lines 312 & 313 to paired bulk methanators 316 & 318, and via lines 314 and 315 to paired bulk methanators 320 & 322, each containing a bed of a particulate methanation catalyst. Upstream of methanators 316 and 318, fresh feed gas in line 312 is combined with a recycle methanated gas stream 354. The resulting mixed gas feed stream 313 is divided and fed via a

line 324 to bulk methanator 316 and line 326 to bulk methanator 318. The methanated gas stream 317 recovered from bulk methanator 316 is cooled in heat exchanger 332 to produce a cooled methanated gas stream 340. The methanated gas stream 319 recovered from bulk methanator 318 is cooled in heat exchanger 334 to produce a cooled methanated gas stream 342. The cooled methanated gas streams 340 and 342 are combined and fed via line 343 to be mixed with the feed stream 314. The resulting mixed gas feed stream 315 is divided and fed via a line 328 to bulk methanator 320 and line 330 to bulk methanator 322. The methanated gas stream 321 recovered from bulk methanator 320 is cooled in heat exchanger 336 to produce a cooled methanated gas stream 344. The methanated gas stream 323 recovered from bulk methanator 322 is cooled in heat exchanger 338 to produce a cooled methanated gas stream 346. The cooled methanated gas streams 344 and 346 are combined to form a cooled product gas stream 347. A portion of the product gas stream 347 is taken as a recycle loop via line 350 to a compressor 352, where it is compressed and provided via line 354 to be mixed with fresh feed in line 312. The remaining portion of the cooled product gas stream 348 is passed in to one or more subsequent trim methanators (not shown). The product SNG is withdrawn from the trim methanator and then is cooled and dried.

In Figure 4 a comparative flow sheet is depicted in which the arrangement of first 412, second 414, third 416 and fourth 418 bulk methanators is the same as depicted in Figure 1 except that the recycle loop of methanated gas 442 feed to the first bulk methanator 412 is recovered from the cooled methanated gas stream obtained from the first bulk methanator 412, rather than the second bulk methanator. Hence, desulphurised feed gas rich in carbon monoxide is fed in line 410 to the bulk methanation section which consists of four bulk methanators 412, 414, 416, 418, each containing a bed of particulate methanation catalyst. The first bulk methanator 412, the second bulk methanator 414, third bulk methanator 416 and fourth bulk methanator 418 are each fed with a diluted portion of the feed gas 410 by lines 420, 422, 424 and 426 respectively. The feed gas is methanated in the bulk methanators 412, 414, 416, 418. The methanated gas stream from the first bulk methanator 412 is passed in line 428 to heat exchanger 430 where it is cooled. A portion of the methanated gas stream from the heat exchanger 430 is passed in a recycle loop in line 438 to a compressor 440. The compressed methanated gas from the compressor 440 is passed via line 442 to dilute the inlet feed gas fed to the first bulk methanator 412. The remaining portion of the stream from heat exchanger 430 is passed via line 432 to dilute the inlet feed gas to the second bulk methanator 414. The methanated gas stream from the second bulk methanator 414 is passed in line 434 to a heat exchanger 436 where it is cooled before being passed by line 444 to the inlet of the third bulk methanator 416. The methanated gas stream from the third bulk methanator 416 is passed in line 446 to a heat exchanger 448 where it is cooled before being passed by line 450 to the inlet of the fourth bulk methanator 418. A product stream 452 is recovered from the fourth bulk methanator and cooled in heat exchanger 454. It is then passed in line 456 to one or more subsequent trim

methanators (not shown). The product SNG is withdrawn from the trim methanator and then is cooled and dried.

