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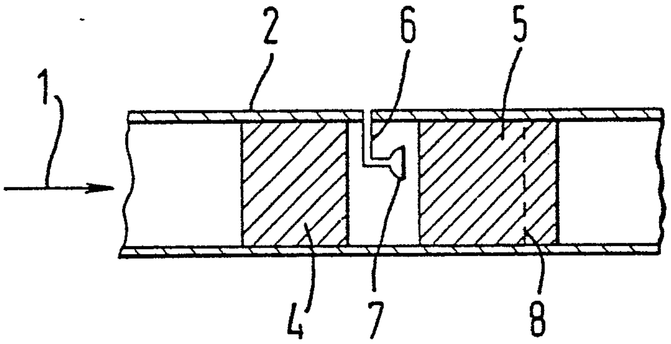

(57) Abstract

Methanation reactions and, more particularly an improved process for the catalytic methanation of gases such as "synthesis gas". In more detail a process for the methanation of synthesis gas comprises reacting together CO, CO_2 and H_2 (1) by successive contact steps thereof with: (a) a catalyst (4) comprising a solid support having deposited thereon a metal selected from the group consisting of Fe, Co, Ni, Cu, W, Ru, Rh, Pd, Ir, Pt alloys of the said metals with each other and alloys containing an aggregate of at least 10% by weight of one or more of the said metals with other metals, and, (b) an inert body or assembly of bodies (5) having a substantial surface area with which the gases make contact subsequent to their contact with the said catalyst, the said inert body or assembly of bodies having sprayed on to it or them (6, 7) a liquid medium which removes heat from the gases and thereby has its temperature raised and/or is evaporated, the rate of supply of the liquid medium, its specific heat, its latent heat of vaporisation and the other conditions of the process being such that the temperature of the gas emerging from the body or assembly of bodies is not higher than 600°C and that the entire quantity of liquid medium is evaporated before its passage along the inert body or assembly of bodies is complete (8).

"ISOTHERMAL METHANATION"

This invention relates to methanation reactions and, more particularly is concerned with an improved process for the catalytic methanation of gases such as "synthesis gas".

By "synthesis gas" is meant a mixture of carbon monoxide and hydrogen, and also, possibly some carbon dioxide and nitrogen, depending upon the method of preparation employed. Common methods of preparation include the steam reforming of hydrocarbons, such as naphtha distillates and the gasification of coal.

The "methanation" of synthesis gas, namely its conversion in whole or in part to methane, especially to pipeline quality methane for use as "substitute natural gas" (SNG) is a commercially important process.

The main reactions involved are:

$$3H_2 + Co \rightleftharpoons CH_4 + H_2O \qquad (A)$$

$$4H_2 + Co_2 \rightleftharpoons CH_4 + 2H_2O \qquad (B)$$

Some of the carbon monoxide present will be converted to carbon dioxide and a measure of the selectivity of the process to methane formation is provided by the proportion of input carbon monoxide which is converted to methane. This conversion may be direct in accordance with reaction (A) or via carbon dioxide which is then converted to methane as in reaction (B).

The ratio of H_2 to CO in the synthesis gas may be adjusted to a value in the region of 3 to 1 which is required for the methanation reaction (A) by subjecting the synthesis gas to the well known water gas shift reaction:-

$$CO + H_2O \longrightarrow CO_2 + H_2.$$

For this purpose any of the commonly used water gas shift catalysts, such as an iron catalyst, may be employed.

A problem which occurs with methanation is that reactions (A) and (B) are both highly exothermic, the heat evolved being approximately 50 Kcals. per mole of carbon monoxide in the case of reaction (A) and 40 Kcals. per mole of carbon dioxide in the case of reaction (B). A further problem is that the reaction constants favour reactants rather than products at temperatures higher than about 600°C, so that it is important to keep the temperatures down during the course of the methanation process.

According to one aspect of the present invention a process for the methanation of synthesis gas comprises reacting together CO, CO_2 and H_2 by successive contact steps thereof with

(a) a catalyst comprising a solid support having deposited thereon a metal selected from the group consisting of Fe, Co, Ni, Cu, W, Ru, Rh, Pd, Ir, Pt, alloys of the said metals with each other and alloys containing an aggregate of at least 10% by weight of one or more of the said metals with other metals, and

(b) an inert body or assembly of bodies having a substantial surface area with which the gases make contact subsequent to their contact with the said catalyst, the said inert body or assembly of bodies having sprayed on to it or them a liquid medium which removes heat from the gases and thereby has its temperature raised and/or is evaporated, the rate of supply of the liquid medium, its specific heat, its latent heat of vaporisation and the other conditions of the process being such that the temperature of the gas emerging from the body or assembly of bodies is not higner than 600°C and that the entire quantity of liquid medium is evaporated before its passage along the inert body or assembly of bodies is complete.

