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ENTRADA EN FASE NACIONAL wo

1) SOLICITUD DE:

lI Patente de invención 0 Patente de Modelo de Utilidad

IXI Capitulo I. i:i Capitulo
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II.

2) IDENTIFICACION

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5) PCT (86)
Solicitud Internacional No. PCT/GB2006/050096 Fecha: Mayo 9, 2006

PublicaciOn Internacional No. W02006/126017 Al Fecha: Nov. 30, 2006
6)TituIo (54) SINTESIS DE METANOL

7) Clasificación Internacional: C07C 29/151 C07C 29/162 C07C 291153
8) PRIORIDAD 33) Pals de Origen (32) Fecha (31) Nümero do

Solicitud
GRAN BRETAA MAYO 27, 2005 051 08238
Si El NO
9) Comprobante de pago N° 07-93,039 DE NOV 15, 2007

Instrucciones para el diligenciamiento del presente formulario. Ver reverso de esta pagina

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Documento do cesiOn del inventor at solicitante o a su causante
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1. Reporte internacional de bt:isqueda

12) Solicitud concesión do la patente,

NOMBRE: DUJA RODRGUEZ[YALE(4AN

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RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

SUPINTENDLNCA DE INDUSTRIAY COMERCIO

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Art. 411 PRESENTACION Folios: 48

SUPERINTENDENCIA DE INDUSTRIA V CONERCIG

NIT: 600176089-2

RECIBU OFICIAL DE CAJA: 07 - 93,039
FECHA NOVIENBRE 15 DE 2007

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CANT. RENTISTICO CONCEPTO TOTAL CONCEPTO ---------------------------------------------------------------------------------------------------------------------

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TOTAL $ 482,000.00

SON: CIJATROCIENTOS OCHENTA V DOS NIL PESOS

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

(19) World Intellectual Properly OrganizationI
International Bureau liii IMII II Hill 1111111011111111111111111 11111 VII 11111 III IIIIV I ill! III

(43) International Publication Date PCT (10) International Publication Number

30 November 2006 (30.11.2006) WO 2006/126017 Al

(51) International Patent ClassificatIon: (81) Designated States (unless otherwise Indicated, for every
C07C 29/151 (2006.01) C07C 29/153(2006.01) kind ofnational protection available): AS, AG, AL, AM,
C07C 291152 (2006.01) AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CF, CU, CZ, DE DK, DM, DZ, BC, BE, EG, ES, Fl,
(21) International Application Number GB, GD, GE, GH, GM, HP, Jill, ID, IL, IN, IS, JP, KE,
PCT/GB2006/050096 KG, EM, EN, KP, KR, KZ, LC, LK, LR, LS, IT, LU, LV,
LY, MA, MD, MG, ME, MN, MW, MX, MZ, NA, NG, NI,
(22) International Filing Date: 9 May 2006 (09.05.2006) NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SO,
SK, SL, SM, SY, Ti, TM, TN, TR, ’IT, TZ, UA, 130, US,
(25) Filing Language: English lIZ, VC, VN, YtJ, ZA, ZM, ZW.

(84) Designated States (unless otherwise Indicated, for every (26) Publication Language: English kind of regional protection available): ARIPO (SW, OH,

GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, 130, ZM,

(30) Priority Data: ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, Ti, TM), 0510823) 27 May 2005 (27.052005) GB European (AT, BE, BG, CH, CY, CZ, DE, DK, BE, ES, Fl,

FR, GB, OR, RU, IS, IS, IT, IT, LU, LV, MC, NL, PL, PT,

(71) Applicant (for all designated States except US): JOHN- RU, SE, SI, SE, TR), OAPI (SF, BI, CF, CG, CL CM, GA,

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(72) Inventor; and with international search report
(75) Inventor/Applicant (for US only): FITZJATRICK,1kI. before the expiration of the time limitfor amending the
he in the cane, Jam[GB/GBJ; Waingarth, Busb Lane, Kirkby In claims and to republished event of receipt of
 Cleveland, Middlesbrough Cleveland TS97AW (GB). amendments
ForIwo-letter codes and other abbreviations, refer to the "Geld-
(74) Agent: RIDLAND, John; P0 Box 1, Belasis Avenue, ance Notes on Codes andAbbreviasions" appearing at the begin-
Billingham Cleveland TS23 1LB (GB). ning ofeach regular issue ofthe PC).’ Gazette.

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(57) Abstraet A process for synthesising methanol is described comprising the steps of; (i)reforming a hydrocarbon feedstock and
- separating water from the resulting reformed gas mixture to generate a make-up gas comprising hydrogen and carbon oxides, said make-up gas mixture having a stoichiometric number, R, defined by the formula; R = ([1-12] - [CO2]) / ([CO2] + [CO]) of less than 2.0, (ii) combining said make up gas with an unreacted synthesis gas to form a synthesis gas mixture, (iii) passing the synthesis gas mixture at elevated temperature and pressure through a bed of methanol synthesis catalyst to generate a product stream comprising "1 methanol and unreacted synthesis gas, (iv) cooling said product stream to recover a crude methanol stream from said unreacted syn-thesis gas, (v) removing a portion ofsaid unreacted synthesis gas as a purge gas, and (vi) feeding the remaining unreacted synthesis gas to step (ii), characterized in that hydrogen is recovered from at least a portion ofsaid purge gas and a portion ofsaid make up gas, and the recovered hydrogen is included in the synthesis gas mixture.

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Methanol Synthesis.

This invention relates to methanol synthesis and in particular to methanol synthesis from a synthesis gas that Is deficient in hydrogen.

Methanol synthesis is generally performed by passing a synthesis gas comprising hydrogen, carbon oxides and any inert gases at an elevated temperature and pressure through one or
more beds of a methanol synthesis catalyst, Which Is often a copper-containing composition. Methanol is generally recovered by cooling the product gas stream to below the dew point of
10 the methanol and separating off the product as a liquid. The process is usually operated in a
loop: thus the remaining unreacted gas stream is usually recycled to the synthesis reactor as
part of the synthesis gas via a circulator. Fresh synthesis gas, termed make-up gas, is compressed and added to the recycled unreacted gas to form the synthesis gas stream. A
purge stream is often taken from the circulating gas stream to avoid the build up of inert gases.
15 Such a process is described for example in EP 0329292.

This arrangement is, however, unsuitable for gases whose stoichiometric number (R), defined
by the formula;

R [H2][co2]

20 is less than 2, signifying that the gas is deficient in H2 for the manufacture of methanol.
Synthesis gases deficient in hydrogen may be obtained from reforming processes including a
step of partial oxidation, such as autothermal reforming. In such a case, the hydrogen will be consumed in the methanol synthesis reaction while a su ’ball portion of the carbon oxides remain unreacted leading to a composition in the synthesiibpwhich has very high levels of
25 carbon oxides but is low In hydrogen. This has several consequences, among them that the
required catalyst volume will be high and that the level of by-products (higher alcohols and
ketones In particular) will be much higher than normal.

