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(54) **Title**: PROCESS FOR THE PRODUCTION OF METHANE RICH GAS

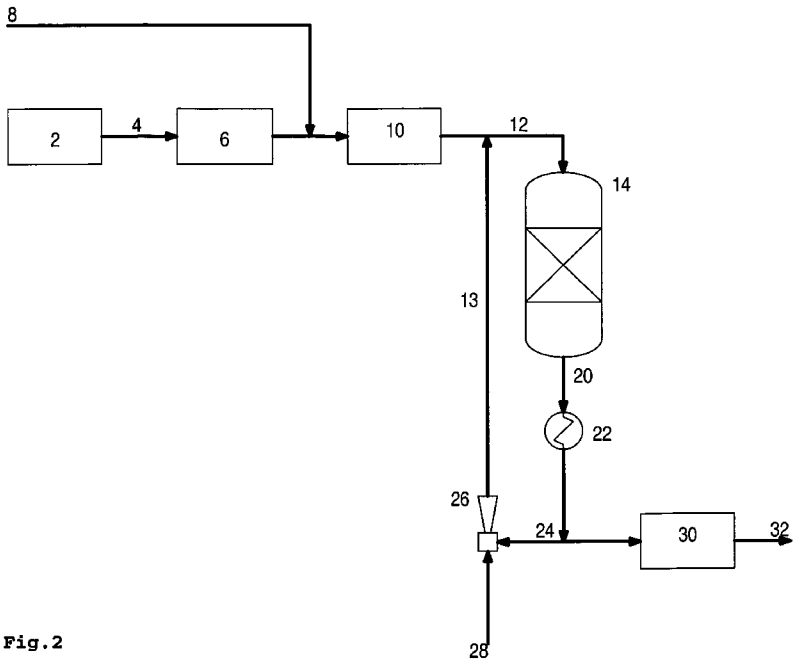

Fig.2

(57) **Abstract**: A process is disclosed for production of a methane rich product gas comprising the steps of (a) providing a feed comprising carbon oxide such as carbon monoxide and/or carbon dioxide, hydrogen and at least 1% C2+ hydrocarbons. (b) adding a flow comprising steam to said feed forming a reacting feed mixture, (c) reacting said reacting feed mixture in the presence of a catalyst forming a product gas rich in methane (d) withdrawing the methane rich product gas wherein the ratio of water molecules to carbon atoms in higher hydrocarbons, S/HHC, is below 25, the maximum catalyst temperature T is at least 460°C, preferably at least 480°C, and even more preferably 500°C, and the maximum catalyst temperature is less than the critical carbon formation temperature for the S/HHC value for said catalyst. In a preferred embodiment the recycle is driven by an ejector with steam feed as motive gas.

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Title: PROCESS FOR THE PRODUCTION OF METHANE RICH GAS

The present invention relates to a process for the production of substitute natural gas (SNG) from carbonaceous materials. Particularly the invention relates to a process for the production of SNG from a carbonaceous material in which the carbonaceous material is converted to a synthesis gas, and mixed with an amount of steam and a recycled stream prior to a methanation reaction, and the steam addition is made in an ejector withdrawing the recycle stream from the product stream rich in methane.

The low availability of fossil liquid and gaseous fuels such as oil and natural gas has revived the interest in developing technologies capable of producing combustible gas synthetically from widely available resources such as coal, biomass as well as off-gasses from coke ovens. The produced gas goes under the name substitute natural gas or synthetic natural gas (SNG) having methane as its main constituent.

Coke is a solid fuel produced from coal, by baking the coal in an airless furnace. During coke production, volatile coal constituents are driven off, purified and an off-gas comprising i.e. one or both of carbon dioxide and carbon monoxide, as well as hydrogen and hydrocarbons is produced. This coke oven off-gas is energy rich, and may often be combusted for generation of heat, e.g. for heating the coke furnace, when coke is produced in relation to steel works. However, especially when coke is produced as a solid fuel in a plant without other requirements for energy, excess off-gas may be available.

In relation to gasification of biomass or waste, similar gases comprising carbon oxides, hydrogen and hydrocarbons may also be produced.

In such production of substitute natural gas from a feed gas comprising hydrocarbons with 2 or more carbon atoms (C2+hydrocarbons), there is a significant risk that the presence of C2+hydrocarbons results in formation of carboneous material, which may damage the methanation catalyst.

Therefore, there has been a prejudice against the use of gases rich in C2+hydrocarbons for methanation, and even with operating conditions with minor amounts of C2+hydrocarbons present, a significant safety margin has been implemented, at the cost of i.e. reactor size.