In Figure 5 a desulphurised feed gas rich in carbon monoxide is fed in line 510 to the bulk methanation section which consists of six bulk methanators 512, 514, 516, 518, 520 and 522 each containing a bed of particulate methanation catalyst. The first bulk methanator 512, the second bulk methanator 514, third bulk methanator 516, fourth bulk methanator 518, fifth bulk methanator 520 and sixth bulk methanator 522 are each fed with a diluted portion of the feed gas 510 by lines 524, 526, 528, 530, 532 and 534 respectively. The feed gas is methanated in the bulk methanators. The methanated gas stream from the first bulk methanator 512 is passed in line 536 to heat exchanger 538 where it is cooled before being added via line 540 to dilute the feed to the second bulk methanator 514. The methanated gas stream from the second bulk methanator 514 is passed in line 542 to a heat exchanger 544 where it is cooled before being added via line 546 to dilute the feed to the third bulk methanator 516. The methanated gas stream from the third bulk methanator 516 is passed in line 548 to a heat exchanger 550 where it is cooled before being added via line 552 to dilute the feed to the fourth bulk methanator 518. The methanated gas stream from the fourth bulk methanator 518 is passed in line 554 to a heat exchanger 556 where it is cooled. A portion of the stream from the heat exchanger 556 is passed in a recycle loop in line 558 to a compressor 560. The compressed methanated gas from the compressor 560 is passed via line 562 to dilute the inlet feed gas fed to the first bulk methanator 512. If desired the compressed methanated gas may be heated to a suitable methanation inlet temperature in a heat exchanger (not shown). The remaining portion of the stream from heat exchanger 556 is passed via line 564 to dilute the inlet feed gas to the fifth bulk methanator 520. The methanated gas stream from the fifth bulk methanator 520 is passed in line 566 to a heat exchanger 568 where it is cooled before being passed via line 570 to dilute the inlet feed gas to the sixth bulk methanator 522. The product from the sixth bulk methanator 522 is removed in line 572 and passed through heat exchanger 574 where it is cooled. It is then passed in line 576 to one or more subsequent trim methanators (not shown). The product SNG is withdrawn from the trim methanator and then is cooled and dried.

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The invention is further illustrated by reference to the following Examples.

Example 1

A first example considers the case where the feed gas comprises hydrogen, carbon oxides and some methane, and is based on a SNG production capacity of 250,000 Nm³/h.

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The desulphurised feed gas composition is as follows;

	vol%
Water	0.10
Hydrogen	63.74
Carbon Monoxide	20.00
Carbon Dioxide	1.00
Methane	14.93
Nitrogen & Argon	0.21
Ethane	0.030

The product specification is as follows;

	vol%
Hydrogen	< 2%
Carbon Dioxide	< 1%
Methane	> 95%

- 5 In a process according to the flow sheet depicted in Figure 1, there are 4 bulk methanators in series, with 2 methanators placed inside the recycle loop and the 2 methanators placed outside the recycle loop. The following Table sets out the operation of this flow sheet using Katalco™ CRG-S2R, and Katalco™ CRG-S2CR.

Stream Number	110	120	128	122	134	124	146	126	152	142
Temperature (°C)	225	320	620	320	620	320	620	320	620	353
Pressure (MPa abs)	4.57	4.02	3.97	3.93	3.88	3.80	3.75	3.80	3.75	4.02
Vapour Flow (kNm ³ /h)	684.1	527.2	464.2	698.6	616.4	363.1	320.7	479.6	423.7	358.1
Composition (mol%)										
H ₂ O	0.10	11.98	20.15	13.43	21.28	14.18	22.06	14.78	22.75	17.58
H ₂	63.74	33.42	17.82	33.22	18.24	33.49	18.67	33.60	18.82	19.10
CO	20.00	7.39	1.37	7.62	1.37	7.61	1.39	7.55	1.37	1.43
CO ₂	1.00	2.92	3.55	2.69	3.65	2.76	3.75	2.84	3.79	3.83
N ₂	0.21	0.32	0.36	0.31	0.35	0.30	0.34	0.30	0.34	0.37
CH ₄	14.93	43.97	56.75	42.72	55.10	41.64	53.79	40.91	52.93	57.69
C ₂ H ₆	0.03	0.01	-	0.01	-	0.01	-	0.01	-	-

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The catalyst volumes are as follows;

Bulk Methanator	112	114	116	118
Catalyst Bed Diameter (mm)	4755	5500	4055	4630
Catalyst volume (m ³)	41	54	28	37

The equipment count and required catalyst volumes remains the same as the comparative process depicted in Figure 3, however, the equipment items related to the recycle are smaller by 40 % due to reduced flow. The required recycle gas flow is approximately 16,000 kmol/h and recycle compressor shaft power is approximately 1,860 kW. The shaft power has been calculated using a 75% polytropic efficiency and 4% losses.