It Is known that hydrogen can be recovered from the purge gas stream using a hydrogen
30 recovery unit and recycled back into the feed gas so that the gas within the synthesis loop Is

40 significantly more H2-rich than is the synthesis gas. However, one of the difficulties with this
approach is that for synthesis gases that are very deficient in H2, it is necessary to recover
large quantities of H2 from the purge gas, and to have such a large flow of purge gas means
either operating the synthesis loop at low pressure or having a low ratio of flow of recycle gas
35 to flow of fresh synthesis gas. Running the synthesis loop at low pressure Is not attractive for
large commercial scale plants due to the size of the pipework, vessel diameters, etc., whereas
running with a low recycle ratio can impose restrictions on the methanol synthesis reactor that
may be unacceptable. For instance, a low recyde ratio means that using the circulating gas to

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cool the reaction, either In a quench cooled or tubular reactor, is impossible, so the only option
is a steaimraising reactor. Furthermore, the low recycle ratio means that the reactant concentration at the Inlet to the reactor Is high as will be the reaction rates, so In order to
prevent excessive temperatures In the catalyst bed, the catalyst will have to be Installed inside
S the tubes of a tubular steam raising reactor. This is an unattractive choice as this leads to poor
utilisation of the volume within the shell of the reactor as well as the requirement for extremely thick, heavy tube sheets. There is also a limit to the pressure at which steam can be raised, so utilisation of this steam may complicate the design of the steam system on such a plant so increasing cost and reducing operability and reliability.
10

Another alternative is to take a side-stream of the frOsh synthesis gas, also termed make-up
gas (MUG), recover hydrogen from it using a hydrogen recovery and feed this hydrogen
back into the synthesis gas. However, the drawback to this arrangement is that some
hydrogen is lost within the hydrogen recovery unit before it ever gets to the synthesis loop, and
15 the synthesis gas, after enrichment with this hydrogen will now have a stoichiometry number
greater than 2, so the purge gas will now consist of a significant portion of unreacted H2. The effect of this is that the quantity of methanol produced from a fixed quantity of synthesis gas is reduced, and so a large synthesis gas generation unit Is required for a given production
capacity. Since the synthesis gas generation unit is the most expensive part of the plant,
20 increased spending In this area Is uneconomic.

Thus there Is a need to provide a methanol synthesis process Including a step of hydrogen recovery without the disadvantages of either method.

25 Accordingly the Invention provides a process for synthesising methanol comprising the steps
of

(i) reforming a hydrocarbon feedstock and separating water from the resulting
reformed gas mixture to generate a make-up gas comprising hydrogen and carbon
oxides, said make-up gas mixture having a stoichiometric number, R, defined by
30 the formula; R = (11-12) -[CO2)) I ([CO2) + [CO)) of less than 2.0,
(Il) combining said make up gas with an unreacted synthesis gas to form a synthesis
gas mixture,
(iii) passing the synthesis gas mixture at elevated temperature and pressure through a bed of methanol synthesis catalyst to generate a product stream comprising
35 methanol and unreacted synthesis gas,
(iv) cooling said product stream to recover a crude methanol stream from said unreacted synthesis gas,
(v) removing a portion of said unreacted synthesis gas as a purge gas, and
(vi) feeding the remaining unreacted synthesis gas to step (ii)

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characterized in that hydrogen Is recovered from at least a portion of said purge gas and a
portion of said make up gas, and the recovered hydrogen is included in the synthesis gas
mixture.

5 The make up gas comprising hydrogen and carbon oxides is obtained by reforming a
hydrocarbon feedstock such as methane, natural gas, associated gas or naphtha and removing water from the resulting reformed gas mixture. The reforming process may comprise one or
more steps of steam reforming and/or partial oxidation. For example, the reforming may
comprise a step of primary steam reforming In which a hydrocarbon and steam, and optionally
10 carbon dioxide, are passed through externally-heated catalyst-filled tubes In a combustion-fired
or gas-heated reformer and a step of secondary reforming In which the primary reformed
gases, optionally with further hydrocarbon, are subjected to a step of partial combustion with an oxygen-containing gas, preferably substantially pure oxygen, and the partially combusted
gases passed through a bed of steam reforming catalyst In one preferred embodiment, the
15 secondary reformed gases are used to externally heat the catalyst-filled tubes of the primary
reformer. Alternatively, the reforming process may comprise a step of autothermal reforming in which the hydrocarbon feedstock is fed to a reformer where it is first subjected to partial
oxidation with an oxygen-containing gas and the resulting hot partially combusted gases
passed through a bed of a steam reforming catalyst. Steam may be added to the hydrocarbon
20 and/or oxygen-containing gas.

Primary steam reforming catalysts typically comprise nickel on a refractory support e.g. alumina
or calcium aluminate. Secondary and autothermal steam reforming catalysts also typically comprise nickel on a refractory support. Alternatively a precious metal catalyst may be
25 employed such as platinum, palladium and/or rhodium.

Additionally the reforming process may comprise one or more steps of adiabatic steam
reforming over a bed of supported nickel steam reforming catalyst at temperatures between
450 and 650°C. Such adiabatic low-temperature steam reforming, often termed pre-reforming,
30 has the advantage that higher hydrocarbons are converted to methane and some hydrogen is
generated, thus reducing the possibility of carbon formation in the primary steam reformer or autothermal reformer, especially at low steam ratios.

The reformed gas mixture, depending on the reforming process used, may be at a temperature
35 in the range 400 1150°C, a pressure of 10-30 bar abs and comprises different amounts of
steam, hydrogen, carbon oxides, i.e. carbon monoxide and carbon dioxide, methane, and inert gases such as nitrogen and argon.

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Make up gas is preferably obtained from the reformed gas mixture by cooling It to below the dew point of steam and separating condensed water from the gas mixture. Cooling may be performed by heat exchange with water to generate steam. The reformed gas mixture Is preferably cooled to below 100°C, more preferably below 60°C to condense water. The cooled mixture is preferably fed to a separator where the condensed water may be separated from the
gas mixture. The separated water may usefully be recycled to generate steam for performing
the reforming step.

Howsoever the make up gas is generated; it should have a stoichiometric number (R), defined
10 by the formula;

R-- [H2]-[CO2]

In which 11-123, [CO23 and [CO3 are the concentrations of hydrogen, carbon dioxide and carbon monoxide respectively of less than 2.0, preferably less than I.S. Thus it is deficient in
hydrogen for the methanol synthesis step.
15

10 remainder

the present invention a side-stream of make up gas is taken to hydrogen recovery. The
remainder is fed to a methanol synthesis loop in which a synthesis gas mixture comprising
make up gas and unreacted synthesis gas containing hydrogen and carbon oxides is fed to one
or more steps of methanol synthesis by means of one or more circulators. The temperature
20 and pressure of the make up gas are preferably adjusted to be suitable for methanol synthesis
prior to feeding It to the methanol synthesis loop by means of compressors and heat
exchangers known to those skilled in the art. The methanol synthesis may desirably be
performed at pressures in the range 40- 150, and more conveniently in the range 45- 120, bar
abs. The temperature of the synthesis catalyst is suitably in the range 160 - 300°C; preferably
25 the peak temperature is below 285°C. The synthesis gas preferably enters the catalyst bed at
a temperature in the range 200 - 250°C and leaves the beds at temperatures preferably in the range 220-260°C. Such temperatures provide for an acceptable methanol output rate (owing to favourable equilibrium) without producing the greater content of by-product impurities, and
reduction in catalyst life, that would result from operation at higher temperatures.
30

The methanol synthesis catalyst Is preferably a copper-based catalyst. Particularly suitable are catalysts containing copper and compounds, e.g. oxides of zinc, aluminium, chromium,
titanium, zirconium, and/or magnesium. The catalyst may be in the form of pellets, tablets or extrudates. Particularly preferred catalysts are described in US 4788175.