Preferably successive contact steps (a) and (b) may be repeated either by recycling or by passing the gas mixture through a number of zones containing supported catalyst and sprayed inert body or bodies.

Preferably the liquid medium has a latent heat of vaporisation within the range 150-600 calories per gram. Preferably, also, the liquid medium is water because, under equilibrium conditions, steam, when mixed with the reactants has relatively little effect on the reaction. Indeed we have found that at a temperature less than 400°C a change in the reactant ratio ($H_2 : CO : H_2O$) from 3:1:0 to 3:1:15 results in less than a 20% change in the volume percentage of CO converted to CO_2 and CH_4 although, of course, high concentrations of steam do result in a reduction of the percentage selectivity of the reaction to CH_4.

Liquid media other than water may be used but they need to be such that they do not have a deleterious effect upon the methanation process. A liquid medium which may be used is an inert solvent sold under the Registered Trade Mark "Dowtherm" by the Dow Chemical Company.

Preferably the catalyst comprises ruthenium and/or nickel or alloys of one or other or both of these metals with other metals. The catalyst metals or alloys may be deposited upon a particulate support such as pelleted alumina or granular silica. A preferred support is a ceramic or metallic honeycomb monolith preferably "washcoated" with a layer of alumina. Such ceramic monoliths are described in British patent No.882,484 and the metallic monolith in German Offenlegungsschrift No.2450664. Suitable alloys for the construction of metallic monoliths are described in German Offenlegungsschrift 2450664.

The catalyst unit, or the first catalyst unit of a multi-unit assembly according to the invention may advantageously be preceded by a unit containing a water gas shift catalyst so that the H_2 to CO ratio in the reactant gases may be adjusted to a desired value, such as 3:1, as previously indicated.

Suitable temperatures and pressure ranges for the process when water is the liquid medium are 175-500°C, preferably 250-400°C and about

By the use of the above described reaction conditions, which may be operated as a continuous process, the product gas is obtained at a temperature only slightly higher than that of the feed gas and this is believed to constitute a very considerable advance on prior art processes. Water and carbon dioxide are removed from the product gas, thus resulting in a gas consisting essentially of methane and a final methanation unit may be used to remove trace quantitites of reactants.

The following is an example of the way in which the invention has been carried out. The example will be described with reference to fig.1 in which a stainless steel tubular reactor 2 contains metal honeycomb monoliths 4 and 5 each having 400 passageways per square inch and a spray head 7. The monoliths 4 and 5 are washcoated with alumina and the washcoating in monolith 4, which constitutes the catalyst unit, is loaded with 0.5 grams of ruthenium metal.

Reacting gases generally designated 1 and comprising synthesis gas having a H_2 : CO ratio of approximately 3:1 enter the catalyst unit 4 at a temperature of 400°C and a pressure of 75 p.s.i.

The temperature of the gases rises considerably in unit 4 due to the highly exothermic nature of the catalytic reactions which ensue there and on leaving unit 4 the hot gases enter the "contact" unit 5. Water under pressure is introduced into the reactor through a tube 6 and is sprayed on to the support 5 by the nozzle 7.

The rate of supply of water through nozzle 7 is adjusted by trial and experiment to form a thin layer over the surfaces of the honeycomb unit 5 up to about boundary line 8, and to be evaporated by contact with the hot gases so that when line 8 is the water has been completely evaporated. Boundary line 8 is a line drawn somewhat short of the end of contact unit 5 and the reaction conditions are adjusted so that the remainder of the contact unit 5 remains free of liquid water.

Values of CO conversion and of the selectivity of the reaction to CH_4 obtained under the conditions just described are set forth in Table 1.

TABLE 1

Reactant Ratio (H_2:CO:H_2O)	Total CO Conversion (vol.%)	CH_4 Selectivity (i.e. proportion of CO converted to CH_4) (vol.%)
3:1:0	66	81
3:1:2	73	59
3:1:5	75	44
3:1:10	77	34
3:1:15	74	29

In practice, reactant gases may be re-cycled more than once through a reactor of the type illustrated in fig.1 or they may be led to further reactor units arranged in tandem. In this latter case, the catalyst units of subsequent reactors may have higher ruthenium metal contents than in the earlier units.

Other types of washcoated supports may of course be used in the catalyst and contact units other than the metal supports described. Ceramic honeycomb supports supplied by Corning Glass under the name "CERCOR" (Registered Trade Mark) or by E.I. du Pont de Nemours under the name "TORVEX" (Registered Trade Mark) may be used.

Further, alternatives to ruthenium metal catalysts include Ni or Fe or Ni-Fe alloys for the initial catalytic unit although ruthenium metal is probably advantageous for the subsequent zones where the steam concentration is higher.