In a process according to the flow sheet depicted in Figure 2, there are 4 bulk methanators in series, with 3 placed inside the recycle loop and the 4th place outside the recycle loop. The following Table sets out the operation of this flow sheet using Katalco™ CRG-S2R, and Katalco™ CRG-S2CR.

Stream Number	210	220	228	222	234	224	246	226	252	242
Temperature (°C)	225	320	620	320	620	320	620	320	620	352
Pressure (MPa abs)	4.57	4.02	3.97	3.93	3.88	3.85	3.79	3.71	3.66	4.02
Vapour Flow (kNm ³ /h)	684.1	389.4	342.7	515.7	455.0	683.3	603.4	480.0	424.1	267.0
Composition (mol%)										
H ₂ O	0.10	11.83	20.15	13.43	21.28	14.20	22.11	14.75	22.66	17.20
H ₂	63.74	33.58	17.81	33.21	18.23	33.44	18.59	33.68	18.97	19.76
CO	20.00	7.29	1.37	7.62	1.37	7.59	1.37	7.60	1.40	1.46
CO ₂	1.00	3.04	3.55	2.69	3.65	2.77	3.74	2.82	3.81	3.97
N ₂	0.21	0.32	0.36	0.31	0.35	0.30	0.34	0.30	0.34	0.37
CH ₄	14.93	43.94	56.76	42.73	55.11	41.69	53.85	40.84	52.83	57.24
C ₂ H ₆	0.03	0.01	-	0.01	-	0.01	-	0.01	-	-

The catalyst volumes are as follows;

Bulk Methanator	212	214	216	218
Catalyst Bed Diameter (mm)	4030	4800	5485	4660
Catalyst volume (m ³)	30	40	53	37

The equipment count and required catalyst volumes remains the same as the comparative process depicted in Figure 3, however, the equipment items related to the recycle are smaller

by 55 % due to reduced flow. The required recycle gas flow is approximately 11,900 kmol/h and recycle compressor shaft power is approximately 1,750 kW.

- Whereas each additional bulk reactor in series adds 0.8 – 1 bar pressure drop across the plant,
5 the lower product pressure has a small impact on product quality.

- In comparison, Figure 3, which represents current practice for large scale SNG plants, uses 2 bulk methanators in series and the reactors/equipment items inside the bulk methanation recycle loop are twinned due to manufacturing and transportation limitations. The required
10 recycle gas flow is approximately 27,100 kmol/h and recycle compressor shaft power is approximately 3,800 kW. The following Table sets out the operation of this flow sheet using Katalco™ CRG-S2R, and Katalco™ CRG-S2CR.

Stream Number	310	313	317+319	315	321+323	354
Temperature (°C)	273	320	620	320	620	337
Pressure (MPa abs)	3.97	3.96	3.91	3.87	3.82	3.97
Vapour Flow (kNm ³ /h)	684.8	894.2	787.4	1185.7	1046.3	607.6
Composition (mol%)						
H ₂ O	0.10	12.00	20.17	13.43	21.27	17.62
H ₂	63.74	33.48	17.91	33.30	18.36	19.21
CO	20.00	7.40	1.38	7.64	1.39	1.45
CO ₂	1.00	2.93	3.56	2.70	3.67	3.84
N ₂	0.21	0.32	0.36	0.31	0.35	0.37
CH ₄	14.93	43.86	56.61	42.61	54.97	57.51
C ₂ H ₆	0.03	0.01	-	0.01	-	-

- 15 The catalyst volumes are as follows;

Bulk Methanator	316	318	320	322
Catalyst Bed Diameter (mm)	4380	4380	5180	5180
Catalyst volume (m ³)	34.5	34.5	45.5	45.5

- In comparison, Figure 4, which represents an alternative comparative process, has 1 bulk methanator inside the recirculation loop and 3 bulk methanators outside the recirculation loop.
20 In comparison to process depicted in Figure 1 and Figure 2, the equipment items related to the recycle are larger by 78% and 139%. The required recycle gas flow for process in Figure 4 is approximately 28,400 kmol/h and recycle compressor shaft power is approximately 2,380 kW.

