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(54) Title: METHANOL SYNTHESIS

(57) Abstract

Methanol synthesis in a synthesis loop having at least two synthesis stages wherein at least the final synthesis stage of the loop is effected in indirect heat exchange with pressurised water whereby a stream of heated pressurised water is produced, and the make–up gas fed to the loop is produced by a process including catalytically reacting a hydrocarbon feedstock with steam and at least part of that steam is introduced by direct contact of the hydrocarbon feedstock with the stream of heated pressurised water.

<u>Methanol synthesis</u>

This invention relates to methanol synthesis. Methanol is conventionally synthesised at elevated and pressure in a methanol synthesis loop where synthesis gas, containing hydrogen, carbon oxides, and, usually, some inerts such as nitrogen and methane, is passed over a copper

5   catalyst at an elevated temperature, typically 200-300°C, and pressure, typically 40-150 bar abs., and then the product reacted gas is cooled, condensed methanol is separated and the unreacted gas is recycled to the synthesis reactor. Fresh synthesis gas, hereinafter termed make-up gas, is added to the loop at a suitable location, usually to the recycled unreacted gas before the latter is fed to the synthesis reactor. A purge is taken from the loop at a suitable point to avoid the build-up of

10 inerts to an uneconomically high level. The make-up gas may be added to the loop before or after the separation step.

Methanol synthesis is an exothermic process and it is necessary to limit the amount of reaction occurring in a bed of catalyst and/or to cool the bed, to avoid overheating the catalyst. To this end, a variety of reactor types have been employed. For example it has been proposed to employ a

15 reactor with means to inject cool quench gas (generally a mixture of make-up gas and unreacted recycle gas) into the catalyst bed or between beds. Examples of such quench bed reactors are described in GB 1105614, EP 0297474, EP 0359952 and US 4859425. It has also been proposed to employ reactors having heat exchangers within the beds so that heat evolved by the reaction is transferred to a coolant. Thus in the arrangement described in US 4778662 the synthesis reactor

20 has coolant tubes which extend through at least the inlet part of the catalyst bed and open into the space above the inlet to the catalyst bed: the coolant is the mixture of recycled unreacted gas and make-up gas so that the reactants are heated to the desired inlet temperature by the evolved heat. In the arrangement described in GB 2046618 the catalyst is disposed as a single bed through which the reactants flow radially and heat exchange tubes are provided through which a coolant, e.g.

25 pressurised boiling water, is circulated.

It is often desirable to increase the amount of methanol synthesised. In US 5252609 and US 5631302 methods are described wherein the make-up gas is subjected to a preliminary synthesis step before it is added to the synthesis loop. In the aforesaid US 5631302 the second synthesis stage, i.e. that in the synthesis loop, is effected in heat exchange with boiling water,

30 thereby producing steam which may be exported. In EP 0790226 an arrangement is described where there are two synthesis reactors in series in the loop; the first reactor being cooled by heat exchange with boiling water while the second is cooled by heat exchange with the mixture of make-up gas and recycled unreacted gas.

In the aforementioned arrangements wherein the coolant is boiling water, the reactor operates

35 under essentially isothermal conditions and the temperature and pressure of the steam produced is largely dependent upon the temperature at which the reactants leave the synthesis reactor. In order to achieve a high conversion per pass, this temperature is desirably relatively low, for example in the

range 200 to 250°C . As a result the temperature and pressure of the steam is such that the steam is of little utility elsewhere in the methanol plant.

The make-up gas is often produced by a steam reforming process wherein a hydrocarbon feedstock, such as natural gas, is reacted with steam at an elevated pressure, e.g. in the range 20 to 80 bar abs., and at an elevated temperature, e.g. in the range 700 to 1100°C, in the presence of a catalyst. This reforming reaction is strongly endothermic and at least part of the reforming reaction is generally operated with the catalyst disposed in tubes through which the feedstock/steam mixture passes while the tubes are heated externally by a suitable medium.

It is known, e.g. see US 4072625, to recover heat from reacted methanol synthesis gas leaving a methanol synthesis reactor by heat exchange with water under pressure to give a stream of heated water which is used to provide at least some of the steam required for steam reforming by contacting the stream of hot water, preferably after further heating, directly with the hydrocarbon feedstock. Such direct contact of the hydrocarbon feedstock with hot water is herein termed saturation. We have realised that, instead of recovering the heat from the reacted synthesis gas after it has left the synthesis reactor, by using a reactor operated in heat exchange with water under such a pressure that the water does not boil, hot water useful for saturation can be obtained, while at the same time enabling an adequate temperature profile to be achieved in the synthesis reactor.

In the present invention, the synthesis loop comprises two or more synthesis stages in series with at least the final stage being effected in indirect heat exchange with water under sufficient pressure to prevent boiling, and the resultant heated pressurised water is used to supply at least some of the process steam required for the aforesaid reforming reaction by contacting the hydrocarbon feedstock with the pressurised heated water. It will be appreciated that since the water is contacted directly with the hydrocarbon feedstock, the pressure of the pressurised water is equal to or greater than that employed in the reforming reaction.

