(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 August 2021 (12.08.2021)

WIPO | PCT

(10) International Publication Number
WO 2021/156179 A1

(51) International Patent Classification:
B01J 8/04 (2006.01) *C07C 31/04* (2006.01)
C07C 29/152 (2006.01)

(21) International Application Number:
PCT/EP2021/052262

(22) International Filing Date:
01 February 2021 (01.02.2021)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PA 2020 00146 05 February 2020 (05.02.2020) DK

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to the identity of the inventor (Rule 4.17(i))*
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

(54) **Title:** PROCESS AND REACTION SYSTEM FOR THE PREPARATION OF METHANOL

(57) **Abstract:** Process and reaction system for the preparation of methanol. The process comprises the steps of (a) providing a fresh methanol synthesis gas containing hydrogen, carbon monoxide and carbon dioxide;(b)) introducing and reacting the fresh methanol synthesis gas stream in a first methanol reaction unit in presence of a methanol catalyst and obtaining a first effluent stream containing methanol and unconverted synthesis gas; (c) providing a recycle gas stream containing the unconverted methanol synthesis gas contained in the first effluent stream and unconverted methanol synthesis gas from a second methanol reaction unit;(d) introducing and reacting the recycle gas stream in the second methanol reaction unit in presence of a methanol catalyst; (e) withdrawing a second effluent stream containing methanol and the unconverted methanol synthesis gas from the second methanol reaction unit; (f)) combining the first and a part of the second effluent stream;(g) cooling and separating the combined effluent into a methanol-containing liquid stream and the recycle stream; and (h) withdrawing the remaining part of the second effluent stream a purge gas stream,wherein the remaining part of the second effluent stream is withdrawn as a purge gas stream prior to combining the first and second effluent stream.

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Title: Process and reaction system for the preparation of methanol

The present invention relates to a process for the preparation of methanol by catalytic conversion of methanol synthesis gas and a reaction system for carrying out the process.

More particularly, methanol is by the invention prepared in two reaction units, in which a first unit is operated in once-through mode on fresh synthesis gas optionally admixed with unconverted synthesis gas separated from effluent of a second reaction unit and in which the second reaction unit is operated in a synthesis loop with unconverted synthesis gas optionally admixed with fresh synthesis gas.

The reaction of carbon oxides and hydrogen to methanol is equilibrium limited and conversion of the synthesis gas to methanol per pass through a methanol catalyst is relatively low, even when using a high reactive synthesis gas.

Because of the low methanol production yield in a once-through methanol conversion process, the general practice in the art is to recycle unconverted synthesis gas separated from the reaction effluent and dilute the fresh synthesis gas with the recycle gas.

This typically results in the so-called methanol synthesis loop with one or more reactors connected in series being operated on fresh synthesis gas diluted with either recycled unconverted gas separated in a separator from the reactor effluents or on the reactor effluent containing meth-

anol and unconverted synthesis gas. The recycle ratio (recycle gas: fresh synthesis feed gas) is 1 : 1 up to 7 : 1 in normal practice.

In methanol process designs with a once-through reaction unit and a reaction unit operated on recycled unconverted synthesis in a methanol synthesis loop, optimal gas compositions can be set to the once-through reaction unit or reaction unit operated on recycled unconverted synthesis by the recycle gas and feed bypass gas. The effluent from the once-through reaction unit is mixed with the effluent from the reaction unit in the synthesis loop. Produced methanol is separated from the mixed effluent after cooling upstream separation unit. Separated unconverted synthesis gas contained in the mixed effluent combined from the reaction units is recycled to the reaction unit in the synthesis loop.

In order to save equipment, the cooling and separation of the methanol containing effluent gas can be made in a combined cooling train. However, the combined cooling train will have mixed the two different recycle gasses, i.e one from the once through reaction unit and one from the synthesis loop reaction unit. To prevent built up of inert gases, a part of the combined recycled unconverted synthesis gas must be purged from the loop, thereby purging out more active reactants than necessary.

For the sake of simplicity, in the following description and claims the “once through reaction unit” is termed “first methanol methanol reaction unit” and the “synthesis

loop reaction unit" is termed "second methanol reaction unit"

The term "methanol catalyst" used in the following description and in the claims refers to any catalyst being active in the conversion of hydrogen, carbon monoxide and carbon dioxide to methanol. Those catalysts are not part of the invention and are extensively disclosed in the patent literature.