The methanol synthesis step may be carried out in a methanol synthesis reactor of the quench converter type or in a reactor in which the catalyst bed has immersed therein heat exchange tubes through which the synthesis gas passes an route to the catalyst bed, for example as

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described in EP 0082070. Alternatively there may be used a reactor ofthe tube-cooled type,
for example as described in EP 0081948, where the exothermic heat of methanol synthesis Is removed by a flow of coolant, particularly water, through coolant tubes disposed In the catalyst bed or beds. Alternatively the tube-cooled catalyst bed may be disposed in a reaction vessel as
5 an annular bed with synthesis gas inlet means adjacent the outer periphery of the bed and
reacted synthesis gas outlet means adjacent the axis of the vessel, so that the synthesis gas
flows radially inwards through the catalyst bed, i.e. in a radial flow reactor. In a radial flow arrangement, the coolant tubes will generally be disposed In planes perpendicular to the vessel axis. An example of a suitable radial flow reactor design is shown in EP 1060788.
10

By passing the synthesis gas mixture at elevated temperature and pressure through a bed of methanol synthesis catalyst, a product stream comprising methanol and unreacted synthesis
gas Is generated.

15 Methanol is recovered by cooling the product stream to condense crude methanol, which
contains water and small amounts of higher alcohols and other compounds, from unreacted synthesis gas. The crude methanol may then be used but is preferably sent to one or more distillation steps in which pure methanol is separated from the water, higher alcohols and other by-products.
20

Because the methanol synthesis step consumes hydrogen and carbon oxides the unreacted synthesis gas can become enriched in Inert gases such as nitrogen and argon, which are Impurities in the hydrocarbon and/or oxygen-containing gas. Unreacted methane from the reforming step may also build up. The build up of such gases Is undesirable and therefore a
25 portion of the unreacted synthesis gas is removed as a purge gas. The amount of purge gas
Will depend on the exact flowsheet. Preferably the remaining unreacted synthesis gas is compressed prior to mixing it with the make up gas. The resulting synthesis gas mixture Is preferably heated prior to feeding it to the methanol synthesis reactor.

30 In the present Invention hydrogen Is recovered from at least a portion of the purge gas and
from a portion of make up gas and said recovered hydrogen Is included in the synthesis gas mixture fed to the methanol synthesis reactor. The purge and make up gases comprise
hydrogen and carbon oxides as well as small amounts of unreacted methane and Inerts.
Hydrogen may be recovered from these gases, which may or may not be combined
35 beforehand, using one or more hydrogen recovery units. Such units are known and may
function by so-called pressure-swing absorption (PSA) in which an absorbent material Is
disposed in the unit that captures the non-hydrogen components of the gas stream, thereby allowing a gas rich In hydrogen to pass through. The advantage of a PSA hydrogen recovery
unit is that the gas rich in hydrogen is recovered at the PSA operating pressure and the waste

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gas, which may be used as fuel, Is recovered at low pressure. A disadvantage is that the absorbent has to be periodically cleansed of captured material by adjusting (i.e. lowering) the pressure In the unit. An alternative to PSA hydrogen recovery Is a membrane hydrogen
recovery unit, which functions continuously. The membrane functions by allowing the hydrogen
5 to pass through while holding back non-hydrogen components ofthe gas stream fed to it. The
membrane recovery unit however recovers a gas stream rich In hydrogen at a reduced
pressure below that of the partial pressure of hydrogen in the feed stream to the unit, whereas
the waste gas Is recovered at the membrane operating pressure.

10 Accordingly, where a PSA hydrogen recovery unit Is employed, the recovered hydrogen may
either be fed to the make-up gas prior to its addition to the synthesis loop, or the recovered hydrogen may be fed directly to the synthesis loop by adding It to either the unreacted
synthesis gas before or after the purge stream has been removed or to the synthesis gas
mixture (comprising the combined make up gas and unreacted synthesis gas). In contrast,
15 where the hydrogen recovery unit is a membrane recovery unit, the recovered hydrogen is
preferably fed to the make-up gas stream destined for the synthesis loop prior to its
compression. In a preferred process, the recovered hydrogen is fed to the make up gas. The resulting hydrogen-adjusted make up gas Is then compressed, fed to the synthesis loop where
it Is mixed with the remaining unreacted synthesis gas, i.e. after the purge stream has been
20 removed, heated and fed to the methanol synthesis reactor.

Adding hydrogen increases the value of R In the synthesis gas mixture towards the optimum stoichiometry value for methanol synthesis. Preferably the quantity of hydrogen added raises
the value of R towards 2.0, preferably up to 2.2, especially to 2.1 – 0.1.
25

The quantity of hydrogen recovered from the purge gas or make up gas may be varied
depending upon the precise flowsheet adopted and the contents of hydrogen and carbon
oxides in the make up gas provided by the reforming stage. For example the purge gas may provide between 5 and 95% of the required hydrogen on a molar basis to bring the value of R
30 towards 2.0 and the make up gas consequently between 95 and 51/16. Preferably all the purge
gas is fed to the hydrogen recovery unit, more preferably to provide >50% on a molar basis of
the required hydrogen, with the remainder provided by the make up gas stream. Thus in a preferred arrangement, the purge gas Is routed to the hydrogen recovery unit and this
hydrogen source is supplemented with a side-stream of the make-up gas.
35

Preferably the side-stream of make up gas fed to the hydrogen recovery unit comprises<20%, preferably 10% by volume of the make up gas provided by the reforming stage. Hence preferably ’80%, more preferably 90% by volume of the make up gas is fed to the synthesis loop. In this way, the design of the synthesis loop can be set to allow the most appropriate

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equipment to be selected, while still maintaining a very high level of conversion of hydrogen to methanol.

The invention Is illustrated by reference to the accompanying drawings in which Figure 1
5 depicts a flow sheet of a preferred embodiment of the present invention wherein hydrogen is
recovered from combined purge gas and make up gas side-stream using a membrane recovery unit, and fed to the remaining make up gas, which is then compressed and fed to the synthesis
loop. Figures 2 and 3 by way of comparison depict flowsheets not according to the present invention in which only partial hydrogen recovery either from purge gas or make up gas is
10 affected.

In Figure 1, make up gas supplied via line 10 divided into two portions. A first portion 121
controlled by valve 14 is combined with a hydrogen stream 16 fed from PSA hydrogen recovery
unit 18 and the combined gases passed via a line 20 to compressor 22 where their pressure is
15 increased before feeding them via line 24 to compressed unreacted synthesis gas in line 26.
The combined synthesis gas is fed via line 27 to heat exchanger 28 where It is heated then fed
. via line 30 to the inlet zone 32 of a methanol synthesis reactor 34 defined by the reactor wails
and tubesheet 35. The synthesis gas passes up though a plurality of tubes 36 extending from
tubesheet 35 upwards through a bed of a particulate copper/zinc/alumina synthesis catalyst 38
20 into a space 40 above the bed and thence down through the bed to an outlet zone above
tubesheet 35. Methanol synthesis takes place as the gases pass down through the catalyst
bed and the resulting product stream is fed from the outlet zone via line 42 to heat exchanger
44 where it is used to raise steam, thence to the heat exchanger 28 where it is used to heat the synthesis gas and then heat exchanger 48 where it Is cooled with cold water to condense crude
25 methanol. The cooled mixture is fed via line 49 to separator 50 that separates the crude
methanol via line 52 from unreacted synthesis gas in line 54. A purge stream 56 is taken from
line 54 and the remaining unreacted synthesis gas is fed via line 58 to compressor 60. The compressed unreacted synthesis gas leaves compressor 60 via line 26 and is combined with
the make up gas from line 24. The second make up gas stream 62 taken from line 10 is
30 combined with the purge gas stream 56 and the combined stream fed via line 54 to the PSA
recovery unit 18. Waste gases depleted in hydrogen are removed from the hydrogen recovery
unit 18 via line 66.