According to the present invention we provide a process wherein methanol is synthesised in a loop from a synthesis gas mixture comprising hydrogen and carbon oxides in at least two synthesis stages, synthesised methanol is separated, at least part of the unreacted synthesis gas is recycled to the first stage, and make-up gas is added to the loop, characterised in that in at least the final synthesis stage of the loop, the synthesis is effected in indirect heat exchange with water under sufficient pressure to prevent boiling, whereby a stream of heated pressurised water is produced, and the make-up gas is produced by a process including catalytically reacting a hydrocarbon feedstock with steam at an elevated temperature and at an elevated pressure equal to or less than the pressure of said stream of heated pressurised water and at least part of said steam is introduced by direct contact of said hydrocarbon feedstock with said stream of heated pressurised water.

In contrast to the process of the aforesaid EP 0790226 where the first stage is effected in indirect heat exchange with boiling water, in the present invention at least the final stage is effected

in heat exchange with water under sufficient pressure to prevent boiling. The reactor used for synthesis in indirect heat exchange with pressurised water is herein termed a water-cooled reactor.

In its simplest form the synthesis loop has two stages of methanol synthesis with one or both stages being effected in a water-cooled reactor. The first stage is preferably effected in a quench

5   reactor or a heat exchange reactor wherein the synthesis catalyst is cooled by transferring heat evolved by the synthesis reaction by heat exchange to the feed gas of that reactor, e.g. as described in the aforesaid US 4778662. Where more than two stages are employed, it is again preferred that the first stage is effected in a quench reactor or a heat exchange reactor as aforesaid and at least the last of the subsequent stage or stages is effected in the water-cooled reactor.

10   Where, as is preferred, the first synthesis stage is not effected in a water-cooled reactor, it may be desirable that at least part of the make-up gas is added to the loop after the synthesis gas has been subjected to the first synthesis stage and before it is subjected to the synthesis stage employing the water-cooled reactor. One advantage of this arrangement is that the throughput may also be increased by operating the loop at a lower circulation ratio, which is defined herein as the

15   ratio of the flow rate of the gas recycled from the separator to the rate at which make-up gas is fed to the loop. In a conventional methanol synthesis process, this circulation ratio is generally in the range 3 to 7. By adding at least part of the make-up gas after the first synthesis stage, low circulation ratios, e.g. in the range 1 to 4, particularly 1 to 3, may be employed. The addition of part of the make-up gas after the first synthesis stage is of particular benefit at circulation rates below

20   2.5, especially below 2. If, in a loop operating at a low circulation rate, all the make-up gas is added to the recycled unreacted gas before the first synthesis stage, the partial pressures of the reactants of the gas fed to the first stage may be relatively high leading to excessive reaction, and heat evolution, in the first stage.

It is preferred that at least 5% of the make-up gas is added to the recycled unreacted gas

25   before the latter is fed to the first synthesis stage. While all of the make-up gas may be added to the recycled unreacted gas before the latter is fed to the first synthesis stage, it is preferred that at least 10%, particularly at least 30%, of the make-up gas is added to the loop after the first synthesis stage, especially if the circulation rate is low, e.g. below 2. The proportion of the make-up gas that is added to the loop after the first synthesis stage will depend upon the type of reactor employed for

30   the first synthesis stage and on the circulation ratio.

The first synthesis stage is preferably effected adiabatically.

Thus in one form of the invention, the first stage employs a quench reactor wherein some or all of the recycled unreacted gas, optionally to which part of the make-up gas has been added, is fed to the inlet and some or all of the remainder of the make-up gas, or make-up gas in admixture with

35   recycled unreacted gas, is used as the quench gas. The gas from the outlet of the quench reactor is then fed to the water-cooled reactor.

Where a quench reactor is employed for the first synthesis stage, typically only about 20-25% of the recycled unreacted gas is fed to the quench reactor inlet: the balance, to which make-up gas may be added, is used as the quench gas. The quench reactor may have several beds of synthesis catalyst with injection of quench gas between each bed. With such a reactor it is preferred that at

5   least 50% of the make-up gas is added as some or all of the quench gas and/or to the reacted gas from the quench reactor after the first synthesis stage, i.e. before it is fed to the water-cooled reactor.

Where a heat exchange reactor, e.g. of the type described in US 4778662, wherein the catalyst is cooled by transferring heat evolved by the synthesis reaction by heat exchange to the

10   feed gas to that reactor, is employed for the first stage, a larger proportion, for example 30 to 90%, particularly 40 to 70%, of the make-up gas may be added to the recycled unreacted gas before the latter is fed to the first synthesis stage. Indeed, unless operating at very low circulation rates, e.g. below 2, all the make-up gas may be added to the recycled unreacted gas before the latter is fed to the first synthesis stage. After leaving the first synthesis stage, the remainder, if any, of the

15   make-up gas is added and the mixture passed through one or more further catalyst beds, disposed in the water-cooled reactor.

