PATENT SPECIFICATION

Inventors: RUDOLF WENDLANDT and GERHARD HOFFMANN

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COMPLETE SPECIFICATION

Improved process for the production of Methane and Methane Mixtures from Carbon Monoxide and Hydrogen

We, LONZA ELEKTRIZITATSWERKE UND CHEMISCHE FABRIKEN AKTIENGESELLSCHAFT, a Joint Stock Company, organised under the Laws of the Confederation of Switzerland, of 72, Aeschenvorstadt, Basel, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known to produce methane by catalytic reaction of carbon monoxide and hydrogen. This reaction has hitherto generally been carried out in accordance with the equation:

$$CO+3H_2=CH_4+H_2O \qquad (I)$$

and takes place from about 250°—300° C. with considerable evolution of heat. The high exothermy necessitates cooling of the catalyst, which it is difficult to carry out on a large industrial scale. However, increased temperatures not only unfavourably displace the equilibrium, but at the same time lead to a partial decomposition of the carbon monoxide in accordance with the equation:

$$2CO=C+CO_2 \qquad (II),$$

whereby the catalyst rapidly becomes unusable owing to the separation of carbon.

Attempts have therefore been made to avoid this disturbing subsidiary reaction either by employing at least 5 parts by volume of hydrogen and more, whereby only a gas mixture with methane and hydrogen is obtained in the ratio of, at the most, 1:2, or by admixing water vapour with the starting gas in order to remove the carbon or to prevent the separation of carbon. For controlling the reaction temperature alone, it has also already been proposed to return the gas mixture containing methane without altering the fundamental working conditions described. In such cases, the necessary high hydrogen excess, which even in theory is $3H_2$ and in practice is generally over $5H_2$ to 1CO, is particularly disturbing in practice, especially as hydrogen is only obtained in a considerably lower quantity by volume in relation to the carbon monoxide in technical gases containing carbon monoxide (for example water gas), while on the other hand the additional production of hydrogen is costly and is impossible without special expensive means

Having regard to these facts, it is surprising and highly noteworthy that it has been found possible according to the invention to overcome these difficulties in the technical production of methane and in particular, despite hydrogen concentrations in which the mixing ratio of H_2 to CO is substantially less than 3:1, to discover an advantageous continuous process without separation of carbon at the contact. The new method of operation consists of catalytically converting into methane carbon monoxide and hydrogen, or mixtures containing the said substances in a ratio of substantially less than $3H_2$ to 1CO, and returning the reaction mixture formed, in a volume at least equal to the volume of the fresh gas and amounting more especially to 2—6 times the quantity of fresh gas, into the fresh gas containing carbon monoxide and hydrogen at temperatures above 100° C., the said fresh gas being in turn so preheated by the heat exchange with the unreturned fraction of gas that, after combination with the return gas, it flows to the catalyst at temperatures of from 200°

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to 300° C.

The invention accordingly concerns a cyclic process in which the hydrogen concentrations are adjusted to relatively low values which have hitherto not been usual in practice and which have been regarded as extremely objectionable owing to the danger of the separation of carbon, and the avoidance of which has been regarded as necessary, and considerable quantities of the reaction mixture are returned at temperatures which do not necessitate a separation of water, and in addition the temperatures of the returned and escaping gas fractions are specially controlled and adjusted, the waste heat being utilised by heat exchange.

While the separation of carbon in accordance with Equation II has hitherto constituted a serious problem, obviously due to local overheating, and has had to be prevented by special steps which unfavourably influence the equilibrium conditions, it has surprisingly been found possible, by means of the relatively large quantity of gas returned, to moderate the temperatures and to prevent even local temperature excesses which might cause separation of carbon. This is even more surprising since, not only is the great hydrogen excess, which has a heat-dissipating effect owing to the fact that its heat conductivity is several times greater, avoided and even reduced to below the concentration theoretically considered necessary, but even under these conditions a partial reaction according to the equation:

$$2CO + 2H_2 = CH_4 + CO_2 \qquad (III)$$

occurs, the exothermy of which is even greater than that of Equation I (59 kcal as against 49 kcal in Equation I).

Moreover, owing to the particular nature of the waste gas economy and of the circulation without any additional external heat supply, it is possible for the gas to be fed to the catalyst at temperatures of from 200° to 300° C. if the fresh gas is correspondingly preheated by heat exchange with the unreturned gas fraction and is then mixed with the return gas which is still at a temperature of more than 100° C.