In Figure 2 (comparative) there is hydrogen recovery from purge gas stream 56 only. Thus
35 purge gas stream 56 passes to the hydrogen recovery unit 18, make up gas stream 62 is
absent and the recovered hydrogen 16 is added to stream 10. In this case the synthesis
reactor is necessarily a steam-raising converter with pressurised-water cooling within the bed
and therefore heat exchanger 44 is omitted. In this flowsheet, it is necessary to use a steam raising converter rather than the smaller, cheaper tube-cooled converted used in Figure 1,

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because the circulation ratio of synthesis gas Is too tow to permit effective use of the TCC.
This Is because a larger amount as purge gas has to be removed to provide the required
hydrogen.

5 In Figure 3 (comparative) there Is hydrogen recovery from make up gas via stream 62 only. Purge gas in line 56 Is simply combusted. The synthesis reactor is according to that In Figure 1
and accordingly heat exchanger 44 Is again present to cool the product stream 42 before it
passes to heat exchanger 28..

10 The invention Is further Illustrated by reference to the following calculated examples.

Example I

According to the embodiment depicted in Figure 1.
15
Stream 10 62 16 20 30 42 58 56 52

Temperature [CI 45.0 45.0 45.0 44.9 220.0 255.0 45.0 45.0 45.0
Pressure [bar] 34.0 34.0 34.0 34.0 81.5 80.0 77.7 77.7 77.7
Molar Flow [k9mole/h] 15210.6 1181.0 1336.8 15386.4 75366.4 66877.1 60000.0 1583.1 5294.2
Mass Flow [kg/h] 186073 14447 2695 174321 844492 U44671670171 17683 158637

Hydrogen 63.63% 100.00% 66.79% 59.86% 53.50% 56.08% 56.08%10.24-/.
Co 24.71% 24.71% 0.001* 22.56% 7.61% 3.49% 3.79% 3.79% 0.09%

CO2 721% 7.21% 0.00% 6.58% 1 5.88% 5.37% 5.70% 5,70% 1.49%
Methane 3.15% 3.15% 0,00% 2.88% 119.46% 21.93%123.70% 23.70% 1.27%
Nitrogen 0.79% 0.79% 0.00% 0.72% 5.44% 8.13% 6.64% 8.64% 0.11%
Argon 0.17% 0.17% 0.00% 0.15% 1.11% 1.25% 1.35% 1.35% 0.040/6
Methanol 0.00% 0.000/0 0.00% 0.00% 0.53% 6.95% 0.67% 0.67% 79.97%
H20 0.340A 0.34% 0.00% 0.31% 0.11% 1.38% 0.06% 0.08% 16.78%

Methanol production Is high using a low volume of synthesis catalyst

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Comoarative Examoles

A) H2 Recovery from purge gas stream only (Figure 2)

Stream 10 16 20 30 42 58 56 52

Temperature [C] 45.0 45.0 44.8 220.0 255.0 45.0 45.0 45.0
Pressure [bar] 34.0 34.0 34.0 81.5 80.0 77.7 77.7 77.7
Molar Row (kgmolelh] 15210.6 4410.1 19620.7 41543.7 33535.7 21923.0 6918.8 4694.0
Mass Flow [kg/h] 186073 8891 194964 381988 361984 167025 52712 142248

Hydrogen 63.63% 100.00% 71.80% 75.96% 68.57% 79.68% 79.68% 0.35%
Co 24.71% 0.00% 19.16% 11.34% 3.76% 4.35% 4.35% 0.11%
CO2 721% 0.00% 5.59% 6.12% 5.941/6 6.591/6 6.59% 1.90%
Methane 3.15% 0.00% 2.440/6 4.67% 5.79% 6.67% 6.67% 0.39%
NItrogen 0.79% 0.00% 0.61% 1.20% 1.48% 1.72% 1.72% 0.03%
Argon 0.17% 0.00% 0.13% 0.25% 0.31% 0.36% 0.36% 0.01%
Methanol 0,00% 0.00% 0.00% 0.31% 12.33% 0.60% 0.60% 84.42%
H20 0.34% 0.00% 0.26% 0.14% 1.82% 0.04% 0.041/16112.78%

B) H2 Recovery from MUG only (Figure 3)

Stream 10 62 16 20 30 42 58 56 52

Temperature (C] 45.0 45.0 45.0 44.9 220.0 255.0 45.0 45.0 45.0
Pressure [bar] 34.0 34.0 34.0 34.0 81.5 80.0 77.7 77.7 77.7
Molar Flow [kgmole/h] 15210.6 2162.1 1100.6 14149.0 89149.0 81157.8 75000.0 1142.2 5015.7
Mass Flow [kg/hl 186073 26449 2219 161842 1081684 1081680 919842 14009 147834

Hydrogen 653.631/6163.63% 100.00% 66.46% 53.53% 47.95% 51.09% 51.09% 0.21%
CO 24.71% 24.71% 0.00% 22.79% 6.74% 3.49% 3.71% 3.71% 0.09%
CO2 7.21% 7.21% 0.00% 6.65% 5.32% 4.83% 5.06% 5.06% 1.30%
Methane 3.15% 3.15% 0.009/6 2.91% 25.06% 27.530/6 29.24% 29.24% 1.540/6

Nitrogen 0.79% 0.79% 0.00% 0.73% 7.21% 7.92% j 8.43% 8.45% j 0.140/.
Argon 0.17% 0.17% 0.00% 0.15% 1.45% 1.59% 1.70% 1.70% 0.05%
Methanol 0.00% 0.00% 0.000/6 0.00% 0.59% 5.57% 0.70% 0.70% 78.50%
1420 0.34% 0.34% 0.000/0 0.31% 0.10% 1.12% 0.07% 0.071Y. 17.16%

10 The calculations demonstrate that in the case of hydrogen recovery from the purge gas only, the excess carbon oxides are being eliminated from a gas stream that is relatively low in
carbon oxides and so large quantities of hydrogen are being lost with the waste gas leading to

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a lower methanol production rate. Furthermore in the fiowsheet of Figure 2, a more complex,
and therefore more expensive steam-raising converter Is required. In the case of hydrogen
recovery from MUG only, hydrogen is being lost with the waste gas from the hydrogen recovery
unit as well as being lost in the purge gas stream. Again, the high hydrogen loss leads to lower
5 methanol production.

Furthermore, calculations also demonstrate that If no hydrogen recovery is affected, compared
to the flowsheet depicted in Figure 1, the process requires 75% higher catalyst volume due to
the low partial pressure of hydrogen and results in 3x higher by-products due to the high CO:H2
10 ratio. Thus hydrogen recovery according to the present invention is able to reduce the catalyst volume and amount of waste product therefore reducing the size of reaction vessels and simplifying purification of the crude methanol, which reduces the overall cost of the process.

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I. A process for synthesising methanol comprising the steps of;
(I) reforming a hydrocarbon feedstock and separating water from the resulting reformed
gas mixture to generate a make-up gas comprising hydrogen and carbon oxides,
said make-up gas mixture having a stoichiometric number, R, defined by the
formula; R = ([H2] - (CO2]) I ([CO2] 1- [CU]) of less than 2.0,
(ii) combining said make up gas with an unreacted synthesis gas to form a synthesis
gas mixture,
(iii) passing the synthesis gas mixture at elevated temperature and pressure through a bed of methanol synthesis catalyst to generate a product stream comprising
methanol and unreacted synthesis gas,
(iv) cooling said product stream to recover a crude methanol stream from said unreacted synthesis gas,
(v) removing a portion of said unreacted synthesis gas as a purge gas, and
(vi) feeding the remaining unreacted synthesis gas to step (ii)

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characterized in that hydrogen is recovered from at least a portion of said purge gas and portion of said make up gas, and the recovered hydrogen is included in the synthesis
gas mixture.