In the prior art it is known to operate the methanation reactor with a noble metal catalyst at elevated temperatures. On such a more expensive catalyst carboneous whisker formation is absent, and this enables operation at increased temperatures, with limited potential of carbon formation.

The methanation process of carbon oxides with hydrogen is exothermal, so after activation of the process, the process will proceed towards equilibrium with significant heat development. An increased allowable temperature of the catalyst will thus allow for increased concentrations of carbon oxides in the reactor feed, and thus reduced reactor volume.

We have now surprisingly found that by careful analysis of thermodynamics and reaction conditions, it is possible to identify an optimal reaction window, by combination of temperature control and steam addition.

We have further found that the use of an ejector for driving the recycle of product gases, is especially beneficial in the case of presence of C2+hydrocarbons, as the effect of increased steam addition via an ejector will have an effect of increased recycle, and the combined increase in steam addition and recycle will have a synergistic effect in reducing the carboneous material formation.

It has now been found by us that the operational range for the process is surprisingly expanded by selection of the temperature in the range close to the carbon formation curve, while the ratio between steam and higher hydrocarbons is kept in an intermediate range.

The temperature of the reactants and products will increase during the passage through a catalyst bed in an adiabatic reactor. On the other hand, such increasing temperature will tend to displace the equilibrium towards lower methane concentration. Consequently, complete or close to complete reaction will only be possible if the temperature increase is limited by cooling the reacting gas in one way or another, for instance by recycling of cooled product gas, as it is disclosed in US 4,130,575.

It is well known that the temperature of the methanation reaction may be controlled by addition of steam to the

synthesis gas, as disclosed e.g. by application EP 2 110 425. Such a steam addition, especially in the case of a feed comprising higher-hydrocarbons (C>1), has the effect of reducing whisker carbon formation, which potentially may damage the catalyst.

We have found that by feeding the steam through an ejector drawing a recycle stream of the methane rich product gas into the syngas feed comprising CO and/or CO_2 and H_2 a reduced amount of steam is required by such a recycling.

The extraordinary effect of the combination of steam addition, recycling and use of a steam driven ejector for providing the recycle is that the use of an ejector not only utilizes the pressure difference between the steam and the syngas to drive the recycle, but also at the same time reduces outlet temperature and increases the steam to higher hydrocarbon ratio which is very important to avoid carbon formation.

As used herein the terms "C2+ hydrocarbons" and "higher hydrocarbons" mean any hydrocarbon and/or oxygenate comprising at least 2 carbon atoms.

As used herein the term "S/HHC" indicates the "steam to higher hydrocarbon ratio", and is calculated as the ratio between the number of moles of water and the number of moles of carbon atoms comprised in C2+ hydrocarbons, both taken at the inlet of the catalytic reactor. The term steam to carbon in higher hydrocarbons ratio shall be used with the same meaning. Actually there will be some formation of water in the reactor prior to the reaction of the C2+

hydrocarbons, so the true critical "S/HHC" values to be evaluated is in practice the values corresponding to inlet concentrations of higher hydrocarbons and outlet concentrations of water.

As used herein critical S/HHC value shall mean an S/HHC value for a given temperature and a given catalyst, for which S/HHC value below the critical S/HHC value gives a significant increased risk of carbon formation on the catalyst.

As used herein critical temperature shall mean a temperature for a given S/HHC ratio and a given catalyst, for which temperatures above the critical temperature gives a significant increased risk of carbon formation on the catalyst.

As used herein critical temperature vs. S/HHC curve or carbon formation curve shall mean a curve corresponding to temperatures and S/HHC ratios for a given catalyst, for which temperatures and S/HHC ratios above the critical temperature and/or below the S/HHC ratio gives a significant increased risk of carbon formation on the catalyst.

In its broadest form the invention involves
A process for production of a methane rich product gas comprising the steps of
(a) providing a feed comprising carbon oxide such as carbon monoxide and/or carbon dioxide, hydrogen and at least 1% C2+ hydrocarbons (b) adding a flow of steam to said feed forming a reacting feed mixture, (c) reacting said reacting

feed mixture in the presence of a catalyst forming a product gas rich in methane (d) withdrawing the methane rich product gas wherein the ratio of water molecules to carbon atoms in higher hydrocarbons, S/HHC, is below 25, the maximum catalyst temperature T is at least 460°C, preferably at least 480°C, and even more preferably 500°C, and the maximum catalyst temperature is less than the critical carbon formation temperature for the S/HHC value for said catalyst, with the benefit of providing production of methane, without catalyst deactivation by carbon formation.

In a further embodiment the critical carbon formation temperature for the S/HHC value for said catalyst is determined experimentally with the benefit of establishing operational conditions specifically matching the catalyst analysed.