In a particularly advantageous embodiment of the process, heat is extracted from the reaction mixture before the returned fraction is branched off—preferably with generation of useful steam—and is employed to operate a steam generator, a waste heat boiler or the like. Despite the circulation with heating of the fresh gas by the admixture of hot or still warm reaction mixture, it is thus possible to utilise a substantial proportion of the waste heat with steam generation and to feed it to a steam supply system.

The new process is carried out, for example, by mixing the fresh gas with at least an equal volume of still warm or hot return gas and thereby preheating it to 200°—300° C. at which temperature the gas mixture is fed to the catalyst. On leaving the catalyst, the reaction mixture has a temperature of 300°—400° C., or more and is then generally guided through a waste heat boiler in which it generates useful steam. The reaction mixture leaving the steam generator can then yield, in a further heat exchanger, further heat which is employed to preheat the fresh gas.

Under the operating conditions according to the invention, partial reaction according to Equation III will always occur, since the hydrogen concentration is insufficient even theoretically for Equation I. For example, only 2.7 parts by volume of H_2 to 1 part by volume of CO are employed, or this quantity is made even smaller.

A particular embodiment of the process resides in feeding the fresh gas with very considerably less than $3H_2$ to 1CO, more especially only 1.1—1.5 H_2 to 1CO. In this case, the reaction takes place predominantly or mainly in accordance with Equation III, with the formation of methane and carbon dioxide. In all cases, water vapour is only present either in small proportions or up to considerable concentrations. It has surprisingly been found that even in the latter case (i.e. when Equation I predominates) the return of the hot gas mixture can be effected without the separation of water, whereas having regard to the equilibrium conditions a disadvantageous effect should have been expected therefrom. It was not to be foreseen that this separation of water with considerable cooling even of the fraction to be returned can be avoided and is unnecessary under the special working conditions of the invention.

The gas mixture fed to the catalyst is preferably preheated to temperatures between 230° and 270° C. the said preheating being obtained more especially by heat exchange with the reaction mixture coming from the catalyst or from a waste heat boiler connected beyond the catalyst. Here again, no special preheater is generally required, and the fresh gas is simultaneously so diluted that the temperature beyond the catalyst can be maintained at 350° to 450° C. The quantity of circulating gas amounts, for example, to 2.5 times the volume of fresh gas or the admixed quantity of circulating gas is made even higher.

In accordance with the invention a preferred embodiment affording optimum heat economy and circulation of the quantities of gas consists in returning the reaction mixture after it has passed through the steam boiler and is in part still warm, into the fresh gas leaving a heat exchanger, while the other part of the reaction gas flows through the same heat exchanger and heats the fresh gas, the steam boiler first mentioned being so dimensioned and operated that the issuing hot gas, together with the preheated fresh gas has the temperature necessary at the catalyst without any additional external heat supply. It is thus possible by the choice of the operating conditions of the steam boiler to adjust as required the manner of operation of the methane oven and the temperature and concentration conditions in the formation of the methane. The remainder of the waste heat is in this case further utilised to preheat the fresh gas in the following heat exchanger. This special control of the gas paths with circulation of a large quantity of reaction mixture for steam generation constitutes a particularly advantageous novel method of obtaining methane from carbon monoxide and hydrogen, which is of particular importance for the large-scale production of CH_4.

However, in some cases the method of control described above may be modified or only partially employed by withdrawing part of the return gas directly beyond the reaction zone and another part after it has passed through a heat exchanger or steam boiler, at temperatures lying about the dew point. This step is particularly expedient if danger exists of the gas being insufficiently heated before the catalyst or if greater preheating of the quantity of fresh gas is required owing to considerable withdrawal of heat from the reaction zone. In general, however, the method described in the preceding paragraph of utilising the entire hot reaction mixture in a steam boiler will be preferable.

The new process may be further developed by separating carbon dioxide either completely or partially from the reaction mixture before the separation of the circuit gas, or from the circuit gas before or after combination with the fresh gas. In this way, one of the possible reaction products is removed from the gas mixture fed to the catalyst, whereby the yield and the output of the installation are increased. For the separation of carbon dioxide, for example, a process performed at higher temperatures may be employed, for example the carbon dioxide may be removed by combining it with metallic oxides at higher temperatures. It has been found advantageous to remove the carbon dioxide at temperatures below 140° C. and preferably between 90° and 130° C. by means of drying masses containing potassium carbonate in the presence of the existing (or admixed) water vapour or water of hydration, according to the reaction:—

