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(56) Documents Cited

**GB 2255516 A GB 0589342 A EP 0430699 A2**

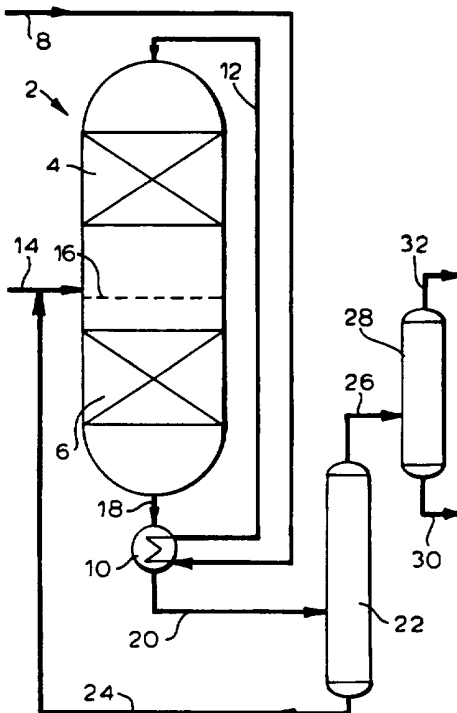
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## (54) Process for carrying out chemical equilibrium reactions

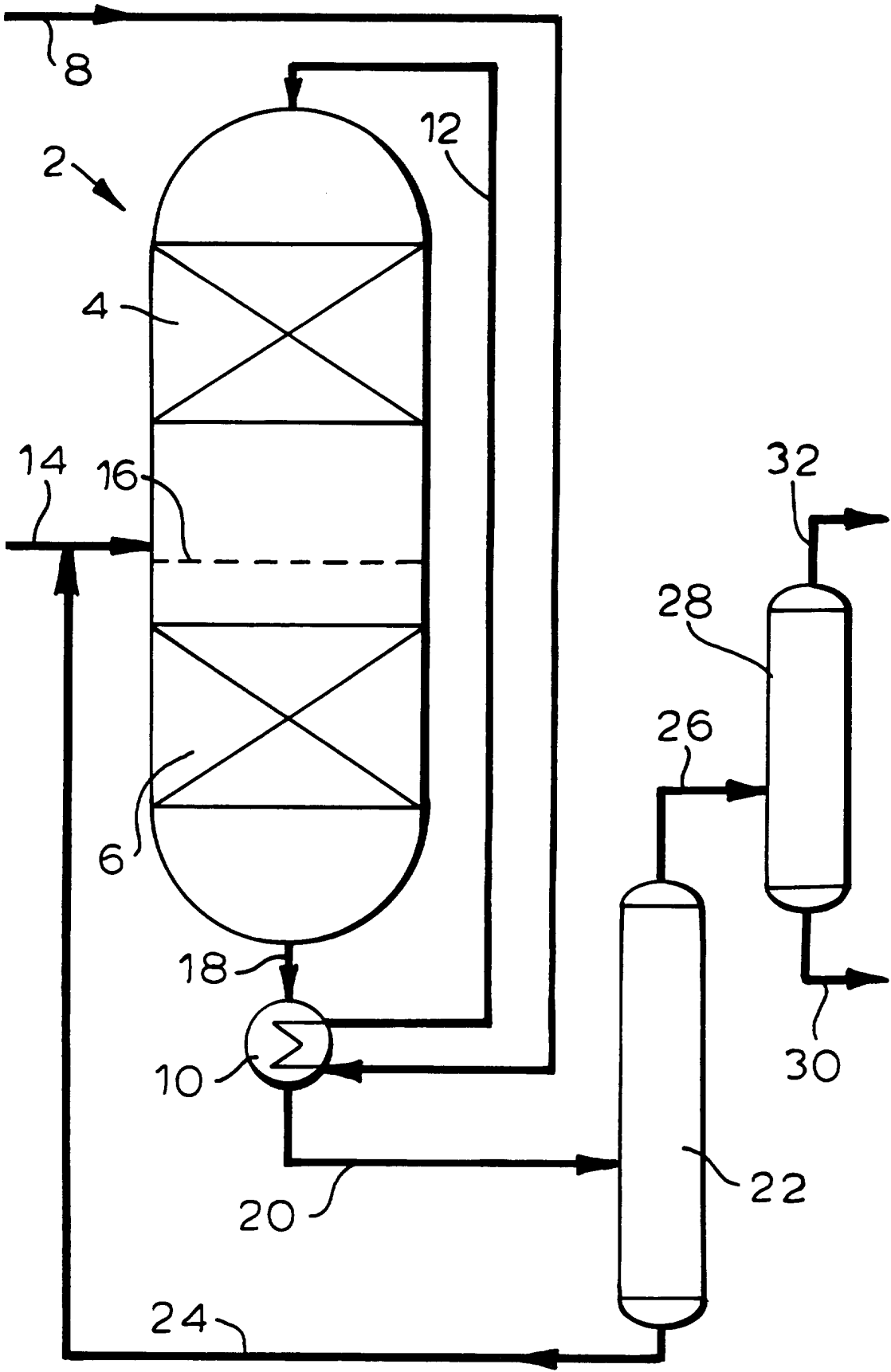
(57) A two-stage process for carrying out equilibrium reactions is disclosed. In the first step the reagents are contacted with a fixed catalyst bed under such conditions that both reagents and products are gaseous. The product of this step is then passed to another fixed-bed catalyst where the reaction proceeds in the presence of an absorbent for one of the products.