In a further embodiment the critical carbon formation temperature for the S/HHC value for said catalyst is defined as T_{crit}=425+30*S/HHC with the benefit of providing a prediction of operational conditions without experiments.

In a further embodiment the catalyst comprises nickel as a catalytically active constituent, which is a catalyst with good activity at a moderate price compared to noble metal catalysts such as Ruthenium.

In a further embodiment the catalyst is provided on a support which may comprise alumina, and specifically a combination of one or more of alumina, MgAl spinel, alumina-zirconia, and calcium aluminates with the benefit

of providing a high active surface area, at a moderate cost of expensive metal.

In a further embodiment the flow of steam is added by use of an ejector driven by a recycled stream of product gas with the benefit of not requiring any additional energy for the recycle stream.

In a further embodiment additional carbon dioxide is added to the feedstock with the benefit of optimising the stoichiometric balance in the feedstock, where hydrogen is present in excess.

In a further embodiment the ratio of steam to higher hydrocarbons is kept above 1.5, which has the effect of reducing carbon formation from C2+ hydrocarbons.

In a further embodiment the source of feedstock gas is generated from a carbonaceous material selected from the group consisting of coke, coal, petcoke, biomass, oil, black liquor, animal fat and combinations thereof, which has the benefit that a methane rich gas is produced from what would otherwise be a wasted gas.

Another aspect of the invention involves a reactor system for production of a methane rich product gas from a syngas feed originating from a coke oven, configured for combining said feedstock line with a second feed line into a reactor inlet line being configured for feeding a reactor comprising a methanation catalyst characterised in that said second feed line comprises an ejector configured for having a steam feed as motive gas and a recycled methane

rich product gas as driven gas, with the associated benefit of providing recycle without requiring energy for pumping or requiring a pump with moving parts.

In a further embodiment such a reactor system is configured for operating at a highest catalyst temperature in the range 460-750°C, preferably 500-700°C, and even more preferably 550-650°C. The temperature range balances that an increased catalyst temperature provides the benefit of minimizing the required inert and product flow and thus increases conversion per reactor volume, with the fact that a low temperature drives the product mixture towards increased methane concentration.

In such methanation processes the formation of methane from carbon oxides and hydrogen proceeds quickly to equilibrium in the presence of a catalyst and in accordance with either or both of the following reaction schemes:

$$CO+3H_2 \Leftrightarrow CH_4+H_2O \qquad (1)$$

$$CO_2+4H_2 \Leftrightarrow CH_4+2\ H_2O \qquad (2)$$

These reactions will be coupled to an equilibrium between carbon monoxide and carbon dioxide as follows:

$$CO+H_2O \Leftrightarrow CO_2+H_2 \qquad (3)$$

The net reaction of methane formation whether by reaction (1) or (2) or both will be highly exothermic.

It is known from the field of steam reforming that catalysts and equipment exposed to a syngas atmosphere may form carbon if certain elements such as nickel or noble metals are present in the material formulation. The most common types of carbon are: Whisker carbon, gum or encapsulating carbon and pyrolitic carbon. The type of carbon is highly dependent on the operating temperature and ultimately the formation of carbon is determined by the combination of: material formulation, feedstock, temperature, and steam content. The potential for carbon formation from simple molecules can be evaluated considering the thermodynamics of the following reactions:

$$CH_4 \Leftrightarrow C(s) + 2H_2 \quad (4)$$

$$2CO \Leftrightarrow C(s) + CO_2 \quad (5)$$

$$CO + H_2 \Leftrightarrow C(s) + H_2O \quad (6)$$

While the potential for formation of carbon from higher hydrocarbons is a kinetic competition between carbon formation and steam reforming according to the reaction below:

$$C_nH_m \Rightarrow \text{Olefins} \Rightarrow C(s) \quad (7)$$

$$C_nH_m + nH_2O \Rightarrow nCO + (n+\tfrac{1}{2}m)H_2 \quad (8)$$

The formation of carbon takes place after an induction period t_0 reflected by the kinetics, and subsequently carbon grows at a constant rate: $\frac{dC_w}{dt} = k_c(t - t_0)$. The risk of carbon formation may be assessed by the critical steam to C2+ hydrocarbon ratio $(S/HHC)_{Crit}$, which decreases with temperature and depends on the type of hydrocarbon and the

type of catalyst applied. Thus, in order to avoid carbon formation the potential must be assessed at all points using thermodynamics for simple molecules and for higher hydrocarbons the steam to higher hydrocarbon ratio must be kept above the critical steam to higher hydrocarbon ratio at the operating temperature for any point in the reactor.