The water-cooled reactor may have the catalyst disposed in tubes with the pressurised water circulating past the exterior of the tubes. However it is preferred that the catalyst is disposed as a single bed with the pressurised water passing through cooling tubes disposed within the catalyst

20   bed.

In the present invention, the heated pressurised water is employed to supply at least part of the steam required for making the make-up gas. Thus the heated pressurised water, preferably after further heating, is directly contacted with the hydrocarbon feedstock before the latter is subjected to the reforming reaction. Such direct contact of the hydrocarbon feedstock with hot water

25   is herein termed saturation. It will be appreciated that since the water is contacted directly with the hydrocarbon feedstock, the pressure of the pressurised water is equal to or greater than that employed in the reforming reaction. Normally, the feedstock, e.g. natural gas, at an elevated pressure is subjected to desulphurisation prior to reforming. It is generally desirable to effect the contacting with the pressurised water after any such desulphurisation step.

30   In a preferred arrangement, the reforming is effected in two stages. In the first, primary reforming, stage the feedstock/steam mixture is passed over a steam reforming catalyst, usually nickel supported on an inert support, e.g. alumina or a calcium aluminate cement, disposed in externally heated tubes. In the second stage, the primary reformed gas mixture is subjected to a secondary reforming stage wherein it is partially combusted with oxygen and passed through a

35   secondary reforming catalyst. The secondary reforming catalyst is normally disposed as a single bed, again usually of nickel supported on an inert support, e.g. alumina or a calcium aluminate cement. By adjusting the amount of oxygen employed relative to the amount of feedstock, a

secondary reformed gas that approximates to the stoichiometric composition for methanol synthesis may be obtained. If the secondary reforming stage is omitted, the reformed gas is liable to have an excess of hydrogen over that required for methanol synthesis, especially where the feedstock is natural gas. In a preferred version of a reforming process employing primary and secondary

5   reforming, the primary reforming is effected in a heat exchange reformer with the heating required for the primary reforming stage being provided by passing the secondary reformed gas past the tubes containing the primary reforming catalyst.

The reformed gas is cooled and excess steam condensed therefrom before compression, if any, of the reformed gas to the synthesis loop pressure. The cooling of the reformed gas preferably

10   includes further heating of the pressurised water before the latter is contacted with the hydrocarbon feedstock. It may also include other heat recovery, e.g. heating of pressurised water fed to the synthesis reactor, and the provision of heat for distillation of product methanol.

The invention is illustrated by reference to the accompanying drawings wherein

Figure 1 is a flowsheet of one embodiment of the invention;

15   Figure 2 is a flowsheet of an alternative methanol loop arrangement for use in the flowsheet of Figure 1;

Referring to Figure 1, a hydrocarbon feedstock, such as natural gas, at elevated pressure, e.g. 45 bar abs., is fed as stream A via line 10, mixed with a hydrogen-containing gas 11 (stream B), and fed to heat exchangers 12 and 13 wherein it is heated to a temperature suitable for desulphurisation.

20   The gas is passed through a bed of a hydrodesulphurisation catalyst, e.g. nickel and/or cobalt molybdate, and a bed of a sulphur absorbent, e.g. zinc oxide, in vessel 14 to effect desulphurisation of the gas. The desulphurised gas serves as the heating medium in heat exchanger 12 and then is passed as stream C to a saturator 15. In saturator 15, the desulphurised feedstock is contacted with heated water, at a pressure similar to that of the desulphurised feedstock, fed as stream D via

25   line 16. The saturated feedstock, i.e. a feedstock/steam mixture, is then fed via line 17 to a heater 18 where it is further heated and then fed via line 19 as stream E to a heat exchange reformer 20. Heat exchange reformer 20 has a plurality of tubes 21 containing a steam reforming catalyst, e.g. nickel supported on a calcium aluminate cement rings. The reformer tubes 21 are heated by a hot gas flowing through the shell space 22 of the heat exchange reformer 20. The

30   feedstock/steam mixture undergoes primary reforming in the tubes 21 and is then fed as stream F via line 23 to a secondary reformer 24. In secondary reformer 24, the primary reformed gas is partially combusted with oxygen fed as stream G via line 25 and the partially combusted mixture is fed through a bed 26 of a secondary reforming catalyst, e.g. nickel supported on a support of calcium aluminate cement, where it undergoes secondary reforming. The resultant hot gas,

35   comprising hydrogen and carbon oxides plus unreacted steam and a little unreacted methane, is then fed as stream H via line 27 to the shell space 22 of the heat exchange reformer wherein it serves to heat the reformer tubes 21. The partially cooled secondary reformed gas leaves the heat

exchange reformer 20 as stream I via line 28. The secondary reformed gas is then further cooled by heat exchange in heat exchangers 29, 30 and 31 to below the dew point of the steam in the secondary reformed gas. The unreacted steam thus condenses and is separated as stream J from the secondary reformed gas in a separator 32. The resultant dewatered gas is then compressed in

5 compressor 33 to form fresh synthesis gas, i.e. the make-up gas, (stream K) at about the desired synthesis pressure. The make-up gas is fed to a synthesis loop via lines 34 (stream L) and/or 35 (stream M).