2. A process according to claim I wherein the hydrogen recovery Is performed using a
pressure swing hydrogen recovery unit.

3. A process according to claim I wherein the hydrogen recovery is performed using a
membrane hydrogen recovery unit.

4. A process according to claim 2 wherein the recovered hydrogen is added to said
unreacted synthesis gas or added to the make up gas that is combined with said
unreacted synthesis gas.

5. A process according to claim 3 wherein the recovered hydrogen Is fed to the make up gas
that is combined with said unreacted synthesis gas.

6. A process according to any one of claims Ito 5 wherein the bed of methanol synthesis
catalyst is disposed in a reactor in which the catalyst bed is cooled by the synthesis gas
mixture passing through tubes disposed within the catalyst bed.

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7. A process according to any one of claims I to S wherein the product stream Is cooled In
separate stages of heat exchange with water under pressure, the synthesis gas mixture
fed to the catalyst bed and cold water.

8. A process according to any one of claims I to 7 wherein the purge gas provides between
5 and 95% of the required hydrogen on a molar basis to bring the value of R towards 2.0.

9. A process according to any one of claims I to 8 wherein all the purge gas is fed to the
hydrogen recovery unit.

10. A process according to any one of claims I to 9 wherein the amount of make up gas fed
to hydrogen recovery comprises <20% by volume of the make up gas provided by the
reforming stage.

11. A process according to any one of claims I to 10 wherein the reforming is autothermal
reforming.

S12. A process according to any one of claims I to 11 wherein the crude methanol Is distilled
to obtain a substantially pure methanol product.

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Figure 2 (Comparative)

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Figure 3 (Compiatfve)

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A. CLASSIFICATION Of SUBJECT MATTER

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ADD. C07C29/152 C07C29/153

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Electronic data base consulted during the International search (name of data base and Where practical, search termused)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category* Citation of dccumerd with Indication, where appropriate, of the relavant passages Relevant to claim No,

X US 4 650 814 A (KELLER El AL) 1-12

17 March 1987 (1987-03-17) figure 3

column 1, lines 9-13,40-48,62-65
column 3, lines 17-22,46-55
column 4, lines 21-66
column 13, lines 10-19
claims 1,7

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S–NTESIS DE METANOL

Esta invenciôn se relaciona con la sintesis cia metanol y en particular con la sintesis de metanol a partir de un gas de sintesis que es deficiente en hidrógeno.
La sintesis metanol se ileva a cabo de manera general
haciendo pasar un gas de sintesis que comprende hidrógerio, óxidos de carbono y cualquier gas inerte a una elevada temperature y presión a travØs de uno o mÆs lechos de un catalizador pare la sintesis de metanol, que a menudo as una composición qua cornprende cobre. El metanol as generalmente racuperado machaste el enfriamiento la corriente de gas de producto per clebajo del punto de condensación del metanol y separando el producto come us liquido. El proceso se lieva a cabo usualmente en us bucle: de esta manera la corriente remanente del gas qua no reaccionó as normalmente reciclada hacia el reactor de sintesis come parte del
gas de sintesis a travds us circulador. El gas sintesis
fresco, denomiriado gas de raposición, se comprime y se afade al gas que no reaccionó reciclado con el fin de formar la corriente de gas de sintesis. Una corriente de purga as meziudo tomada cia la corriente de gas circulante para evitar la acuxsulación de gases inertes. Dicho proceso se describe, per ejernpj.o, en la EP 0329292.

Eats disposicióri as, no obstante, inadecuada pars los gases
cuyo indice estequiemØtrico (R), definido per la formula;

as manor cia 2, lo qua significa que al gas as deficiente en H, pars la fabricaciOn de metanol. Los gases de sintesis deficientes en hidrOgeno pueden ser obtenidos a partir de los procesos de

reformación que incluyen una etapa de oxidación parcial, taj.
como, la reformaciôn autotØrrnica. En dicho caso, el hidrógeno
serÆ consumido en is racción cia sintesis del metanol mientras qua una porción substancial de los óxidos de carbono permariecen sin reaccionar lo que conduce a una composición en el bucle sintesis que tiene niveles muy elevados de oxides de carbonc,
pare es bajo en hidrógeno. Esto tiene varias corisecuencias, entre
alias, qua el volumen de catalizaclor requerido serÆ elevado y qua el nivel de subproductos (alcoholes superiores y cetonas, en particular) serb mucho mayor qua el normal.
Es conocido qua el hidrógeno puede ser recuperado de la corriente de gas purga utiiizando una unidad de recuperaciOn cia hidrogeno y reciclado de retorno al gas de alimentación de manera qua el gas dentro del bucle de sintesis sea significativamente mao rico en H2 que el gas de sintesis. Sin embargo, una de las dificultados eon eats enfoque es qua para los gases de sintesis qua son muy deficientes en H2 es necesario
.recuperar grandes cantidades H2 del gas cia purge, y tener dicho
gran flujo de gas purga significa ya sea operar el bucle de
sintesis a baja presión o tamer una baja relación de flujo de gas de reciclaje a flujo de gas de sintesis fresco Correr el bucle de sintesis a baja presiOri no as atractivo pars las piantas comerciales a gran escala debido al tamaæo de las tuber5.as, diOmetros de los recipientes, etc., mientras qua correr con una baja re].ación reciclado puede imponer restricciones sobre el
reactor sintesis de metanol qua pueden oar inaceptables. Por
ejexnpio, una baja relación de reciclado quiere decir qua utilizar el gas circulante para enfriar la reacciOn, ya sea en un reactor tubular o cia enfriamiento rÆpido, es imposible, de manera que la cinica opcióri as un reactor de producciOn de vapor. AdemÆs, una

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baja relación de reciclado quiere decir que la concentración cia
reactivo en la eritrada al reactor es elevada coma serÆn las tasas
de reacción, ad, can el fin de evitar las excesivas temperaturas en el lecho de catalizador, el catalizador tendrA que ear instalado dentro de los tubos o de un reactor tubular qua produce vapor. Esta es una alterriativa poco atractiva ya que conduce a la pobre utilización del volumen dentro del casco del reactor asi coma tambiØn al requerimiento de placas tubulares pesadas y extrerrtadaxnente gruesas. TambiØn hay un limite a la presión a la cual el vapor puede ser producido, de manera que la utilización de este vapor puede cornplicar el cliseæo del sisterna de vapor en dicha planta, lo que cia coma resultado incremento del costo asi cons la reducción de la operabilidad y la confiabilidad.
Otra alternativa es tomar una corriente secundaria de gas de sintesis fresco, taxnbiØn denominada gas de reposición (GDR), recuperar hidrôgeno del mismo utilizarido una unidad de recuperación de hidrógeno, y alicnentar este hidrógeno de regreso al gas de sintesis. No obstante, la desventaja de esta
disposición as que se pierde algo del bidrógeno en la unidad de
recuperacidn de hidrógeno siempre antes de que Øste ilegue al bucle de sintesis, y el gas de sintesis despuØs del enriquecimierito con este hidrógeno, tendrÆ ahora us indice estequiomtrico mayor de 2, de manera que el gas de purga consistirÆ de una porciÆn significativa deH2 que no reaccionó. El efecto de esto es que la cantidad de nietanol producido a partir de una cantidad fija de gas de sintesis se reduce, y de esta manera se requiere una gran generación de gas de sintesis para una capacidad de producción dada. Ya qua la unidad de generaciÆn
de gas de sintesis es la parte rnÆs costosa de la planta, el
incremento en el gasto en estÆ area es antieconÆmico.