Furthermore for process in Figure 4, the first bulk methanator and downstream effluent cooling system may require parallel items due to large reactor diameter required for a single vessel. (estimated catalyst bed diameter = 6400 mm). The following Table sets out the operation of this flow sheet using Katalco™ CRG-S2R, and Katalco™ CRG-S2CR.

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Stream Number	410	420	428	422	434	424	446	426	452	442
Temperature (°C)	225	320	620	320	620	320	620	320	620	354
Pressure (MPa abs)	4.03	4.02	3.97	3.89	3.84	3.80	3.75	3.72	3.67	4.02
Vapour Flow (kNm ³ /h)	684.1	947.6	834.8	273.4	241.3	362.4	320.0	480.0	424.1	636.5
Composition (mol%)										
H ₂ O	0.10	12.15	20.15	13.41	21.24	14.17	22.07	14.74	22.67	18.04
H ₂	63.74	33.20	17.81	33.25	18.31	33.49	18.66	33.68	18.96	18.28
CO	20.00	7.51	1.37	7.64	1.38	7.60	1.38	7.59	1.39	1.41
CO ₂	1.00	2.77	3.55	2.69	3.66	2.77	3.74	2.83	3.81	3.64
N ₂	0.21	0.32	0.36	0.31	0.35	0.30	0.34	0.30	0.34	0.37
CH ₄	14.93	44.03	56.76	42.69	55.06	41.65	53.80	40.85	52.84	58.26
C ₂ H ₆	0.03	0.01	-	0.01	-	0.01	-	0.01	-	-

The catalyst volumes are as follows;

Bulk Methanator	412	414	416	418
Catalyst Bed Diameter (mm)	6415	3495	4025	4660
Catalyst volume (m ³)	74	21	28	37

10 Example 2

A second example considers the case where the feed gas comprises hydrogen, carbon oxides and no methane, and is based on a SNG production capacity of 250,000 Nm³/h. The desulphurised feed gas composition is as follows;

	vol%
Water	0.10
Hydrogen	74.44
Carbon Monoxide	24.16
Carbon Dioxide	0.57
Methane	0.00
Nitrogen & Argon	0.74

The product specification is as follows;

	vol%
Hydrogen	< 2%
Carbon Dioxide	< 1%
Methane	> 95%

In a process according to the flow sheet depicted in Figure 5, there are 6 bulk methanators in series, with 4 methanators placed inside the recycle loop and 2 methanators placed outside the recycle loop. The equipment count is reduced when compared to the process depicted in Figure 3 because the production capacity in this example can be achieved via a single train using process depicted in Figure 5, but two trains are necessary for the process depicted in Figure 3. The required catalyst volumes remain the same as the comparative process depicted in Figure 3; however equipment items related to the recycle for Figure 5 are smaller by 70 % due to reduced flow via a single train versus the combined flow of two trains for Figure 3. The required recycle gas flow is approximately 16,800 kmol/h and recycle compressor shaft power is approximately 4,850 kW.

The following Table sets out the operation of this flow sheet using Katalco™ CRG-S2R, and Katalco™ CRG-S2CR.

Stream Number	510	524	536	526	542	528	548	530	554	532	566	534	572	562
Temperature (°C)	195	320	620	320	620	320	620	320	620	320	620	320	620	352
Pressure (MPa abs)	2.95	2.90	2.85	2.82	2.77	2.73	2.68	2.65	2.59	2.48	2.43	2.39	2.34	2.91
Vapour Flow (kNm ³ /h)	964.3	484.6	426.8	586.8	520.0	712.5	632.3	864.5	768.0	459.9	409.1	557.3	496.1	377.1
Composition (mol%)														
H ₂ O	0.10	11.36	20.35	14.83	22.43	16.40	24.10	17.66	25.43	18.61	26.37	19.38	27.22	14.57
H ₂	74.44	36.23	20.14	34.94	20.90	35.36	21.53	35.74	22.11	36.21	22.83	36.56	23.29	25.33
CO	24.16	6.86	1.70	7.83	1.68	7.75	1.68	7.71	1.68	7.74	1.73	7.69	1.74	1.93
CO ₂	0.57	4.07	3.94	3.02	4.13	3.17	4.29	3.29	4.43	3.39	4.57	3.50	4.66	5.07
N ₂	0.74	1.52	1.73	1.46	1.65	1.40	1.58	1.35	1.52	1.31	1.47	1.28	1.44	1.74
CH ₄	-	39.96	52.14	37.92	49.21	35.92	46.82	34.24	44.82	32.75	43.03	31.58	41.65	51.35