The process is illustrated by the production of methanol from synthesis gas. The reactants are passed to first bed 4 via heat-exchanger 10 and line 12. The product is then passed to second bed 6 together with liquid absorbent added through line 14. The absorbed methanol and unreacted reagents pass through heat-exchanger 10 to desorber 22 and then to separator 28, from which methanol is withdrawn via line 30. Absorber and unreacted synthesis gas components are recycled.



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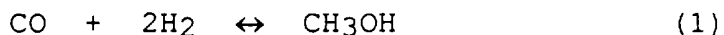
PROCESS FOR CARRYING OUT CHEMICAL EQUILIBRIUM REACTIONS

The present invention relates to a process for carrying out chemical equilibrium reactions involving reactants and products which are present as gases under the prevailing reaction conditions. In particular, the present invention is directed to a process for the preparation of methanol, from mixtures of carbon monoxide and hydrogen.

A number of chemical process involve chemical reactions which are equilibrium reactions. A number of these reactions involve reactants and products which are gaseous under the prevailing reaction conditions. For such reactions, it has been found possible to select the processing conditions in order to shift the equilibrium of the reaction and favour the formation of the desired end products. One such reaction is the reaction by which methanol is formed from mixtures of carbon monoxide and hydrogen, often referred to as synthesis gas.

Methanol is a valuable material useful, for example as a feed stock for chemical processes. Accordingly, there is a need for a process which may be operated on a commercial scale to produce methanol in high yields with a minimum of by-products. The process should preferably require a minimum of processing equipment and machinery and, therefore, is preferably simple to operate.

One method for preparing methanol is by the reaction of carbon monoxide and hydrogen, mixtures of which are referred to in the art as synthesis gas. The preparation of methanol from carbon monoxide and hydrogen proceeds by means of the following, highly exothermic, equilibrium reaction



In order to achieve an acceptable rate of conversion of carbon monoxide and hydrogen to methanol for operation on a commercial scale, it is necessary to operate the reaction (1) at elevated temperatures. However, the level of conversion achieved is limited by the thermodynamic equilibrium. In order to obtain an acceptably high level of conversion, it has been found necessary to operate the reaction (1) at very high pressures. Operation at the high pressures required is very expensive and requires a large investment in operating plant and machinery.

A number of process schemes have been proposed to accommodate the thermodynamic limitations of chemical equilibrium reactions in general and the methanol synthesis reactions in particular in order to provide attractive processes for commercial application.

The use of an interstage quench to cool the reaction mixture between successive conversion stages and hence favour the forward exothermic reaction yielding methanol has been proposed.

Thus, US patent No. 4,670,473 (US-A-4,670,473) a synthesis process scheme is disclosed in which synthesis gas is converted in at least two beds of catalyst. Lower alkanols, including methanol, prepared in the process are recycled and used as an interstage quench between successive catalyst beds. US-A-4,670,473 discloses that, in this way, methanol may be recycled to extinction in order to prepare higher alkanols.