Appropriate methanol catalysts for use in the invention are as an example the known copper-zinc based catalysts.
The main principle of the invention is, thus, to withdraw a hot purge gas from the effluent of the second methanol reaction unit, prior to the effluent is combined with the effluent from the first reaction unit.

The hot purge gas will allow combined equipment in cooling train and at the highest content of inert components and the lowest activity, which allows more effective purging without losing too much reactants with only one extra small cooler.

The term "inerts" refers to components contained in methanol synthesis gas, which are not chemically reactive in the methanol synthesis.

Accordingly, this invention is a process for the preparation of methanol, comprising the steps of
(a) providing a fresh methanol synthesis gas containing hydrogen, carbon monoxide and carbon dioxide;

(b)) introducing and reacting the fresh methanol synthesis gas stream in a first methanol reaction unit in presence of a methanol catalyst and obtaining a first effluent stream containing methanol and unconverted synthesis gas;

(c) providing a recycle gas stream containing the unconverted methanol synthesis gas contained in the first effluent stream and unconverted methanol synthesis gas from a second methanol reaction unit;

(d) introducing and reacting the recycle gas stream in the second methanol reaction unit in presence of a methanol catalyst;

(e) withdrawing a second effluent stream containing methanol and the unconverted methanol synthesis gas from the second methanol reaction unit;

(f)) combining the first and a part of the second effluent stream;

(g) cooling and separating the combined effluent into a methanol-containing liquid stream and the recycle stream; and

(h) withdrawing the remaining part of the second effluent stream a purge gas stream,

wherein the remaining part of the second effluent stream is withdrawn as a purge gas stream prior to combining the first and second effluent stream.

In some applications of the process according to the invention, it will be desirous to adjust the module $M=(H_2-CO_2)/(CO+CO_2)$ of the fresh synthesis gas by addition of hydrogen to the gas. Hydrogen can be recovered from the purge gas and recycled to the process upstream the synthesis gas compressor.

Thus, in an embodiment of the invention at least a part of hydrogen contained in the purge gas stream is recovered and recycled to step b).

To provide optimum conditions for the methanol reaction in the first methanol reaction unit, a part of the recycle stream is introduced into the first methanol reaction unit in further an embodiment.

In still an embodiment, a part of the fresh methanol synthesis gas is introduced into the second methanol reaction unit to provide optimum condition for the methanol synthesis in the second methanol reaction unit.

The first and second methanol reaction unit can comprise one or more reactors selected from boiling water cooled reactors, gas cooled reactors, quench reactors and adiabatic operated reactors, connected in series and/or in parallel.

The invention provides furthermore reaction system for use in a process for the preparation of methanol, the system comprises a first and second methanol reaction unit containing each a methanol catalyst;
a process gas stream passageway for introducing a process gas stream of a fresh synthesis gas into the first methanol reaction unit and a circulation passageway for circulating unconverted synthesis gas to the second methanol reaction unit;
a first effluent passageway for withdrawing and passing a first methanol containing effluent stream from the first reaction unit to a mixing point in a second effluent pas-

sageway for withdrawing a second methanol containing effluent from the second reaction unit;
separating means arranged downstream the mixing point in the second effluent passageway for separating methanol from the unconverted synthesis gas;
a circulator arranged in the circulation passageway between the separating means arranged upstream the second methanol reaction unit; and
a purge gas line connected to the circulation passageway and arranged upstream the mixing point in the second effluent passageway.

In an embodiment of the reaction system according to the invention, the purge gas line is connected to hydrogen recovery unit.

In an embodiment of the invention, a passageway is connected to the hydrogen recovery unit and to the process gas stream passageway for passing hydrogen to the gas stream of a fresh synthesis gas.

In an embodiment of the invention, the reaction system further comprises a passageway connected to the hydrogen recovery unit and to the process gas stream passageway for passing hydrogen to the gas stream of a fresh synthesis gas.

In an embodiment of the invention, the reaction system further comprises a split stream passageway for passing a part of the unconverted synthesis gas from the circulation passageway to the process gas stream passageway.