The catalyst volumes are as follows;

Bulk Methanator	512	514	516	518	520	522
Catalyst Bed Diameter (mm)	4440	4980	5490	5895	4470	4935
Catalyst volume (m ³)	37	45	55	67	36	43

In comparison, a process as depicted in Figure 3, where the reactors/equipment items inside the bulk methanation recycle loop would be twinned due to manufacturing and transportation limitations, and for the same reason two trains would be required, the number of bulk methanator reactor vessels increases to eight. The required recycle gas flow would be approximately 2 x 28,100 kmol/h and recycle compressor shaft power approximately 2 x 5,470 kW. The following Table sets out the operation of this flow sheet using Katalco™ CRG-S2R, and Katalco™ CRG-S2CR.

Stream Number	310	313	317+319	315	321+323	354
Temperature (°C)	262	320	620	320	620	333
Pressure (MPa abs)	2.87	2.86	2.81	2.77	2.72	2.87
Vapour Flow (kNm ³ /h)	483.3	836.0	737.9	1015.3	899.9	630.1
Composition (mol%)						
H ₂ O	0.10	12.06	20.36	14.82	22.40	15.97
H ₂	74.44	35.51	20.24	35.05	21.04	22.79
CO	24.16	7.34	1.72	7.85	1.71	1.85
CO ₂	0.57	3.53	3.95	3.03	4.15	4.50
N ₂	0.74	1.52	1.72	1.46	1.64	1.78
CH ₄	-	40.04	52.01	37.80	49.06	53.12

10 The catalyst volumes are as follows;

Bulk Methanator	316	318	320	322
Catalyst Bed Diameter (mm)	4125	4125	4635	4635
Catalyst volume (m ³)	2 x 32	2 x 32	2 x 39	2 x 39

In comparison, a process as depicted in Figure 4, the process would need 4 bulk methanators in series, with 1 methanator placed inside the recycle gas loop and 3 methanators placed outside the recycle gas loop. The equipment items related to the recycle would be larger by 37% due to increased recycle flow when compared with the flowsheet depicted in Figure 3. In comparison to process depicted in Figure 5, the equipment items related to the recycle are larger by 174%. The required recycle gas flow is approximately 77,000 kmol/h and recycle compressor shaft power is approximately 12,200 kW. Furthermore, the first bulk methanator and downstream effluent cooling system may require to be twinned / tripled due to significantly large reactor diameter required for a single reactor (catalyst bed diameter = 9700 mm). The following Table sets out the operation of this flow sheet using Katalco™ CRG-S2R, and Katalco™ CRG-S2CR.

Stream Number	410	420	428	422	434	424	446	426	452	442
Temperature (°C)	225	320	620	320	620	320	620	320	620	343
Pressure (MPa abs)	2.93	2.92	2.87	2.77	2.72	2.68	2.63	2.60	2.55	2.92
Vapour Flow (kNm ³ /h)	966.7	2334.8	2063.0	358.7	318.0	435.7	386.7	528.4	469.5	1725.9
Composition (mol%)										
H ₂ O	0.10	12.46	20.36	14.81	22.37	16.35	24.03	17.61	25.37	16.82
H ₂	74.44	34.93	20.10	34.98	21.00	35.44	21.64	35.80	22.20	20.99
CO	24.16	7.61	1.70	7.85	1.70	7.77	1.69	7.72	1.70	1.77
CO ₂	0.57	3.18	3.93	3.01	4.15	3.18	4.31	3.30	4.44	4.11
N ₂	0.74	1.53	1.73	1.46	1.64	1.40	1.58	1.35	1.52	1.81
CH ₄	-	40.29	52.18	37.89	49.15	35.87	46.75	34.21	44.77	54.50

The catalyst volumes are as follows;

Bulk Methanator	412	414	416	418
Catalyst Bed Diameter (mm)	9685	3895	4295	4730
Catalyst volume (m ³)	180	28	34	41

Claims.