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El gas do reposición quo comprende hidrógeno y ôxidos do carbono se obtiene reforntando una carga do alirnentación do hidrocarburo tal comb metano, gas natural, gas asociado a nafta y removiendo el agua de Is mozcla gaseosa reforxnada resultante. El proceso de reformación puede comprender una a mÆs etapas do reformación con vapor yio de oxidación parcial. Por ejemplo, la roformación puede comprender una etapa do roformación con vapor primaria en la cual un hidrocarburo y vapor, y do manera opcional diôxido do carbono, se hacen pasar a travØs de tubos lienos con catalizador calentado externamente en un reformador calentado con gas o enceridido por coxnbustión y una etapa do reformación secundaria en la cual los gases roformados primarios, opcionalmente con hidrocarburo adicional, so someten a una etapa do combustion parcial con un gas que contiene oxigeno, de manera preferible oxigeno substancialmente puro, y los gases parcialmente combustionados son hochos pasar a travØs do un locho de catalizador de reformaciOn con vapor. En una configuraciOn prefericla, los gases reformados secundarios so utilizan para calentar externamente los tubas ilenos con catalizador del reformador primario. Do manera alternativa, el proceso de reformaclOn puede comprender una etapa do reformaciOn autotØrmica en la cual la carga do alimentaciOn do hidrocarburo se alimerita a un reformador, on dondo Øste se somete primero a una oxidaciÆn parcial con gas quo contiene oxigeno y los gases calierites parcialmento combustionados rosultantos so hacen pasar a travØs do un lecho de un catalizador de reforznación con vapor. El vapor puede sor afiadido al hidrocarburo y/o al gas quo contiene oxigeno.
Los catalizadores do reformaciÆn con gas primaria comprenden tipicamento niquel sobre un soporto refractario, por ojemplo,

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alirnina o aluxuinato de calcio. Los catalizadores de reformación con vapor autotØrmica y securidaria tambiØn comprenden tipicamente niquel sobre un soporte refractario. De manera alternativa, se puede emplear un catalizador de metal precioso, tal como, platirio, paladio y/o rodio.
Adicionalmente, el proceso de reformaciôn puede comprender
una o xnÆs etapas de reformación adiabÆtica con gas sobre un lecho de catalizador Us reformación con gas de nlquel con soporte a temperaturas entre 450 y 650 °C. Dioha refcrmación con gas
adiabÆtica a bajas temperaturas, a menudo deriominada pre-
reformación, tiene la ventaja de que los hidrocarburos superiores
se convlerten a metano y se genera algo de hidrôgerio, reducienclo de esta manera la posibili.dad de la formación de carbono en si reformador Us vapor prirnario o reormador autotØrmico, especialmente a bajas relaciones de vapor.
La mezcla de gas reformado, dependiendo del proceso Us
reformación gus se utilice, puede estar a una temperatura en el
range desde 400 hasta 1150 °C, a una presiôn desde 10 hasta 30 bar abs y comprende diferentes cantidades de vapor, hidrÆgenc, oxides Us carbono, es decir, monoxide de carbono y dioxide Us carbono, metano, y gases inertes, tal coma, nitrógenn y argOn.
El gas de reposición se obtiene de manera preferible de la
mezcla de gas reformado enfriªndolo por debajo del punto Us condensaciOn del vapor y separando el agua condensada de la mezcla gaseosa. El enfriamiento se puede llevar a cabo mediante intercamblo tOrmico con agua para generar vapor. La mezcla de gas reformado Se enfria de manera preferible per debajo Us los 100 ° C, mOe preferiblemente por debajo Us los 60 °C con el fin de condensar el agua. La mezcla enfriada as de manera preferible alimentada a un separador en donde el agua condensada se puede

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separar de la mezcla gaseosa. El agua separada se puede reciclar citilmente con el fin de generar vapor para realizar la etapa de reformación.

De cualquier manera como se genera el gas cia reposición;
Øste debe tener un indice estequicmØtrico (R), clefii-iido per la fórise la;

R- [H2}-[co2]
fco2]+[cö}

en la cual [H2], [CO2] y [CO] son las concentraciones hidrógeno, dioxide de carbono y monOxide de carbono, respectivamente, mesas cia 2,0, preferiblemante de macos de 1,8. De esta manera, es deficiente en hidrOgeno para la etapa de sintesis del metanol.
En la presente invenición, se toma una corriente secunidaria
de gas reposiciOn para la recuperaciOn del hidrOgeno. El remanente se alimenta a en bucle de sintesis de metanol en el cual una mazda de gas de sintesis qua comprenda gas de reposiciOn y gas de sintesis qua no reaccionO qua contiene hidrógeno y óxidos de carbono, se alimenta a una o mÆs etapas de sintesis de metanol par maclie de uno o mÆs circuladores. La temperatura y presiOndel gas de reposiciOn se ajustan de manera preferible para ser apropiados para la sintesis del metanol antes de alimentarse al bucle cia sintesis cia metanol per medic de compresores a ix-itercambiadores tOrmicos, conocidos per aquellas personas expertas en la tØcnica. La sintesis del metanol puede ser deseablemente ilevada a cabo a presiones en el rango desde 40 hasta 150, y mÆs convenienitemente en el range desde 45 hasta 120, bar abs. La temperatura del catalizador de sintesis est adecuadainente en el range desde 160 hasta 300 °C; de manera preferible is temperatura mØxima estÆ per debajo de los 285 °C.

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El gas de sintesis ingress preferiblemente en el lecho do catalizador a una temperatura en el range ciesde 200 hasta 250 °C y deja los lechos a temperaturas preferiblemente en el range desdo 220 hasta 260 °C. Dichas temperaturas proveen uris tasa aceptable do producción de metano]. (debido al oquilibrio favorable) sin producir un gran contenido do impurezas come productos secundarios ml reducir la vida del catalizador, in quo podria resultar do is operación a elevadas temperaturas.
El catalizador pars is sintesis del metanol estÆ do manera preferible basado en cobre. Particularmente apropiados son los catalizadores quo contienen cobre asi come compuestos, per ejemplo, óxidos do zinc, aluxninio, cromo, titanic, zirconic y/o magnesio. El catalizador puede estar en la forms do polets, tabletas o formas extruidas. Los catalizadores particuiarrnente preferidos so describen en la US 4788175.
La etapa de sintesis de metanol se puede lievar a efecto en
un reactor de sintesis do metanol del tipo de convertidor con enfriamiento rÆpido o en un reactor en el cual el lecho del catalizador tiene irimerso en el mismo tubos do intercarnbio tØrmico a travØs do los cualee el gas do sintesis pass en la ruts hacia el lecho del catalizador, per ejemplo, come se describe en la EP 0082070. Do manera alternativa, se puede utiiizar un reactor del tipo enfriado per tubes, per ejemplo, conforme so describe en la EP 0081948, en donde el calor exotØrmico de is sintesis del metanol es removido per un flujo de refrigerante, particularmente agua, a travØs do tubos pars ref rigerante dispuestos en el lecho a lechos del catalizador. Do manera altornativa, el lecho do catalizador enfriado per tubes puede estar dispuesto en un recipiente de reacción come un lecho anular con medics pars el ingroso del gas de sintesis adyacentes a is