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3$$

This method of removing carbon dioxide, for example, by means of granules presenting large surfaces containing K_2CO_3 has the particular advantage of simultaneously combining a quantity of water vapour from the gas mixture equal to the quantity of carbon dioxide and thus at the same time removing two of the components which disturb the equilibrium conditions. In this case, there is removed from the two components, i.e. water and carbon dioxide, a quantity of the component of which the larger quantity is present, which is equal to the quantity of the component of which the smaller quantity is present, that is to say, in the case of gas mixtures in which the ratio of H_2 to CO is nearer to 3:1, the entire carbon dioxide is removed with the formation of bicarbonate, while in the case of gas mixtures in which the hydrogen concentration is more nearly equal to the CO concentration the entire quantity of water vapour is removed. In both cases, an advantageous effect on the adjustment of the equilibrium is obtained without the temperatures having to be reduced to below 140° and more especially below 100° C.

In all other respects, all the other known processes for the separation of carbon dioxide may be employed, for example those in which alkazide solutions, aqueous alkali carbonate solutions, pressure washing and the like are employed. In some cases, methods may be employed by which the carbon dioxide can be separated at higher temperatures, for example by the use of hot alkazide solutions or ethanolamines, warm alkali carbonate solutions and the like, so that part of the heat content of the circuit gas is returned into the fresh gas. This method of operation is advantageous if the water vapour content of the gas mixture is not thereby increased.

The new process will be more fully understood from the following example:

EXAMPLE.

A fresh gas mixture a of the following compositions:

	CO_2	CO	H_2	CH_4	N_2	H_2O
Vol.: %	0,69	31,85	43.65	0.98	20.87	1.96

in which, therefore, the ratio of H_2 to CO amounted to 1.37:1, was mixed at normal temperature (20° C.) in a quantity of 1000 litres (referred to dry gas in the normal state, i.e. 0° C. under 760 mm. Hg) or 1020 litres (calculated as moist gas under normal conditions) with a hot circuit gas b which will hereinafter be defined and passed together therewith over a Ni—Mn—Al catalyst which contained these elements in the proportion of 10:2:1. About 1 litre of this catalyst was employed to 1000 litres of fresh gas per hour. The gas admission temperature before the catalyst amounted to 260° C., while the gas temperature beyond the catalyst amounted to 410°—430° C.

The gas mixture leaving the catalyst had the following composition:

	CO_2	CO	H_2	CH_4	N_2	H_2O
% by vol.	21.88	0.93	5.21	29.40	32.51	10.07

and the quantity thereof amounted to 3323 litres (calculated at 0° C. under 760 mm. Hg.—moist). This total quantity of gas was passed through a steam boiler (waste heat boiler) situated beyond the contact chamber and was in this case cooled from about 420° to 340° C. while generating useful steam.

Beyond the steam boiler, the circuit gas b was branched off, without previous separation of water in a quantity of 2669 litres and was fed at a temperature of about 330° C. to the fresh gas a, which was only at room temperature, so that the ratio of circuit gas to fresh gas amounted to 2.62:1 (or 2.4:1 referred to dry gases). By this quantity and temperature of admixed gas, the fresh gas was heated to 260° C. without additional heating, and the entire quantity of gas $a+b=3689$ litres was fed continuously to the catalyst at 260° C. and left it at 410° to 430° C.

That portion of the gases leaving the catalyst (3323 litres) which was not circulated, that is to say $3323-2669=654$ litres, was continuously withdrawn as useful gas. This gas was cooled to 14° C. by cooling water, whereby the water separated off. Referred to dry gas, 588 litres of useful gas were obtained, which had the following composition:

	CH_4	CO_2	CO	H_2	N_2	Total
Litres:	192	143	6	34	213	588

As will be seen from the large quantity of carbon dioxide, the reaction took place for the greater part, not in accordance with Equation I, but in accordance with the equation:

$$2CO+2H_2=CH_4+CO_2 \qquad (III)$$

The yield is very high in accordance with the small quantities of CO and H_2. Calculated on the basis of nitrogen-free gas, the CH_4 content is 51%, and after removal of the carbon dioxide by washing-out or absorption processes, by which it can be recovered in useful form, the methane content amounts to more than 82% CH_4.