In the synthesis loop, any make-up gas that is fed via line 35 is mixed with recycled unreacted gas supplied as stream N via line 36 from a circulator 37. The resultant mixture, stream O, is then

10 fed via line 38 to a heat exchange reactor 39. The synthesis gas passes up through tubes 40 surrounded by a bed 41 of methanol synthesis catalyst. The synthesis catalyst is typically the product of reducing to copper metal the copper oxide in a catalyst precursor containing oxides of copper, and other metals such as zinc, chromium, aluminium, magnesium and/or rare earths. Copper/zinc oxide/alumina catalysts are preferably employed. As the gas passes up through

15 tubes 40 it is heated to the desired synthesis inlet temperature, which is typically in the range 200 to 240°C, and then passes down through the bed of synthesis catalyst. Methanol synthesis occurs with heat evolved heating the incoming gas passing up through tubes 40. The resultant reacted gas, comprising methanol and unreacted gas, is then passed as stream P via line 42 to a water-cooled reactor 43.

20 Make-up gas may be supplied via line 34 as stream L and added to the mixture to give stream Q before it enters water-cooled reactor 43. In reactor 43, the partially reacted synthesis gas passes through a bed 44 of methanol synthesis catalyst through which pass a plurality of tubes 45 through which water at a pressure substantially equal to the reforming pressure, e.g. 45 bar abs., is passed as a coolant. More methanol synthesis occurs as the gas passes through the bed 44 with the heat

25 evolved heating the pressurised water. The reacted gas leaves the water-cooled reactor 44 as stream R via line 46 and is cooled, to below the dew point of the methanol therein, in heat exchanger 47. The condensed crude methanol is separated in separator 48 and is collected as stream S via line 49. The crude methanol may then be subjected to distillation as is well known in the art.

30 The unreacted gas from which the crude methanol has been separated is recycled as stream T via line 50 to the circulator 37. Part of the unreacted gas is taken via line 51 as a purge stream U; part of the purge is fed as the hydrogen-containing gas fed via line 11 as stream B while the remainder is purged via line 52 and used as fuel, e.g. it may be combusted and the combustion products used to heat heat exchanger 18.

35 The hot pressurised water leaves water-cooled reactor 43 via line 53 and is further heated in heat exchanger 29 to provide the hot pressurised water stream D fed to the saturator 15 via line 16. In some cases it may be necessary to heat the hot pressurised water from heat exchanger 29

further in a heat exchanger 54 which may also be heated by the purge gas combustion products. The surplus water from the saturator 15 is drained via line 55. Part of the surplus water is discharged via line 56 as stream V. To the remainder make-up water is added as stream W via line 57 and the mixture heated in heat exchanger 30 and returned to the water-cooled reactor 43 via

5   line 58.

In some cases it may be desirable to increase the temperature of the coolant water entering the water-cooled reactor 43 via line 58 by recycling part of the hot pressurised water leaving the reactor 43 via line 53 directly back to line 58 as stream X via the line 59 shown dotted in Figure 1 so that the coolant stream Y fed to the water-cooled reactor 43 is a mixture of stream X and the water

10 supplied via line 58. This may be desirable to prevent overcooling of the reactants in water-cooled reactor 43, i.e. preventing cooling to a temperature at which the synthesis catalyst is no longer sufficiently active.

The heat exchanger 31 may be used for preheating the make-up water feed 57 and/or to provide heat for distillation of the crude methanol. Some or all of the water separated in

15 separator 32 as stream J and/or a methanol/water stream separated in the distillation stage, may be recycled as part of the make-up water 57.

In the alternative methanol synthesis loop shown in Figure 2, the heat exchange reactor 39 of Figure 1 is replaced by a quench reactor 60 and further heat exchangers 61, 62 and 63 are provided to heat the feed to the quench reactor to the desired synthesis inlet temperature. Make-up gas may

20 be fed as stream M to the loop via line 35 where it mixes with recycled unreacted gas (stream N) which has been heated in heat exchanger 61. Part of the resultant synthesis gas is heated in heat exchangers 62 and 63 to the desired synthesis inlet temperature and is fed as stream O via line 38 to the inlet of the synthesis reactor 60. The remainder of the synthesis gas is fed as stream O' via line 63 to the synthesis reactor 59 as quench gas. Typically quench gas is injected into the

25 synthesis reactor 60 at a plurality of locations. The reacted gas from synthesis reactor 60 is passed via line 43 to heat exchanger 63 and then may be mixed with further make-up gas supplied as stream L via line 34 and fed to the water-cooled reactor 43. The reacted gas from reactor 43 is cooled in heat exchangers 62 and 61 and then further cooled in heat exchanger 47 and then fed to the separator 48. Part of the separated unreacted gas, stream T, is fed to the circulator 37 as

30 recycle gas while the remainder is taken from the loop as a purge stream U via line 51.