For methanation purposes the same principles to assess the potential for carbon formation will apply as described above for steam reforming applications, but the means to control the operating window will deviate significantly. While the methane steam reforming reaction (reverse (1)) is highly endothermic, heat is supplied externally and reaction at the excessive temperatures, which may lead to carbon formation can be avoided by the external heat supply, the methanation reaction (forward (1)) is highly exothermic, and the heat release from the reaction must be controlled in order not to exceed a critical combination of maximum operating temperature and minimum steam to higher hydrocarbon ratio, when higher hydrocarbons are present in the feedstock. Alternatively, the steam content must be adjusted in order to stay above the critical steam to higher hydrocarbon ratio, for the operating temperature.

Several means exist to control the temperature increase; operation in a cooled reactor, dilution of reactants, operation under sub-stoichiometric conditions and recycling of the product stream.

Recycling may be provided using rotary equipment or static installations such as an ejector.

Particularly the use of recycling by addition of steam via an ejector is attractive, since steam can be used to drive the ejector recycling the product stream, without additional consumption of energy. Thus, using an ejector allows for a combined adjustment of temperature and steam content in the feed in order not to exceed a critical combination of operating temperature and the critical steam to higher hydrocarbon ratio, when higher hydrocarbons are present in the feedstock.

The optimal operating window for a methanation process of feedstock containing higher hydrocarbons has been determined and it is defined by the relationship between the operating temperature and the critical steam to carbon in higher hydrocarbon ratio, which is catalysts dependent and requires a certain safety margin, and an upper temperature limit defined by the methane decomposition (4).

These conditions are a major breakthrough from the known conditions, where operating temperatures above 500°C have been associated with S/HHC ratios of far above 30, and thus for synthesis gases with C2+hydrocarbon content beyond minor impurities the requirements have in practice been prohibitive.

In an embodiment of the present disclosure illustrated in Fig.2, a coke oven gas 4 originating from a coke oven 2 is optionally cleaned in 6, optionally mixed with secondary feedstocks 8, and optionally further purified in 10, before forming a feedstock which is combined with a flow comprising steam 16, and directed as a reacting feed mixture 12 to an inlet of a reactor 14 comprising a

catalyst in the presence of which a methanation reaction takes place. From the reactor a methane rich product gas 20 is withdrawn. The gas compositions and temperatures are defined such that the conditions indicated in Fig.1 are fulfilled, possibly by cooling e.g. in a heat exchanger 22.

In a preferred embodiment a recycled stream of product gas 24 is withdrawn from the cooled methane rich product gas.

In a further preferred embodiment, the recycled stream of product gas is directed to an ejector 26 in which steam 28 may be used as a motive gas, and the recycled stream of product gas is driven gas forming the flow comprising steam 16 from the steam and the recycled stream of product gas

The methane rich product gas which is not recycled may be directed to final methanation 30 forming a synthethic natural gas 32.

For a commercial catalyst A the following experimental procedure has determined the upper level of the operational range:

1. Catalyst was loaded in a 35 mm reactor with a total bed height of 200 mm and exposed to a gas mixture comprising 59% CH_4, 43% H_2O, 5.8% C_{2+} and a balance comprising CO, CO_2 and H_2 at 30 barg resulting in a steam to carbon in higher hydrocarbon ratio of 2.38. The linear velocity at the inlet was 8.2 cm/s and the inlet temperature to the reactor was maintained at 500°C for more than 500 hours. The reactor was maintained pseudo adiabatic by compensation heating. Subsequent analysis of the catalyst revealed no signs of

whisker carbon formation. Thus, the conditions were determined to be in the acceptable range of operation.

2. Catalyst was loaded in a 21 mm reactor with a total bed height of 550 mm and exposed to a gas mixture comprising 67% CH_4, 24% H_2O, 6.6% C_{2+} and a balance comprising CO, CO_2 and H_2 at 30 barg resulting in a steam to carbon in higher hydrocarbon ratio of 1.43. The linear velocity at the inlet was 19.5 cm/s and the inlet temperature to the reactor was maintained at 460°C for almost 700 hours. The reactor was maintained pseudo adiabatic by compensation heating. Subsequent analysis of the catalyst revealed no signs of whisker carbon formation. Thus, the conditions were determined to be in the acceptable range of operation.

3. Catalyst was loaded in a 21 mm reactor with a total bed height of 550 mm and exposed to a gas mixture comprising 52% CH_4, 40% H_2O, 5.6% C_{2+} and a balance comprising CO, CO_2 and H_2 at 30 barg resulting in a steam to carbon in higher hydrocarbon ratio of 2.82. The linear velocity at the inlet was 26.8 cm/s and the inlet temperature to the reactor was maintained at 521°C for almost 850 hours. The reactor was maintained pseudo adiabatic by compensation heating. Subsequent analysis of the catalyst revealed no signs of whisker carbon formation. Thus, the conditions were determined to be in the acceptable range of operation.