In an embodiment of the invention, the reaction system further comprises a split stream passageway for passing a part of the process gas stream of a fresh synthesis gas to the circulation passageway.

The first and second reaction unit in the above embodiments can comprise one or more methanol reactors selected from boiling water cooled reactors, gas cooled reactors, quench reactors and adiabatic operated reactors connected in series and/or in parallel.

Claims

1. Process for the preparation of methanol, comprising the steps of

(a) providing a fresh methanol synthesis gas containing hydrogen, carbon monoxide and carbon dioxide;

(b)) introducing and reacting the fresh methanol synthesis gas stream in a first methanol reaction unit in presence of a methanol catalyst and obtaining a first effluent stream containing methanol and unconverted synthesis gas;

(c) providing a recycle gas stream containing the unconverted methanol synthesis gas contained in the first effluent stream and unconverted methanol synthesis gas from a second methanol reaction unit;

(d) introducing and reacting the recycle gas stream in the second methanol reaction unit in presence of a methanol catalyst;

(e) withdrawing a second effluent stream containing methanol and the unconverted methanol synthesis gas from the second methanol reaction unit;

(f)) combining the first and a part of the second effluent stream;

(g) cooling and separating the combined effluent into a methanol-containing liquid stream and the recycle stream; and

(h) withdrawing the remaining part of the second effluent stream a purge gas stream,

wherein the remaining part of the second effluent stream is withdrawn as a purge gas stream prior to combining the first and second effluent stream.

2. The process of claim 1, wherein at least a part of hydrogen contained in the purge gas stream is recovered and recycled to step b).

3. The process of claim 1 or 2, wherein a part of the recycle stream is introduced into the first methanol reaction unit.

4. The process of any one of claims 1 to 3, wherein a part of the fresh methanol synthesis gas is introduced into the second methanol reaction unit.

5. The process according to anyone of claims 1 to 4, wherein the first and second methanol reaction unit comprise one or more reactors selected from boiling water cooled reactors, gas cooled reactors, quench reactors and adiabatic operated reactors connected in series and/or in parallel.

6. A reaction system for use in a process for the preparation of methanol, the system comprises a first and second methanol reaction unit containing each a methanol catalyst; a process gas stream passageway for introducing a process gas stream of a fresh synthesis gas into the first methanol reaction unit and a circulation passageway for circulating unconverted synthesis gas to the second methanol reaction unit;
a first effluent passageway for withdrawing and passing a first methanol containing effluent stream from the first reaction unit to a mixing point in a second effluent passageway for withdrawing a second methanol containing effluent from the second reaction unit;

separating means arranged downstream the mixing point in the second effluent passageway for separating methanol from the unconverted synthesis gas;
a circulator arranged in the circulation passageway between the separating means arranged upstream the second methanol reaction unit; and
a purge gas line connected to the circulation passageway and arranged upstream the mixing point in the second effluent passageway.

7. The reaction system of claim 6, wherein the purge gas line is connected to hydrogen recovery unit.

8. The reaction system of claim 6, further comprising a passageway connected to the hydrogen recovery unit and to the process gas stream passageway for passing hydrogen to the gas stream of a fresh synthesis gas.

9. The reaction system of any one of claims 6 to 8, further comprising a split stream passageway for passing a part of the unconverted synthesis gas from the circulation passageway to the process gas stream passageway.

10. The reaction system of any one of claims 6 to 9, further comprising a split stream passageway for passing a part of the process gas stream of a fresh synthesis gas to the circulation passageway.

11. The reaction system of any one of claims 6 to 10, wherein the first and second reaction unit comprise one or more methanol reactors selected from boiling water cooled reactors, gas cooled reactors, quench reactors and adia-

batic operated reactors connected in series and/or in parallel.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2021/052262

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J8/04 C07C29/152 C07C31/04
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)
B01J C07C

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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2017/121980 A1 (JOHNSON MATTHEY DAVY TECHNOLOGIES LTD) 20 July 2017 (2017-07-20) figure 1 paragraphs [0027], [0044], [0045], [0048], [0050], [0052] claims 1-15 -----	1-11

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 April 2021	10/05/2021

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2021/052262

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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