It will be appreciated that when the cooling liquid is evaporated in the contact unit by the hot gases, the space velocity of the gas stream increases. In the example described with reference to fig.1 for example, the space velocity increased in the contact unit from 60000 hr^{-1} to 90000 hr^{-1}.

CLAIMS

1. A process for the methanation of synthesis gas, comprising reacting together CO, CO_2 and H_2 by successive contact steps thereof with

(a) a catalyst comprising a solid support having deposited thereon a metal selected from the group consisting of Fe, Co. Ni, Cu, W, Ru, Rh, Pd, Ir, Pt, alloys of the said metals with each other and alloys containing an aggregate of at least 10% by weight of one or more of the said metals with other metals, and

(b) an inert body or assembly of bodies having a substantial surface area with which the gases make contact subsequent to their contact with the said catalyst, the said inert body or assembly of bodies having sprayed on to it or them a liquid medium which removes heat from the gases and thereby has its temperature raised and/or is evaporated, the rate of supply of the liquid medium, its specific heat, its latent heat or vaporisation and the other conditions of the process being such that the temperature of the gas emerging from the body or assembly of bodies is not higher than 600°C and that the entire quantity of liquid medium is evaporated before its passage along the inert body or assembly of bodies is complete.

2. A process according to Claim 1 wherein successive contact steps (a) and (b) are repeated by recycling

or passing the gas mixture through a number of zones containing supported catalyst and sprayed inert bodies.

3. A process according to Claim 1 or Claim 2 wherein the liquid medium has a latent heat of vapourisation falling within the range 150- 600 calories per gram.

4. A process according to Claim 1 or Claim 2 wherein the liquid medium is water.

5. A process according to any preceding claim wherein the catalyst comprises ruthenium and/or nickel or alloys of one or other or both of these metals with other metals.

6. A process according to Claim 5 wherein the catalyst ketal(s) or alloy(s) is/are deposited upon a particulate support.

7. A process according to Claim 6 wherein the support is made from alumina or granular silica.

8. A process according to Claim 7 wherein the catalyst support is a ceramic or metallic monolith containing a plurality of flow channels having thereon a layer of alumina.

9. A process according to Claim 8 wherein the monolith

is in the form of a honeycomb.

10. A process according to any preceding claim, wherein the catalyst (a) is preceded by a unit containing a water gas shift catalyst so that the H_2 to CO ratio in the reactant gases may be adjusted to a value of 3:1.

11. A process according to Claim 4 wherein the reaction is carried out at a temperature falling within the range of 175-500°C and at a pressure falling within the range of 70-2000 p.s.i.

12. A process for the methanation of synthesis gas substantially as hereinbefore described.

13. A rocess according to any one of Claims 1 to 4 or 6 to 12 wherein the catalyst comprises nickel, or iron or alloys of one or other or both of these metals with other metals.

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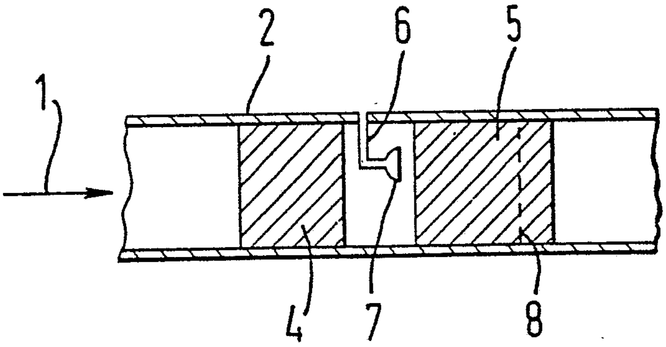

FIG.1

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 78/00040

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

C 07 C 9/04, C 07 C 1/02

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
Int.Cl.^{2}	C 07 C 1/02, C 07 C 1/04, C 07 C 1/12, C 07 C 9/00, C 07 C 9/02, C 07 C 9/04.

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
	Catalysis Reviews, Vol. 8, N° 2, 1973, New York, G.A. Mills et al., "Catalytic methanation", pages 159-210, see pages 181-206 --	1,5-7,11-13
	US, A, 3988334, published 26th October 1976, see claims, Finch et al. --	1,5-7,11-13
A	DE, A1, 2506199, published 13th November 1975, see pages 3-7, 12-13; figure, Air Products and Chemicals --	1,5-7,11-13
A	US, A, 2248734, published 8th July 1941, see pages 2,3; figure, F.T. Barr ------	1,2,12,13

* Special categories of cited documents: [15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 14th February 1979	Date of Mailing of this International Search Report [2] 21st February 1979
International Searching Authority [1] European Patent Office	Signature of Authorized Officer [20] G. L. M. KRUYDENBERG

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