4. Catalyst was loaded in a 13.5 mm reactor with a total bed height of 10 mm and exposed to a gas mixture comprising 38% CH_4, 59% H_2O, 3.3% C_{2+} and a balance comprising CO, CO_2 and H_2 at 20 barg resulting in a steam to carbon in higher hydrocarbon ratio of 3.94. The linear velocity at the inlet

was 15.9 cm/s and the inlet temperature to the reactor was maintained at 535°C for almost 200 hours. The reactor was maintained pseudo adiabatic by compensation heating. Subsequent analysis of the catalyst revealed no signs of whisker carbon formation. Thus, the conditions were determined to be in the acceptable range of operation.

5. Catalyst was loaded in a 39 mm reactor with a total bed height of 1500 mm and exposed to a gas mixture comprising 53.8% CH_4, 39.9% H_2O, 3.3% C_{2+} and a balance comprising CO, CO_2 and H_2 at 36 barg resulting in a steam to carbon in higher hydrocarbon ratio of 2.75. The linear velocity at the inlet was 18.8 cm/s and the inlet temperature to the reactor was maintained at 525°C for almost 1600 hours. The reactor was maintained pseudo adiabatic by compensation heating. Subsequent analysis of the catalyst revealed significant presence of whisker carbon formation. Thus, the conditions were determined to be outside, but close to the acceptable range of operation.

The experiments above summarizes to the following:

	Whisker free				Whisker
Temperature	460	500	521	535	525
S/HHC	1.43	2.38	2.82	3.94	2.75

By linear regression the upper limit of operation ***T = 30*S/HHC + 425*** was found. In the specific example linear regression of the experimental points was calculated, but more complex equations, such as SSH=A+B/T may be found appropriate, depending on the amount of experimental data.

The operating window is defined by the operating temperature **T** obtained by equilibrating the feed gas according to the methanation reaction, and the steam to carbon in higher hydrocarbons molecular ratio **S/HHC** of the methanation equilibrated gas with unconverted higher hydrocarbons. In the broadest form the new and inventive operating window for methanation covers operation in the presence of at least 1% C2+ hydrocarbons at temperatures above 460°C, a S/HHC ratio below 25 and temperature below ***T = 30*S/HHC + 425***. The experimental results of Table 1 are indicated with "Δ" for whicker free operation and "▲" for operation with whisker formation, together with an indication of the claimed range in Fig.1.

Table 1

Typical composition range for a coke oven off-gas.

Constituent	**Concentration**
H_2	50-60%
CH_4	15-30%
CO	5-12%
CO_2	2-10%
C_2+	1-5%
N_2	2-5%

In the following three examples for production of methane rich gas are presented. The points of operation are also indicated in Fig.1.

In a first example, indicated by "□" in Fig.1, for production of a methane rich gas with temperature control by recycling according to the prior art the process involves operation at a temperature of 450°C. To obtain operation at 450°C by recycle would require a recycle of

446,110 Nm^3/hr, in which case the steam present in the recycle stream for operation provides an S/HHC of 21 at the reactor inlet. The total outlet flow is 546,512 Nm^3/h and 19,084 Nm^3/h methane are produced. This example has the drawback of a large total flow, and of high energy requirements for driving the recycle.

In a second example indicated by "◊" in Fig.1 with steam addition according to the prior art a process for production of a methane rich gas involves operation at an S/HHC ratio of 33. With the stated feedstock, this would result in a temperature of 500°C. In this case, 154 ton steam/hr would be required while 13,558 Nm^3/h methane are produced.

In a third example indicated by "o" in Fig.1 with operation at conditions in the temperature and steam to higher hydrocarbon range according to the invention, and with combined steam addition and recycle, which beneficially may be by use of an ejector, the benefit of the invention is clearly seen, as operation at 600°C becomes possible with a S/HHC ratio of 10, which requires addition of 17 ton steam/hr, driving a recycle of 88,213 Nm^3/hr. This corresponds to same total feed flow as in the first two examples and 15,856 Nm^3/hr methane are produced.

From the examples presented it is clearly seen that the energy required for addition of steam or recycle is significantly lower in the third example according to the invention, and the production capacity is increased. In the third example a small sacrifice in the form of CO_2

production is made due to the higher temperature, but this is outweighed by the reduced steam consumption.