Part of the make-up gas may be diverted via line 65 as stream K' and used to augment stream O' to give the quench gas stream Z.

In Figure 2 a further modification is shown by the region enclosed by the dotted line. Thus in order to increase further the amount of methanol formed, the purge gas stream U taken from the

35 loop via line 51 is subjected to a further step of methanol synthesis. Thus the purge gas stream U is fed to a feed/effluent heat exchanger 66 and then to a further heat exchanger 67 where it is heated to the desired synthesis inlet temperature. The heated purge gas is then fed as stream Q' to a

further synthesis reactor 68 which, like reactor 43, may be a reactor cooled by pressurised water. The reacted purge gas, stream R', is then fed to feed/effluent heat exchanger 66 and to a cooler 69 wherein it is cooled to below the dew point of the methanol therein. The cooled reacted purge gas is then fed via line 70 to a separator 71 wherein the condensed methanol is separated as stream S'.

5 The residual unreacted gas stream U' is then taken as the purge 52 while the separated methanol is taken, via line 72, and added to the condensed methanol in line 49 separated in the loop separator 48. The hydrogen-rich gas added to the feedstock via line 11 may be taken from the purge 52.

The invention is further illustrated by the following calculated examples in which all pressures,

10 temperatures and flow rates (in kmol/h) have been rounded to the nearest integer.

Example 1

In this example the flow sheet follows the scheme of Figure 1. The feedstock (stream A) is natural gas and the make-up water (stream W) comprises fresh water together with the condensate (stream J) separated in separator 32 and a stream of water containing some methanol separated in

15 a stage of distillation of the crude methanol. In this example all of the make-up gas (stream K) is added as stream M to the recycled unreacted gas (stream N) from the circulator 37. The loop operates at a circulation rate of 2. In order to avoid overcooling of the catalyst in the water-cooled reactor 43, a substantial proportion of the hot water leaving the reactor 43 via line 53 is recycled directly as stream X. The amount of catalyst required for the water-cooled reactor 43 is about 2½

20 times that required in the heat exchange reactor 39.

The flow rates, temperatures and pressures of the various streams are shown in the following Table 1.

Table 1

Stream	T (°C)	P (bar abs)	Flow rate (kmol/h)							
			CH_4	CO	CO_2	H_2O	H_2	N_2	O_2	CH_3OH
A	20	45	3409*	0	22	0	12	16	0	0
B	40	45	20	4	17	0	105	4	0	1
C	230	45	3429*	4	39	0	116	20	0	1
D	257	45	0	0	2	57652	1	0	0	33
E	450	45	3429*	4	40	7652	117	20	0	34
F	693	40	2936	251	718	6083	3333	20	0	0
G	150	45	0	0	0	0	0	17	1669	0
H	975	40	224	2557	1125	6303	8536	37	0	0
I	528	39	224	2557	1125	6303	8536	37	0	0
J	40	38	0	0	2	6274	1	0	0	0
K	146	84	224	2557	1123	29	8535	37	0	0
L	0	0	0	0	0	0	0	0	0	0
M	146	84	224	2557	1123	29	8535	37	0	0
N	48	84	3278	706	2799	12	17486	587	0	141
O	80	84	3502	3263	3922	41	26022	624	0	141
P	265	82	3502	1857	3230	733	21135	624	0	2238
Q	265	82	3502	1857	3230	733	21135	624	0	2238
R	245	81	3502	751	3104	859	18545	624	0	3470
S	40	78	28	3	138	846	12	2	0	3321
T	40	78	3474	748	2967	13	18532	623	0	149
U	40	78	196	42	167	1	1046	35	0	8
V	202	45	0	0	0	191	0	0	0	0
W	102	45	0	0	2	7843	1	0	0	35
X	244	45	0	0	10	342101	4	0	0	198
Y	240	45	0	0	11	399753	5	0	0	231

* in addition contains 398 kmol/h of higher hydrocarbons expressed as $CH_{2.98}$

The methanol in stream S, less the amount of methanol recycled from the subsequent distillation, amounts to about 2525 tonnes per day.

<u>Example 2</u>

In this example, the feedstock and conditions are the same as in Example 1 except that the loop operates at a circulation rate of 1 and part (about 60%) of the make-up gas stream K by-passes the heat exchange reactor 39 and is fed as stream L and added to the effluent, stream P, from the

5   heat exchange reactor 39. In the following Table 2, the flow rates, temperatures and pressures of the streams are shown. The amount of catalyst required in the heat exchange reactor 40 is about half that required for the heat exchange reactor in Example 1 and the amount of catalyst required for the water-cooled reactor 44 is about 4% more than that required for the water-cooled reactor 44 in Example 1. Since the flow rates, temperatures and pressures of the streams, including the water

10 streams, in the production of the make-up gas are essentially the same as in Example 1, they are omitted for brevity. The slight difference in the composition of the make-up gas stream K results from the different composition and amount of the hydrogen-containing stream B recycled from the synthesis loop.