1. A process for producing a substitute natural gas comprising the steps of: feeding a feed gas comprising hydrogen, carbon monoxide and/or carbon dioxide in parallel to a first bulk methanator, a second bulk methanator and one or more subsequent bulk methanators, each bulk methanator containing a methanation catalyst such that the feed gas is at least partially methanated to form a methanated gas stream, wherein the first, second and at least one subsequent methanators are connected in series so that the feed gas to the second and each of the one or more subsequent bulk methanators is diluted with a methanated gas stream recovered from the previous bulk methanator, wherein all of the methanated gas stream recovered from the first bulk methanator is used to dilute the feed gas to the second bulk methanator, a portion of the methanated gas stream recovered from the second or one or more subsequent bulk methanators is recirculated in a recirculation loop to the first bulk methanator and used to dilute the feed gas fed to said first bulk methanator, and wherein at least one bulk methanator is located outside the recirculation loop.
2. A process according to claim 1 wherein the feed gas is a desulphurised synthesis gas obtained from the gasification of coal or biomass.
3. A process according to claim 1 or claim 2 wherein the methanation catalyst is operated at an inlet temperature in the range 200-450°C, preferably 200-350°C, more preferably 300-350°C.
4. A process according to any one of claims 1 to 3 operated at a pressure in the range 5-80 bar abs.
5. A process according to any one of claims 1 to 4 wherein the process is operated with N bulk methanators, N is in the range 3-10, preferably 3-6,
6. A process according to claim 5 wherein the number of bulk methanators in the recycle loop is N-1, or N-2 when $N \geq 4$.
7. A process according to any one of claims 1 to 6 comprising four bulk methanators, with recycle of the partially methanated gas stream from the second or third bulk methanators to the first bulk methanator such that there are one or two bulk methanators outside the recycle loop.
8. A process according to any one of claims 1 to 6 comprising six bulk methanators, with recycle of the partially methanated gas stream from the fourth bulk methanator to the first bulk methanator such that there are two bulk methanators outside the recycle loop.

9. A process according to any one of claims 1 to 8, wherein the feed gas streams fed to the first, second and one or more subsequent bulk methanators is in the range 10vol% to 60vol% of the total feed gas feedstock.
10. A process according to any one of claims 1 to 9, wherein the re-circulation loop comprises a compressor for the re-circulated gas stream and a pre-heater for heating said diluted gas stream before entering the first bulk methanator.
11. A process according to any one of claims 1 to 10 wherein the proportion of the methanated gas stream recycled to the first bulk methanator is 40-60% vol, preferably 45-55% vol, of the methanated gas recovered from the second or one or more subsequent bulk methanators.
12. A process according to any one of claims 1 to 11 wherein the temperature of the recirculated portion of the methanated gas stream is adjusted to a temperature in the range 100-200°C, preferably 120-180°C.
13. A process according to any one of claims 1 to 12, wherein steam is added at the inlet of at least the first bulk methanator to further dilute the inlet gas.
14. A process according to any one of claims 1 to 13 further comprising subjecting a product gas from the final bulk methanator to further methanation in one or more trim methanators.
15. A process according to claim 14 further comprising subjecting a product gas from the final trim methanator to a drying step.
16. A methanation system for converting a feed gas containing hydrogen, carbon monoxide and/or carbon dioxide into substitute natural gas, said methanation train being adapted to operate according to the process of any one of claims 1 to 15.



Application No: GB1603252.6

Examiner: Mr Martin Price

Claims searched: 1-16

Date of search: 3 August 2016

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X,E	1-16	EP 3018190 A1 Haldor Topsoe - see e.g. figures 2-4
X	1-16	EP 2843031 A1 Sunshine Kaidi - see e.g. figure 3
X	1-16	WO 2012/001401 A1 Davy Process - see e.g. the claims and figures
X	1-16	GB 2060686 A Conoco - see e.g. claim 1
X	1-16	US 2009/0264542 A1 Filippi - see e.g. figure 1
X	1-16	CN 103865600 A China Petroleum - see WPI abstract number 2014-Q26546 and EPODOC abstract

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC

C10K; C10L

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI



International Classification:

Subclass	Subgroup	Valid From
C10L	0003/08	01/01/2006