Table 2

	Example		**1**	**2**	**3**
	Target T	°C	450	500	600
	Feed flow	Nm^3/h	100402	100402	100402
	Steam flow	t/h		154	17
	Recycle flow	Nm^3/h	446110		88213
	Outlet flow		546512	291815	210373
Reactor inlet	T	°C	330	330	330
	H_20	Mole%	19.86	65.62	24.30
	CO	Mole%	1.47	2.75	4.10
	CO_2	Mole%	0.96	1.72	3.45
	CH_4	Mole%	48.43	7.35	25.45
	C_2H_6	Mole%	0.29	0.55	0.76
	C_3H_8	Mole%	0.17	0.33	0.45
	S/HHC (HHC in /H2O in)		18	32	8
Reactor outlet	T	°C	450	500	600
	H_20	Mole%	24.31	71.75	33.21
	CO	Mole%	0.00	0.06	0.66
	CO_2	Mole%	0.05	1.95	2.52
	CH_4	Mole%	54.52	12.65	36.38
	C_2H_6	Mole%	0.00	0.00	0.00
	C_3H_8	Mole%	0.00	0.00	0.00
	S/HHC (HHC in /H2O Out)		21	33	10
	Net CH_4 production	Nm^3/h	19084	13558	15856

CLAIMS

1. A process for production of a methane rich product gas comprising the steps of
(a) providing a feed comprising carbon oxide such as carbon monoxide and/or carbon dioxide, hydrogen and at least 1% C2+ hydrocarbons,
(b) adding a flow comprising steam to said feed forming a reacting feed mixture,
(c) reacting said reacting feed mixture in the presence of a catalyst forming a product gas rich in methane
(d) withdrawing the methane rich product gas
wherein the ratio of water molecules to carbon atoms in higher hydrocarbons, S/HHC, is below 25,
the maximum catalyst temperature T is at least 460°C, preferably at least 480°C, and even more preferably 500°C, and
the maximum catalyst temperature is less than the critical carbon formation temperature for the S/HHC value for said catalyst.

2. A process according to claim 1, wherein the critical carbon formation temperature for the S/HHC value for said catalyst is determined experimentally.

3. A process according to claim 1, wherein the critical carbon formation temperature for the S/HHC value for said catalyst is defined as $T_{crit}=425+30*S/HHC$.

4. A process according to any claim above, wherein the catalyst comprises nickel as a catalytically active constituent.

5. A process according to any claim above, wherein the catalyst is provided on a support comprising alumina.

6. A process according to claim 5, wherein the support comprises one or more constituent from the group consisting of alumina, MgAl spinel, alumina-zirconia and calcium aluminates.

7. A process according to any claim above, wherein the flow of steam is added as motive gas in an ejector driving a recycled stream of product gas.

8. A process according to any claim above, wherein additional carbon dioxide is added to the feedstock.

9. Process according to any claim above, operating at a steam to higher hydrocarbons ratio above 1.5.

10. Process according to any claim above, wherein the feedstock gas is generated from a carbonaceous material selected from the group consisting of coke, coal, petcoke, biomass, oil, black liquor, animal fat and combinations thereof.

11. Process according to any claim above, operating at a steam to higher hydrocarbons ratio above 1.5.

12. Reactor system for production of a methane rich product gas from a feedstock originating from a coke oven, configured for combining said feedstock line with a second feed line into a reactor inlet line being configured for feeding a reactor comprising a methanation catalyst characterised in that said second feed line comprises an ejector configured for having a steam feed as motive gas and a recycled methane rich product gas as driven gas.

13. A system according to claim 13, operating at a highest catalyst temperature in the range 460-750°C, preferably 500-700°C and even more preferably 550-650°C.