Table 2

Stream	T (°C)	P (bar abs)	Flow rate (kmol/h)						
			CH_4	CO	CO_2	H_2O	H_2	N_2	CH_3OH
A	20	45	3409*	0	22	0	12	16	0
B	40	45	9	7	23	0	108	2	1
K	146	84	220	2560	1123	29	8513	35	0
L	146	84	132	1536	674	17	5108	21	0
M	146	84	88	1024	449	12	3405	14	0
N	49	84	772	602	1948	4	8952	127	74
O	75	84	860	1626	2397	16	12357	141	74
P	256	82	860	937	2005	409	9800	141	1156
Q	223	82	993	2473	2679	426	14908	162	1156
R	249	81	993	769	2638	467	11377	162	2901
S	40	78	12	4	164	462	12	1	2807
T	40	78	980	765	2473	5	11365	161	94
U	40	78	208	162	525	1	2413	34	20

* in addition contains 398 kmol/h of higher hydrocarbons expressed as $CH_{2.98}$

In this example, although the methanol production is decreased compared to Example 1, the

15 power requirement of the circulator is only about half that of Example 1, and the total amount of catalyst required is about 89% of that required for Example 1.

Example 3 (Comparative)

By way of comparison, in this example, Example 1 is repeated using the same amounts of feedstock but replacing the water-cooled reactor 43 by a heat exchanger heating the pressurised water stream 58. Because of the omission of the water-cooled reactor 43, the circulation rate is increased to 4. The amount of catalyst required for the heat-exchange reactor 39 is about 60% more than that required for the heat exchange reactor 39 in Example 1. Since there is no catalyst cooled by the water stream 58, there is no need to recycle part of the hot water and so stream X is omitted. In the following Table 3, the flow rates, temperatures and pressures of the streams are shown. Again since the flow rates, temperatures and pressures of the streams, including the water streams (with the exception of stream X and consequently also stream Y), in the production of the make-up gas are essentially the same as in Example 1, they are omitted for brevity. The slight difference in the composition of the make-up gas stream K again results from the different composition and amount of the hydrogen-containing stream B recycled from the synthesis loop.

Table 3

Stream	T (°C)	P (bar abs)	Flow rate (kmol/h)						
			CH_4	CO	CO_2	H_2O	H_2	N_2	CH_3OH
A	20	45	3409*	0	22	0	12	16	0
B	40	45	20	9	13	0	95	4	1
K	146	84	225	2558	1124	29	8534	37	0
N	48	84	7054	3315	4497	26	33582	1275	283
O	67	84	7280	5874	5621	55	42115	1312	283
P	257	84	7280	3413	4731	945	34526	1312	3632
S	40	78	30	6	110	918	12	2	3342
T	40	78	7250	3407	4622	27	34515	1310	290
U	40	78	196	92	125	1	933	35	8

* in addition contains 398 kmol/h of higher hydrocarbons expressed as $CH_{2.98}$

The amount of methanol produced is similar to that produced in Example 1, but the power requirement for the circulator 37 is about twice that required in Example 1.

Example 4

In this example, only the synthesis loop is shown and this follows the flowsheet of Figure 2.

Make-up gas (stream K) supplied at a rate of 27987 kmol/h at about 84 bar abs. and at a temperature of 116°C is divided into three streams. One part, stream M, representing about 21% of the total, is fed to the synthesis loop where it is mixed with recycle gas (stream N) supplied at a rate of 55000 kmol/h from circulator 37 via heat exchanger 61. The system thus operates at a circulation

rate of about 1.97. 25% of the resultant mixture of streams M and N is fed to heat exchangers 62
and 63 where it is heated and fed, as stream O, to the inlet of a quench synthesis reactor 60. The
remainder (stream O') of the mixture of recycle gas and make-up gas streams N and M is then
mixed with the second part (stream K') of the make-up gas to form a quench stream Z. Stream K'

5   represents about 49% of the make-up gas. Stream Z is used as the quench gas in the quench
reactor 60. The quench reactor typically has 5 beds of catalyst and is operated with bed exit
temperatures progressively decreasing from 280°C (first bed) to 260°C (final bed). The quench gas
is introduced between each bed in such proportions that the temperature of the gas leaving the
previous bed is decreased to a temperature in the range 215-220°C before the mixture of reacted

10 gas and quench gas enters the next bed. The reacted gas (stream P) leaves the final bed at a
temperature of 260°C and at a pressure of 82 bar abs. The reacted gas stream P is cooled in heat
exchanger 63 and then the remainder, about 30%, of the total make-up gas is added as stream L to
give a gas stream Q at 245°C which is fed to the water-cooled reactor 43. This reactor is operated
to give an exit temperature of 222°C. The volume of catalyst employed in the water-cooled

15 reactor 43 is about 68% of that used in the quench reactor 60. The reacted gas, at a pressure of
80 bar abs., is then fed as stream R to the heat exchanger train 62, 61 and 47 wherein it is cooled to
35°C and fed to the separator 48. The separated crude methanol is taken as stream S while the
separated unreacted gas (stream T) is divided into a recycle stream and a purge stream U. The
recycle stream at a pressure of 80 bar abs. is fed to the circulator 37 where it is compressed to

20 84 bar abs and fed to heat exchanger 61 to give stream N.