US patent No. 4,766,154 (US-A-4,766,154) discloses a two stage process for the conversion of synthesis gas into methanol. In the process scheme of US-A-4,766,154, a synthesis gas feed containing carbon dioxide, carbon monoxide and hydrogen, is converted in a first, liquid

phase conversion reactor. The product is cooled to  
condense methanol. The remaining, unconverted synthesis  
gas is fed to a second liquid phase conversion reactor,  
the product of which is cooled to yield a methanol  
5 product. The operating conditions of the two reactors  
are selected such that the conversion of carbon monoxide  
to methanol is favoured in the first stage, whilst the  
conversion of carbon dioxide to methanol is favoured in  
the second stage.

10 Several process schemes have been proposed which  
combine separate liquid phase and gas phase methanol  
synthesis reactors in the same scheme.

Thus, US patent No. 4,628,066 (US-A-4,628,066)  
discloses a process for the preparation of methanol, in  
15 which a synthesis gas feed is passed to a liquid phase  
methanol synthesis reactor, thereby converting a portion  
of the feed. The effluent of the reactor is cooled to  
recover the desired products. Unconverted synthesis gas  
is passed to a gas phase synthesis reactor for further  
20 conversion. Synthesis gas remaining unconverted after  
this second conversion step is recycled to the inlet of  
the gas phase reactor.

US patent No. 4,946,477 (US-A-4,946,477) discloses a  
similar, but more complex, process scheme to that of  
25 US-A-4,628,066. The process scheme of US-A-4,946,477  
comprises a first, liquid phase methanol synthesis stage  
in which synthesis gas, together with some added water,  
is converted into methanol. Unconverted synthesis gas is  
fed to a second conversion stage, in which a gas phase  
30 reactor is used to produce additional methanol. Any  
unconverted synthesis gas remaining is used as fuel and  
combusted in a gas turbine, thus generating valuable  
power.

An alternative proposal for overcoming the  
35 limitations on conversion and yield imposed upon a

commercial operation by thermodynamic equilibrium has been to employ an absorbent for the products of equilibrium reactions, again, in particular, methanol.

5 European patent application publication No. 0 326 718 (EP-A-0 326 718) discloses a process for the production of methanol from carbon monoxide and hydrogen, in which the reactants are fed to one or more reaction zones comprising a fixed bed of catalyst using a liquid absorbent to selectively absorb all of the methanol  
10 formed. The methanol product is subsequently recovered from the liquid by desorption. EP-A-0 326 718 states that the absorption of methanol is preferably effected in a separate absorption zone.

15 European patent application publication No. 0 430 699 (EP-A-0 430 699) discloses a further scheme in which an organic absorbent is used to remove methanol from the effluent of a methanol synthesis reactor. EP-A-0 430 699 specifically discloses the use of an organic absorbent having between 3 and 16 carbon atoms and which is  
20 chemically inert with respect to the product of the synthesis reaction. The mass proportion of absorbent to methanol recovered is less than 10 mass units absorbent for each mass unit of methanol.

25 Finally, British patent application publication No. 2 255 516 (GB-A-2 255 516) discloses a process for conducting chemical equilibrium reactions, in which a plurality of fluidised bed catalytic reactors are employed in a series flow arrangement. Between at least  
30 two consecutive stages, the effluent of one reactor is subjected to an absorption treatment using an inert solvent to remove a product of the reaction. The remaining gaseous stream is fed to the following reactor for further conversion. GB-A-2 255 516, although not  
35 limited in this respect, concentrates on the synthesis of methanol from carbon monoxide and hydrogen.

As will be appreciated, although a number of alternative schemes have been proposed for effecting chemical equilibrium reactions in an optimum manner, there is still a need for a simple, inexpensive process scheme which combines a high degree of conversion and yield of the desired product with a minimum of capital and operating expenditure. Surprisingly, it has been found that a process scheme comprising gas phase reaction stage and a combined reaction and absorption stage offers these advantages.

Accordingly, the present invention provides a process for carrying out a chemical equilibrium reaction in which, in a first stage, one or more reactants are contacted with a fixed arrangement of a catalyst under conditions such that the reactants and the products of the reaction are gaseous, the unconverted reactants and products of the first stage being passed to a second stage, in which they are contacted with a fixed arrangement of a catalyst and the reaction allowed to proceed in the presence of an absorbent capable of absorbing a product of the reaction.