Fig.1

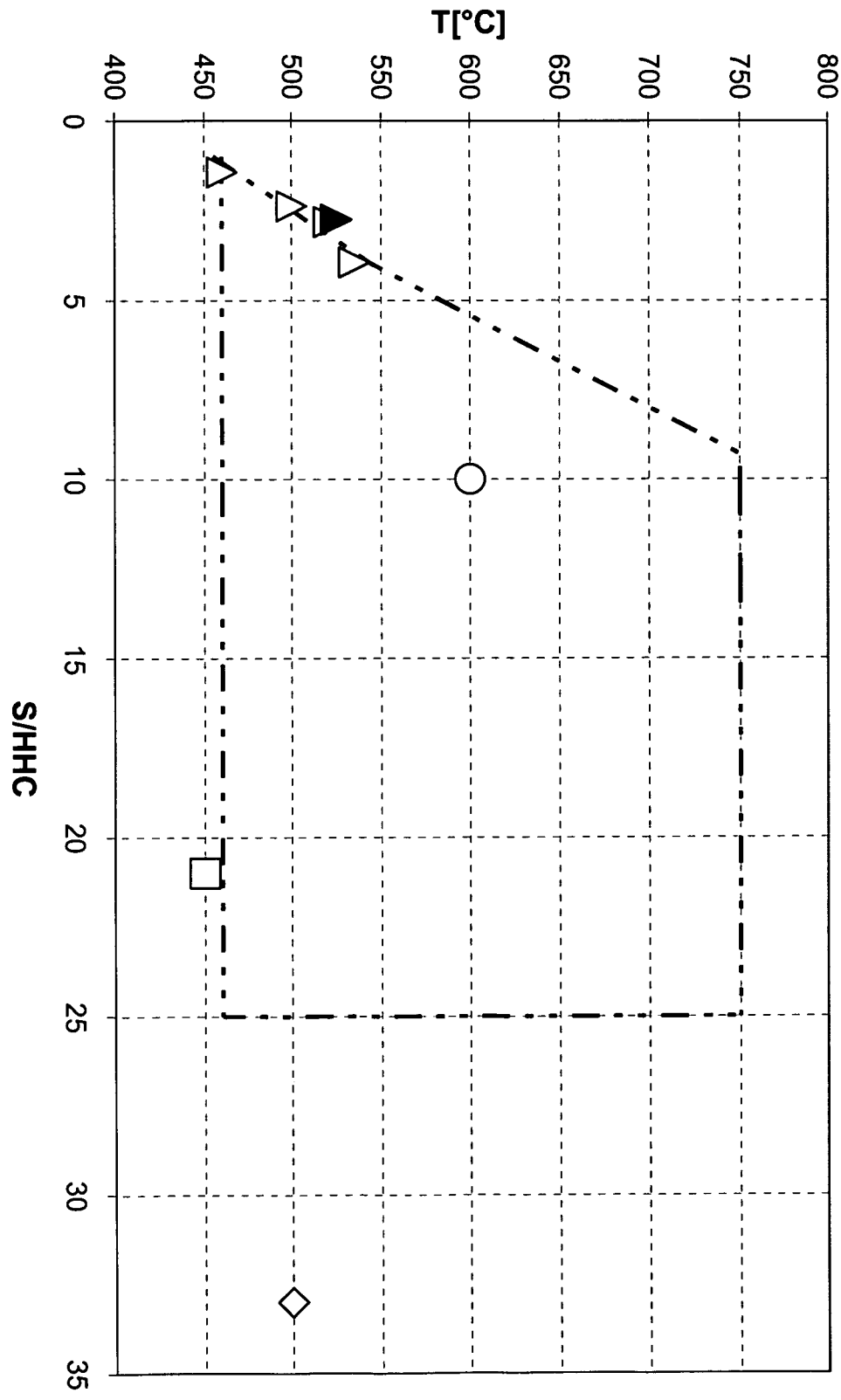
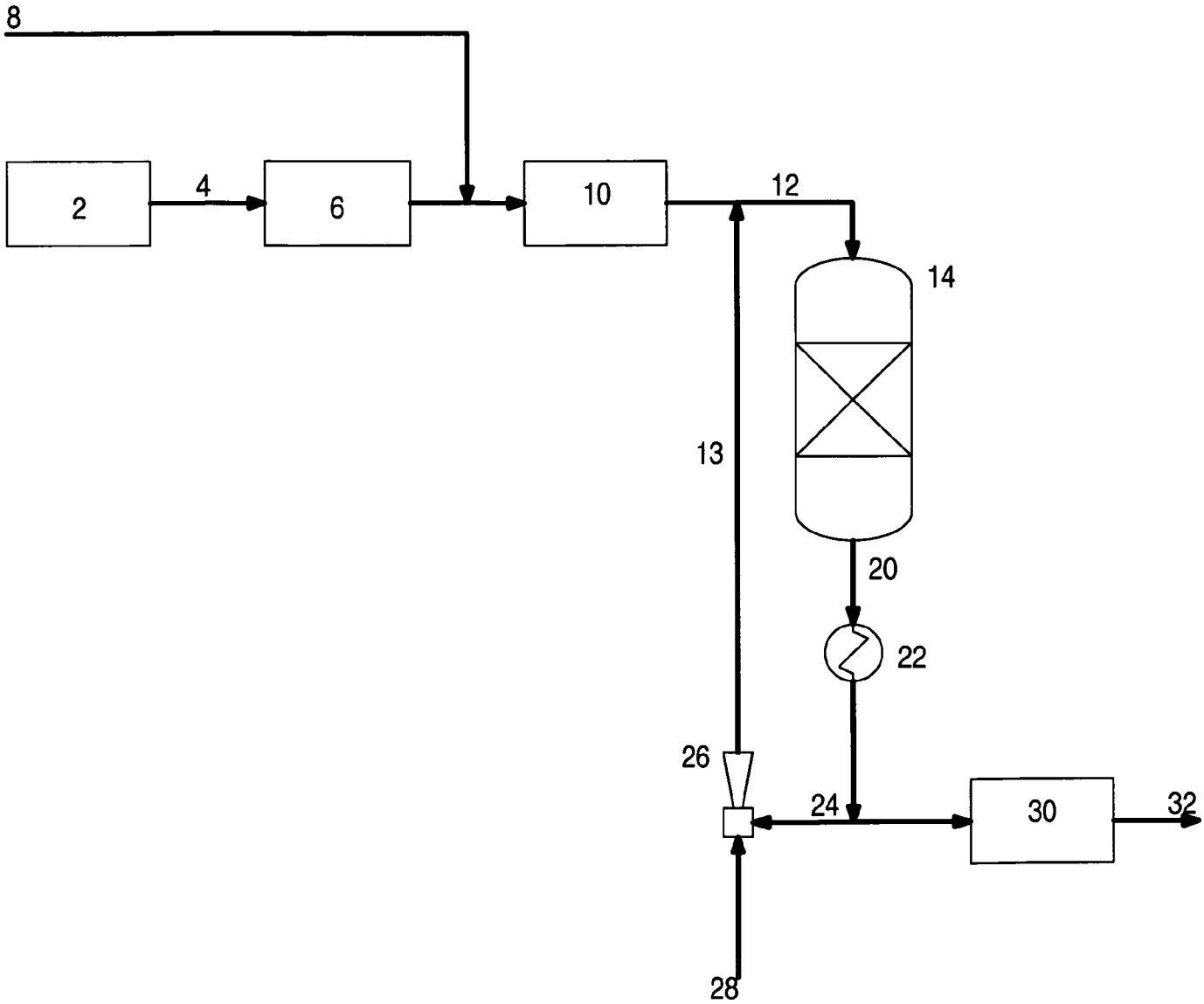