The purge stream U is heated in heat exchangers 66, 67 to 220°C and fed as stream Q' to a
synthesis reactor 68 cooled by pressurised water. The volume of catalyst in reactor 68 is about
10.5% of that used in the quench reactor 60. More methanol is synthesised in reactor 68 to give a
reacted purge gas stream R' at 79 bar abs at a temperature of 221°C. The reacted purge gas

25 stream R' is cooled by heat exchangers 66, 69 to 35°C and fed to separator 71. The unreacted gas
is taken as the purge stream U' and the separated crude methanol stream S' is added to the crude
methanol stream S from loop separator 49 to give a final crude methanol product stream.

The flow rates and temperatures of the components of the streams are shown in the following
Table 4.

Table 4

stream	temp (°C)	Flow rate (kmol/h)						
		CH_4	CO	CO_2	H_2O	H_2	N_2	CH_3OH
K	116	952	4193	2064	46	20648	84	0
M	116	200	881	433	10	4336	18	0
N	114	5540	799	2068	20	45861	501	212
O	223	1435	420	625	7	12549	130	53
O'	114	4305	1260	1876	22	37648	389	159
K'	116	467	2055	1011	23	10118	41	0
Z	115	4772	3314	2887	45	47765	430	159
P	260	6207	1610	2238	1327	52241	560	3611
L	116	286	1258	619	14	6194	25	0
Q	245	6492	2868	2857	1341	58436	585	3611
R	222	6492	934	2493	1704	53478	585	5908
S	35	35	2	83	1681	21	1	5661
T	35	6458	931	2410	23	53457	584	247
U	35	918	132	342	3	7596	83	35
R'	225	918	31	115	231	6710	83	364
U'	35	916	31	113	4	6709	83	25
S'	35	2	0	2	226	1	0	340
S + S'	35	37	2	85	1907	22	1	6001

Example 5 (comparative)

By way of comparison, Example 4 was repeated but heat exchanger 63 and water-cooled reactor 44 are omitted and the reacted gas stream P from quench reactor 60 is fed directly to the exchanger train 62, 61, 47. The total amount of make-up gas (stream K) is decreased to 16804 kmol/h. The system thus operates at a circulation ratio of 3.27. Stream M forms 25% of the total make-up gas. As in Example 4, 25% of the mixture of streams M and N is fed to heat exchanger 62 and is fed as stream O to the inlet of the quench reactor 60. The remaining 75% of the mixture of streams M and N forms stream O' and is mixed with the remaining 75% of the make-up gas (stream K') to form the quench gas stream Z.

The flow rates and temperatures of the components of the streams are shown in the following Table 5.

Table 5

stream	temp (°C)	Flow rate (kmol/h)						
		CH_4	CO	CO_2	H_2O	H_2	N_2	CH_3OH
K	116	572	2517	1239	28	12397	50	0
M	116	143	629	310	7	3099	13	0
N	99	5531	1461	1665	21	45612	500	210
O	218	1419	523	494	7	12178	128	53
O'	100	4256	1568	1481	21	36534	384	158
K'	116	429	1888	929	21	9298	38	0
Z	104	4684	3456	2411	42	45831	422	158
P	260	6103	1609	1871	1082	50171	550	3613
S	35	21	2	40	1059	12	1	3382
T	35	6082	1607	1831	23	50159	550	231
U	35	551	146	166	2	4546	50	21
R'	221	551	12	50	118	3933	50	270
U'	35	550	12	49	2	3932	50	16
S'	35	2	0	1	116	1	0	254
S + S'	35	22	2	41	1174	13	1	3636

By comparison with Example 4 it is seen that the addition of the water-cooled reactor 43 and addition of part of the make-up gas between the quench reactor 60 enables a conventional synthesis loop to be uprated to increase the amount of methanol produced by about 65% without increasing the duty of the circulator 37.

Claims

1.   A process wherein methanol is synthesised in a loop from a synthesis gas mixture
        comprising hydrogen and carbon oxides in at least two synthesis stages, synthesised
        methanol is separated and at least part of the unreacted synthesis gas is recycled to the
        first stage, and make-up gas is added to the loop, characterised in that in at least the final
        synthesis stage of the loop, the synthesis is effected in indirect heat exchange with water
        under sufficient pressure to prevent boiling, whereby a stream of heated pressurised water
        is produced, and the make-up gas is produced by a process including catalytically reacting
        a hydrocarbon feedstock with steam at an elevated temperature and at an elevated
        pressure equal to, or less than, the pressure of said stream of heated pressurised water
        and at least part of said steam is introduced by direct contact of said hydrocarbon
        feedstock with said stream of heated pressurised water.