The process of the present invention is a two stage process. In the first stage, gaseous reactants are contacted with a catalyst. The products of the reaction are gaseous. The catalyst is retained in the form of a fixed arrangement. The catalyst is typically in the form of particles retained in a fixed bed. Suitable techniques for retaining catalysts in fixed bed arrangements are well known in the art. The first stage of the process may comprise one or a plurality of separate reaction stages, in each of which gaseous reactants are contacted with a catalyst to yield gaseous products. The first stage conveniently consists of a single reaction stage.

In the second stage of the process, the products of the first stage, together with the reactants remaining unconverted, are contacted with a catalyst. The catalyst is retained in the form of a fixed arrangement. The catalyst is typically in the form of particles retained in a fixed bed. Suitable techniques for retaining catalysts in fixed bed arrangements are well known in the art. The reaction in the second stage is allowed to proceed in the presence of an absorbent, under conditions such that one or more of the products of the reaction are absorbed. The second stage of the process may comprise one or a plurality of separate reaction stages, in each of which gaseous reactants are contacted with a catalyst to yield gaseous products. The second stage conveniently consists of a single reaction stage.

The products of the reaction, together with any unconverted reactants, are removed from the second stage. The products may be recovered using conventional refining and separation techniques. Unconverted reactants may be recycled to the first stage of the process.

The absorbent, together with the absorbed reaction product, is withdrawn from the second stage. The product may be recovered from the absorbent using conventional desorption techniques well known in the art. The absorbent may be selected so as to absorb one or more than one of the reaction products (in cases in which the reaction yields a plurality of products). In cases in which several reaction products are to be absorbed, the absorbent may comprise one or several different absorbent materials. The absorbent materials may be selected from liquid or solid absorbents. Liquid absorbents may be preferred, as these may be more easily fed to and removed from the second stage in a continuous manner. Solid absorbents may be employed in a continuous trickling mode or, alternatively, in a cycle operation, in which a



period of reaction/absorption is followed by a period of desorption and product recovery.

The first and second stages of the process may be carried out in separate reaction vessels. However, a most convenient mode of operation is to employ two fixed catalyst arrangements, one each for the first and second stage, retained within a single reaction vessel.

In general, the yield at the inlet of the first stage of the process, in terms of the mass of product per unit volume of catalyst per hour, will be greater than that at the inlet of the second stage of the process. However, the yield will decrease as the reactants pass through the catalyst in the first stage. This behaviour results from effects such as the decrease in the partial pressure of the feed gases through the catalyst bed and from the equilibrium nature of the reactions taking place in the catalyst bed. In contrast, the yield of the second stage of the process remains substantially constant along the entire catalyst bed. However, it is a feature of many reactions when operated under the regime of the second stage of the process of this invention, that the reaction may be limited by mass transfer effects. In such cases, the overall yield of the second stage of the process will be lower than that of the first stage. In such cases, it has been found to be very advantageous if the first and second stages of the process are operated such that the yield of the catalyst at the outlet of the first stage is substantially equal to that at the inlet of the second stage.

The process of the present invention is suitable for carrying out a variety of equilibrium reactions, which are well known in the art. Examples of suitable reactions include the etherification and hydration of olefins to ethers or alcohols, in which the ethers or alcohols are absorbed in the second stage. The process

may also be applied in dehydrogenation reactions, such as the dehydrogenation of paraffins to olefins or the dehydrogenation of ethylbenzene to styrene. For these dehydrogenation reactions, an absorbent may be applied in  
5 the second stage which will absorb hydrogen or the dehydrogenated product. Alternatively, the process may be applied in carrying out the water gas shift reaction, involving the reaction of water and carbon monoxide to yield hydrogen and carbon dioxide, in which case an  
10 absorbent to absorb either carbon dioxide or hydrogen may be used in the second stage.

The process of the present invention has been found to be particularly advantageous when applied in the synthesis of methanol from mixtures of carbon monoxide  
15 and hydrogen (commonly known as synthesis gas). Accordingly, in one aspect, the present invention provides a process for the synthesis of methanol from carbon monoxide and hydrogen, in which, in a first stage, carbon monoxide and hydrogen are contacted with a fixed  
20 arrangement of a catalyst active in catalysing the synthesis of methanol under conditions such that the methanol formed is present as a gas under the prevailing reaction conditions, the unconverted carbon monoxide and hydrogen and methanol produced in the first stage being  
25 passed to a second stage, in which they are contacted with a fixed arrangement of a catalyst active in catalysing the synthesis of methanol and the reaction allowed to proceed in the presence of an absorbent capable of absorbing methanol.