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(k periferia externa del lecho asi como medios para la salida del
gas do sintesis que reaccionó adyacentes al eje del recipiente,
de manera que el gas de sintesis fluya radialmente hacia adentro
a travds del lecho del catalizador, es decir, en un reactor de
flujo radial. En una disposición de flujo radial, los tubos eon
refrigerante estarÆn generalmente dispuestos en pianos perpendiculares al eje del recipiente. Un ejemplo de un diseæo do reactor do flujo radial apropiado so muestra en la EP 1060788. Haciendo pasar la mezcia do gas do sintesis a elevada temperature y presión a travds del lecho del catalizador de sintesis de metanol, so genera una corriente de producto que comprende metanol y gas de sintesis quo no reaccionó.
El metanol se recupera enfriando la corriente de producto para condensar el metanol on bruto, quo contiene agua y pequeæas cantidados do alcoholes superiores y otros coinpuestos, del gas do sintesis quo no reaccionó. El metanol en bruto puede entonces ser utilizado, pero es de manors preferible enviado a una o rnÆs etapas do destilación en las cuales so separa el metanol puro del agua, de los alcoholes superiores y de otros subproductos.
Debido a que la etapa do sintesis del metanol consume hidrógeno y óxidos do carbono, el gas de sintesis quo no roaccionó puede ser enriquecido en gases iriertes, tal como nitrógono y argon, quo son impurezas en el hidrocarburo yin gas quo contiene el oxIgerlo. El metano quo no reaccionó do la etapa do reformaciOn tambiØn se puede acumular. La acumulaciOn do dichos gases es irideseable y por in tanto una porciOn dol gas do sintesis quo no reaccionó se remueve como gas do purga. La cantidad de gas do purge dependerÆ del diagrarna do procesos exacto. De manera preferib.le, el gas de sintesis quo no reaccionO restarite se coinprime antes de mezclarlo con el gas do reposición.

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De manors preferible, la mazda de gas de sintesis resultante se calierita antes do alimentarse al reactor do sintesis do metanol. En la presente invención, el hidrógeno so recupera de por in menos una porciórl del gas do purga y de una porción del gas do reposicióri y dicho hidrógerio recuperado se incluye en la mezcia do gas de sintesis quo so alimonta al reactor de sintesis do metanol. Los gases de purga y de reposiciÆn comprendon hidrógeno y Æxiclos de carbono asi coma tambiØn pequefias cantidades de metano quo no reaccionó a inertes. El hidrageno so puede recuperar de estos gases, qua pueden o no ser combinados de antemano, utilizando una o mÆs unidados de recuperacidn do hid.rÆgerio. Dichas unidades son coriocidas y pueden funcionar mediante is denominada absorción con oscilación de presión (AOP) en is cual un material absorbente estÆ dispuosto en la unidad que captura los componentes quo no son do hidrdgeno de is corriente do gas, permitiendo asi que un gas rico en hidrÆgeno pase a travØs. La ventaja de una unidad do recuporación de hidrógono AOP el gas rico en hidrógeno so recupera a is presiôn de
operación de AOP y el gas de desecho, que so puedo utilizar come combustible, so recupera a baja presión. Una desventaja as quo el absorbente tiene quo ser periódicamonte limpiado del material capturado ajustando (es decir, disminuyendo) la presión en la
unidad. Una alternativa a is recuperación de hidrógeno con AOP es
una unidad de recuperación do hidrógeno con membrana, funciona en forma continua. La rnembrana funciona permitiondo
el hidrógeno paso a travis mientras que retienen los componentes
no son hidrógeno de la corriente de gas aiimentada a la Ismisma. No obstante, la unidad de recuperacióri de mernbrana recupera una corriente do gas rica en hidrógeno a una presión
reducida par debajo do aquØlla de la presiÆn parciai do hidrógeno

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en la corriente de alimentación a la ’unidad, mientras que el gas ’27

de desecho se recupera a is presión de opersciOn de is mernbrana
Por consiguiente, cuando se ettplea is unidad de recupersción
de hidrógeno de AOP, el hidrógeno recuperado puede ser ya sea
alimentado al gas de reposición antes de su adición al bucle de
sintesis, o el hidrÆgeno recuperado puede ser alimentado
directarnente al bucle de sintesis agregÆndolo ya sea al gas de
sintesis que no reaccionó antes o despuØs de que se ha reinovido la corriente de purga a a is mezcia do gas do sintesis (que comprende el gas do reposición y el gas de sintesis quo no reaccionó coxnbinados). En contraste, cuando is unidad de recuperación do hidrógeno es una unidad de recuperación do menthrana, el hidrogeno recuperado es preferibiexnente alimentado a
la corriente de gas de roposición destinada al bucle do sintesis
antes do su cornpresión. En un process preferido, el hidrogeno recuperado es alimentado al gas de reposición. El gas de reposición ajustado con hidrôgeno resultants es iuego comprimido, alimentado al bucle de sintesis en cioncle se mezcia con el gas de sintesis quo no reaccionó remsOente, es decir, despuØs de que el gas do purga ha sido removido, se caiienta y ailments al reactor de sintesis do metanol.
La aciición de hidrógeno incrementa si valor de R en is mescia de gas de sintesis hacia el valor estequiomØtrico Æptimo pars la sintesis de inetanol. De manera proferible, la cantidad do hidrogeno afiadido incrementa el valor de R hacia 2,0, do manera preferible hasta 2,2, especiaimente 2,1 – 0,1.
La cantidad de hidrógeno recuperado del gas de purga a del
gas de reposiciÆn puede ser variada dependiendo del diagrama de procesos adoptado asi coma de los contenidos do hidrógeno y ô xidos de carbono en el gas de rsposición provisto en is otapa do

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reformaclón. Por ejemplo, el gas do purga puede proveer entre 5 y 95% del hidrôgeno requerido sobre una base molar para lievar el valor do R liacia 2,0 y ol gas do reposición, en ccnsecuencia, estÆ entre 95 y 5%. De manera preferible, todo el gas do purga se alimenta a la unidad de renuperación do hidrÆgeno, ms preferiblezuente para proveer >50% sobre una base molar del hidrógeno requerido, siendo el restante provisto per in corriente de gas do reposición. De esta manera, en una disposición preferida, el gas do purga so exiruta hacia la unidad de recupemación do hidrógeno y esta fuente do hidrôgeno so complementa con una corriente aecundaria de gas do reposición. Preferiblemerite, la corriente secundaria del gas do reposición alimentado a la unidad do recuperacióri do hidrógeno comprende <20%, do manera preferible:?10% en volumeri del gas de rnposiciÆn provisto por la etapa do reformaciOn. or lo tanto,
- preferiblemente >80%, do manera mae preferible;-?’90% en volumen del gas do reposiciôn so alimenta al bucle de sintesis. En esto sentido, el diseæo del bucie do sintesis so puede establecer para pemmitir quo se seleccione el equipo mÆs apropiado, a is vez quo so mantiene un nivel muy elevado de conversion de hidrogeno a rnetanol.