Fig.2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/005129

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10L3/08 C07C1/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10L C07C C10K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 130 575 A (JORN ERNST) 19 December 1978 (1978-12-19) cited in the application	12,13
Y	abstract; claims; figure 2 column 2, lines 3-16 column 4, lines 1-14	1-11

X	US 2007/245855 A1 (ZENDEJAS-MARTINEZ EUGENIO [MX]) 25 October 2007 (2007-10-25)	12,13
A	abstract; claims; figures 1-4	1-11

Y	GB 1 407 198 A (BRITISH GAS CORP) 24 September 1975 (1975-09-24) page 1, lines 25-43 page 1, paragraph 62 - page 2, line 9	1-11

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/005129

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 436 532 A (YAMAGUCHI KATSUNOBU [JP] ET AL) 13 March 1984 (1984-03-13) figure 2; examples 3,10; table 10	1-13
A	GB 1 080 129 A (KOPPERS GMBH HEINRICH) 23 August 1967 (1967-08-23) page 1, lines 51-73 page 2, lines 36-78 page 3, lines 21-24	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2011/005129

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4130575 A	19-12-1978	AR 205595 A1	14-05-1976
		BR 7507253 A	03-08-1976
		CA 1075906 A1	22-04-1980
		DD 122066 A5	12-09-1976
		DE 2549439 A1	13-05-1976
		DK 495675 A	07-05-1976
		FR 2290410 A1	04-06-1976
		IN 142700 A1	13-08-1977
		JP 1278110 C	29-08-1985
		JP 51068502 A	14-06-1976
		JP 59053245 B	24-12-1984
		SU 1215617 A3	28-02-1986
		US 4130575 A	19-12-1978
US 2007245855 A1	25-10-2007	CN 101460637 A	17-06-2009
		EP 2024521 A2	18-02-2009
		RU 2008146067 A	27-05-2010
		US 2007245855 A1	25-10-2007
		WO 2007122509 A2	01-11-2007
		ZA 200809577 A	25-11-2009
GB 1407198 A	24-09-1975	BE 791915 A1	16-03-1973
		DE 2257239 A1	30-05-1973
		GB 1407198 A	24-09-1975
		IT 975863 B	10-08-1974
		JP 858578 C	16-05-1977
		JP 48060701 A	25-08-1973
		JP 51037645 B	16-10-1976
US 4436532 A	13-03-1984	JP 1370829 C	25-03-1987
		JP 57151693 A	18-09-1982
		JP 61040279 B	08-09-1986
		US 4436532 A	13-03-1984
GB 1080129 A	23-08-1967	NONE	