The production of useful steam is further increased if the useful gas is cooled, not with water, but by heat exchange with the fresh gas. The gas mixture leaving the contact at 420° C. can then be cooled to about 285° C. in the steam boiler and is admixed at about 275° C. with the preheated fresh gas. The preheating is effected by heat exchange with the useful gas, which is thereby cooled to 40° C. with condensation of water, while the fresh gas leaves the heat exchanger at about 210° C. After the admixture of the circuit gas at a temperature of 275° C., the gas mixture again flows to the contact at 260° C. The aforesaid temperatures are to be regarded as approximate figures; since fluctuations may occur in the composition of the gas according to the efficiency of the heat exchange, and the heat insulation of the installation and pipes.

In the accompanying drawing, in which A is the contact chamber, B the steam boiler and C a heat exchanger, the cyclic process hereinbefore described is diagrammatically illustrated.

The reaction conditions illustrated in the drawing apply to a relatively pure hydrogen-carbon-monoxide mixture *a*. This mixture enters at (1) one part of the heat-exchanger C and is mixed at 2 with a CH_4—CO2—H_2O circuit mixture *b*. Mixing can take place in a special mixer or with simultaneous or separate introduction into the contact chamber A. The ratio of fresh gas *a* to circuit gas *b* is 1:4,33 in the process illustrated in the drawing. On leaving the contact chamber A, the reaction gas obtained flows in the direction of the arrow through a steam-boiler B and on leaving the said boiler at 3 is separated into two streams of gas. One gas stream *b* is returned to the point 2 before the contact chamber A. The unreturned fraction is guided at 4 into the heat-exchanger C in which reaction water is separated off. The useful gas obtained is withdrawn at 5 and if necessary freed from carbon dioxide. A high-percentage methane is obtained.

What we claim is:—

1. A cyclic process for the catalytic production of methane from carbon monoxide and hydrogen, characterised in that substantially less than three parts of H_2, for example only about 1.1:1.5 parts of H_2, are employed to 1 part of CO., the gas mixture thus composed is catalytically converted into methane, and the reaction mixture thus formed is admixed with fresh gas consisting of carbon monoxide and hydrogen in a volume a least equal to the volume of fresh gas, and the gas mixture thus obtained is fed to the catalyst at temperatures of about 200° to 300° C.

2. A process according to Claim 1, characterised in that the quantity of reaction gas (return gas) branched off is fed to the fresh gas in a quantity amounting to several times, for example from 2—6 times the quantity of fresh gas.

3. A process according to Claim 1 or 2, characterised in that the fresh gas is preheated by heat exchange with the unturned fraction of the reaction gas.

4. A process according to any one of Claims 1 to 3, characterised in that the return gas is introduced at temperatures of more than 100° C. into the fresh gas consisting of carbon monoxide and hydrogen.

5. A process according to any one of Claims 1 to 4, characterised in that heat is extracted from the reaction gas mixture before the fraction to be returned is branched off, and is utilised, for example, to generate steam.

6. A process according to any one of Claims 1 to 5, characterised in that the gas mixture is preheated before reaching the catalyst to temperatures between about 230° and about 270° C., more especially by heat exchange with the reaction mixture coming from the catalyst or from a waste heat boiler situated beyond the catalyst.

7. A process according to any one of Claims 1 to 6, characterised in that the reaction mixture, after passing through a steam boiler, is returned while in part still warm into the fresh gas leaving a heat exchanger, while the other part of the reaction gas flows through the same heat exchanger and in doing so heats the fresh gas, the steam boiler being so dimensioned and operated that the issuing hot gas, together with the preheated fresh gas, has the gas temperature required before reaching the catalyst without any additional heat supply.

8. A process according to any one of Claims 1 to 7, characterised in that part of the return gas is withdrawn directly beyond the reaction zone, and another part is withdrawn after passing through a heat exchanger or steam boiler, at temperatures above the dew point.

9. A process according to any one of Claims 1 to 7, characterised in that, the carbon dioxide of the reaction gas mixture is completely or partially withdrawn before the separation of the return gas or the carbon dioxide of the return gas is completely or partially withdrawn from the return gas before or after the combination thereof with the fresh gas.

10. A process according to any one of Claims 1 to 9, characterised by the use of a catalyst containing nickel, manganese and aluminium in the proportions of 10:2:1.

11. A cyclic process for the catalytic production of methane substantially as described in the foregoing Example.

12. Methane produced by the process claimed in any one of the preceding claims.

LONZA ELEKTRIZITATSWERKE
UND CHEMISCHE FABRIKEN
AKTIENGESELLSCHAFT.
Per: Boult, Wade & Tennant,
111/112, Hatton Garden, London.
E.C.1,
Chartered Patent Agents.

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1 SHEET

This drawing is a reproduction of the Original on a reduced scale.