La invención se ilustma haciendo referenda a los dibujos
que in acompaæan en los cuales la Figura 1 ilustma un diagrama do operaciones do una configumacion preferida do in prosente invenciOn en clonde el hidrOgeno es recupemado do una corriente de gas do purga y gas do reposiciOn combinados utilizando una unidad do recuperaciOn do membmana, y se alimenta al gas do reposiciOn remanente, que es luego comprirnido y alimentado al bucie do sintesis. Las Figuras 2 y 3, a manera do comparadión, ilustran cliagramas do operaciones quo no estÆn de acuerdo con la presente

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invención, en las cuales se efectüa la recuperación parcial del hidrOqeno ya sea solo del gas de purga a sOlo del gas de rpCSiciOfl
En la Figure 1, al gas de reposiciOn qua se suministra a travØs de is linea 10 Se divide en dos porciones. Una primera porción 12, controlada por la vÆlvula 14 an combine con una corrierite de hidrOgeno 16 aiimentada desde la unidad de recuperaciOn de hidrOgeno de AOP 18 y los gases cornbinados son hechos pasar a travØs de la linea 20 hacia el. compresor 22 en donde su presión se incrementa antes de alimentarlos a travs de is linea 24 a un gas de sintesis que no reaccionO comprimido en is linea 26. El gas de sintesis combinado an alizuenta a travØs de la linea 27 hacia el intercambiador tØrmico 28 en donde se calienta y luego se alimenta a travOs de linea 30 a la zone de entrada 32 de un reactor de sintesis de metanol 34 definido por las paredes de reactor y las piacastubu1are. El gas de sintesis pass en dirección ascendente a travØs de una pluralidad
de tubos 36 que Se extienden desde la place tubular 35 en ------------
direccióri ascendente a travØs de un lecho de catalizador de sintesis de cobre particulado/ zinc! aldmina 38 bade un espacic 40 encirna del lecho y de aili en direcciOn descendente a travØs del lecho bade una zona de salida per encima de is placa tubular
35 La sintesis de metanol se ileva a cabo conforme ins gas-es
pasan en dirección descendente a travØs de la place tubular de catalizador 35. La sintesis de metanol se have a cabo conforme
los gases pasari en direcciÆn descendente a travØs del lecho del
catalizador y la corriente de producto resultante es alimentada desde is zona de sahida a travØs de is linen 42 hacia el intercambiador tOrmico 44 en donde se utilize pare producir vapor, de alhi al intercambiador tOrmico 28 en donde se utiliza

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para calentar el gas de sintesis y luego al intercambiador tØrxnico 48 en doncle se enfrma con agua fria con el fin de condensar el metanoi en bruto. La rnezcla enfriacla es alimentada a travØs de in linea 49 al separador 50 que separa el znetanoi en bruto a travØs de in linea 52 del gas de sintesis qua no reacciorió en in linea 54. Se tome una corriente de purge 56 de in linen 54 y el gas de sintesis que no reaccionô remanente Se alimenta a travØs de in linen 58 al compresor 60. El gas de sintesis qua no reaccionó comprixuido deja el compresor 60 a travØs de is linea 26 y se combine con el gas de reposición de la linea 24. La segunda corriente de gas de reposición 62 tomada de in linea 10 es combinada con la corriente de gas de purga 56 y la corriente coxnbinada se alimenta a travØs de la linea 54 a la unidad de recuperaciôn AOP 18. Los gases de desecho agotados en hidrógeno se remueven unidad de recuperación de hidrógeno 18 a travØs de is linea 66.
En la Figura 2 (comparative) hay recuperación de hidrógeno desde in corriente de gas de purga 56 solamente. De esta manera, in corriente de gas de purga 56 pasa a la unidad cia recupereción de hidrogeno 18, la corriente de gas reposición 62 estÆ ausente y se aflade el hidrógeno recuperado 16 a la corriente 10. En este case, el reactor de sintesis es necesariaxnente un convertidor que produce vapor con enfrmamiento de agua presurizada dentro del lecho y per consiguiente se omite el intercanthiador tØrmico 44. En este diagrama de operaciones, es necesario utilizar un convertidor qua produce vapor en luger del convertidor enfriado per tubes mÆs económico y pequeæo que se utilize en la Figura 1, debido a qua in relación de circulación del gas de sintesis es muy baja pars permitir el uso efectivo del CET. Esto as debido a que se tiene qua remover una mayor cantidad de gas de purga pars

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La invención se ilustra adiciorialmente hacienda referenda los siguientes ejemplos calculados.

Ejemplo 1

De acuerdo con la configuración que se ilustra en la Figura 1

Corriente 10 62 16 20 30 42 58 56 52
Temperatura [CJ 45(0 45,0 45,0 44,9 220,0 255,0 45,0 45,0 45,0
PresiOn [bar] 34,0 34,0 34,0 34,0 81,5 80,0 77,7 77,7 77,7
Flujo molar [jcg-mo1/hl 15210,6 1181,0 1336,8 15366,4 75366,4 66877,1 60000,0 1583,1 5294,2
Flujo de Masa [kg/hl 186073 14447 2695 174321 844492 844487 670171 17683 156637

HidrÆgeno 63,63% 63,63% 100,00% 66,79% 59,86% 53,50% 58,08% 58,08% 0,24%
CO 24,71% 24,71% 0,00% 22,56% 7,61% 3,49% 3,79% 3,79% 0,09%
CO2 7,21% 7,21% 0,00% 6,58% 5,88% 5,37% 5,70% 5,70% 1,49%
Metano 3,15% 3,15% 0,00% 2,88% 19,46% 21,93% 23,70% 23,70% 1,27%
Nitrogeno 0,79% 0,79% 0,00% 0,72% 5,44% 6,13% 6,64% 6,64% 0,11%
Argon 0,17% 0,17% 0,00% 0,15% 1,11% 1,25% 1,35% 1,35% 0,04%

!4etanol 0,00% 1 0,00% 1 0,00% 0,00% 0,53% 6,95% 0,67% 0,67% 79,97%
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Temperatura [C] 45,0 45,0 45,0 44,9 220,0 255,0 45,0 45,0 45,0
9resi6n [bar] 34,0 34,0 34,0 34,0 81,5 80,0 77,7 77,7 77,7
Flujo molar [kg-mol/hI 15210,6 2162,1 1100,6 14149,0 99149,0 81157,8 75000,0 1142,2 5015,7
Flujo de Masa [kg/hl 186073 26449 2219 161842 1081684 1081680 919842 14009 147834

Hidrógeno 63,63% 63,63% 100,00% 66,46% 53,53% 47,95% 51,09% 51,09% 0,21%
Co 24,71% 24,71% 0,00% 22,79% 6,74% 3,49% 3,71% 3,71% 0,09%
CO2 7,21% 7,21% 0,00% 6,65% 5,32% 4,83% 5,06% 5,06% 1,30%
Metano 3,15% 3,15% 0,00% 2,91% 25,06% 27,53% 29,24% 29,24% 1,54%
Nitrogerio 0,79% 0,79% 0,00% 0,73% 7,21% 7,92% 8,43% 8,43% 0,14%
Argon 0,17% 0,17% 0,00% 0,15% 1,45% 1,59% 1,70% 1,70% 0,05%
Metanol 0,00% 0,00% 0,00% 0,00% 0,59% 5,57% 0,70% 0,70% 79,50%
H20 0,34% 0134% 0,00% 0,31% 0,10% 1,129. 0,07% 0,07% 17,61%

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REPUBLICA DE COLOMBIA

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Folio 65
2020
Bogota D.C.,

Doctor (a)
RODRIGUEZ D ALEMAN DILIA MARIA

Apoderado(a) y/o Repre’sentante de
JOHNSON MATTHEY PLC

REFERENCIA Radicaciôn No. 07 121377
Solicitud internacional PCT/G22006/050096
Fecha inicio fase nacional 27/12/2007
Tr&mite 11
Evento 378
Actuación 416
Oficio No. 5322
Folios 1

Teniendo en cuenta que la solicitud de privilegio de patente que se tramita bajo ci expediente indicado en la referencia, reline los requisitos de forma estabiecidos en la Decisiôn 486 de la Comisión de la Comunidad?.ndina, ci Tratado de Cooperación en Materia de Patentes (PCT), ci Reglamento y la Circular Unica de la Superintendencia de Incaustria y Comercio, se envia el extracto de la solicitud a la Of icina de Comunicaciones para efecto de su pu)Dlicación en la Gaceta de Propiedad Industrial.

Cümplase
Dado en Bogota DC,

ALIX CARMENZA
Jefe de la di

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