2.   A process according to claim 1 wherein some or all of the make-up gas is added to the
        recycled unreacted gas after the first synthesis stage.

3.   A process according to claim 1 or claim 2 wherein at least 5% of the make-up gas is added
        to the recycled unreacted gas before the latter is fed to the first synthesis stage.

4.   A process according to any one of claims 1 to 3 wherein the first synthesis stage is effected
        in a quench reactor.

5.   A process according to any one of claims 1 to 3 wherein the first synthesis stage is
        effected in a heat-exchange reactor having a bed of synthesis catalyst with a plurality of
        cooling tubes extending therethrough and the synthesis gas is fed to the tubes and is
        heated by indirect heat exchange with the synthesis gas passing through the bed of
        catalyst.

6.   A process according to claim 5 wherein 30-90% of the make-up gas is added to the
        recycled unreacted gas before the latter is fed to the first synthesis stage.

7.   A process according to any one of claims 1 to 6 wherein the circulation ratio is in the range
        1 to 3.

Fig.1.

Fig.2.
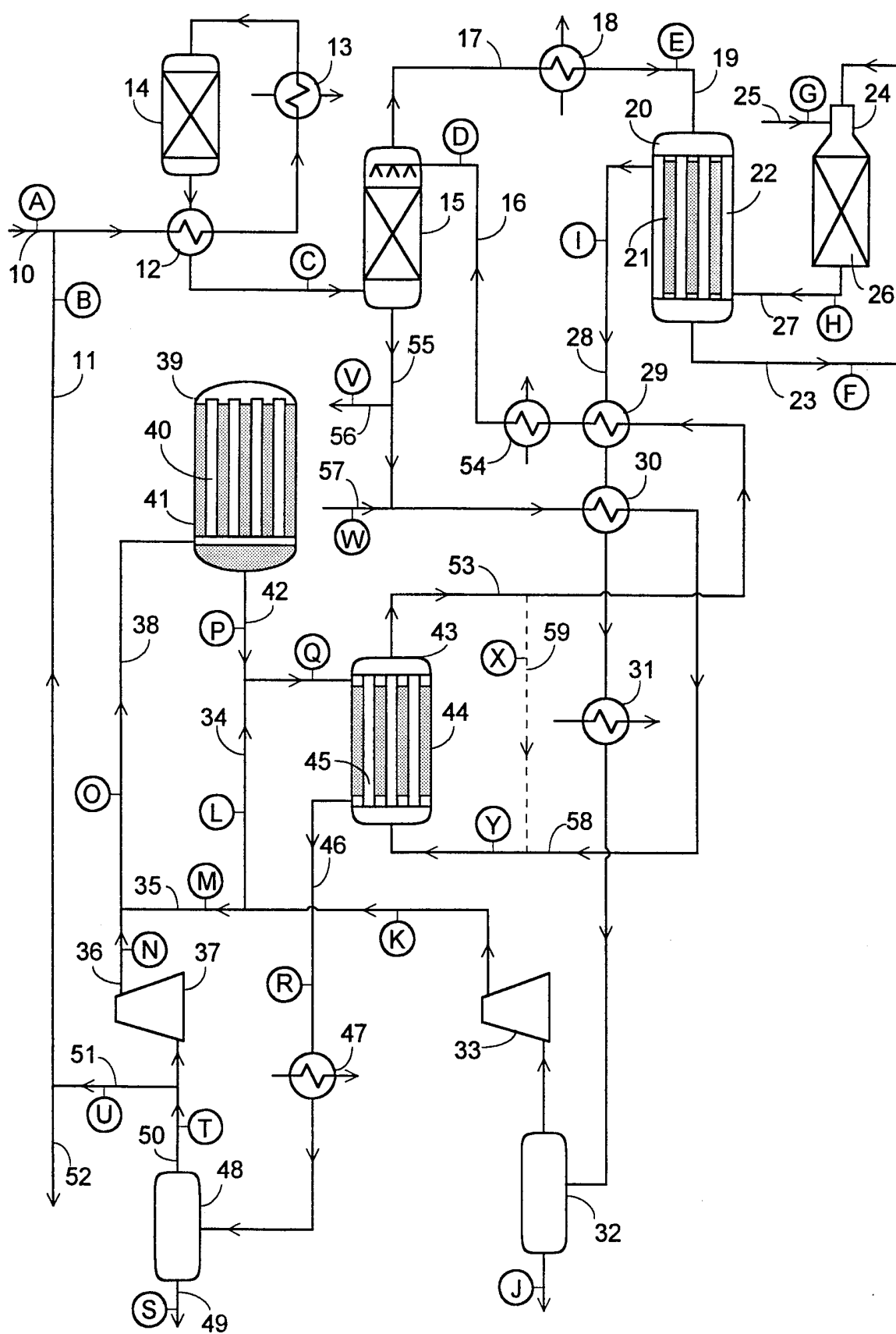
A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C07C29/151

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)
IPC 6   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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search	Date of mailing of the international search report
21 July 1999	30/07/1999

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