30 Suitable operating conditions for carrying out the aforementioned processes are well known and understood in the art. The general engineering aspects of the two stages of the process of this invention is also readily available in the open literature and well understood in  
35 the art. In this respect, reference is made to The

Chemical Engineers Handbook, 5th Edition, edited by R.H. Perry and C.H. Chilton.

The process of the present invention will now be described in more detail by reference to the synthesis of methanol from a mixture of carbon monoxide and hydrogen. It is to be appreciated that this description is for illustrative purposes only and that the principles of the process discussed may be applied more generally.

Reference is made to the Figure, which is a schematic representation of a process for the preparation of methanol from a mixture of carbon monoxide and hydrogen. A reactor, generally indicated as 2, contains a first stage fixed bed of catalyst, 4, and a second stage fixed bed of catalyst 6. Both fixed beds comprise particles of a catalyst active in the synthesis of methanol from carbon monoxide and hydrogen.

A mixture of carbon monoxide and hydrogen is fed via a line 8 to a feed/effluent heat exchanger 10. The mixture of carbon monoxide and hydrogen, heated in the heat exchanger 10 is passed via a line 12 to the inlet of the reactor 2 located above the first stage fixed bed of catalyst 4. The carbon monoxide and hydrogen pass downwards through the catalyst bed 4. The gas leaving the first stage fixed bed of catalyst 4 comprises unconverted carbon monoxide and hydrogen and methanol.

A liquid absorbent is fed via a line 14 to a liquid inlet in the side of the reactor 2 such that the liquid absorbent enters the reactor 2 between the first stage fixed bed of catalyst 4 and the second stage fixed bed of catalyst 6. Once inside the reactor vessel, the liquid absorbent mixes with the gas leaving the first stage fixed bed of catalyst 4. A liquid/gas distributor 16 is located within the reactor 2 below the liquid inlet and above the second stage fixed bed of catalyst 6. The absorbent and the gas are distributed over the top of the

second stage fixed bed of catalyst 6 by the distributor 16 and subsequently flow downwards through the bed 6. The effluent leaving the bottom of the reactor comprises a gas phase and a liquid phase. The gas phase comprises  
5 unconverted carbon monoxide and hydrogen, together with a very minor amount of methanol vapour. The liquid phase comprises the absorbent and the absorbed methanol.

The effluent leaving the bottom of the reactor 2 passes via a line 18 to the feed/effluent heat exchanger  
10 10. Heat produced by the exothermic reaction of carbon monoxide and hydrogen is recovered by indirect heat exchange in the heat exchanger 10 between the hot effluent leaving the reactor 2 and the fresh feed gas. The thus cooled effluent passes from the heat exchanger  
15 10 via a line 20 to a desorber 22. The desorber 22 acts firstly to separate the gas from the liquid present in the reactor effluent and secondly to separate the methanol product from the absorbent. The absorbent recovered is recycled via a line 24 to the liquid inlet  
20 of the reactor 2.

A gaseous stream is recovered from the desorber 22 and is passed via a line 26 to a separator 28. The separator 28 acts to separate unconverted carbon monoxide and hydrogen, together with any minor amounts of by-  
25 products which may have been formed, from the methanol product. The methanol product is withdrawn via a line 30. The unconverted carbon monoxide and hydrogen is withdrawn from the separator 28 via a line 32 and may be recycled via a suitable line and compressor (not shown)  
30 to the inlet of the reactor 2. A portion of this stream may be removed from the process as a purge, in order to avoid the accumulation of inert components in the recycle loop. The purge gas can suitably be used as fuel, for example in a process for the preparation of synthesis  
35 gas.

Suitable catalysts for use in the first and second stage fixed beds of catalyst 4 and 6 are well known in the art. Typical methanol synthesis catalysts for use in the process of the present invention are described in the publications described hereinbefore. Examples of  
5 suitable methanol synthesis catalysts include catalysts comprising zinc and/or copper as the catalytically active components. The catalyst may comprise a promoter in addition to the catalytically active component, for  
10 example aluminium or chromium. The same catalyst may be applied in both the first stage and second stage of the process of this invention.

Suitable operating conditions for the reactor 2 are well known in the art. In order to obtain an acceptable  
15 level of catalyst activity, the process is typically operated at elevated temperatures. Suitable temperatures are in the range of from 100 to 350°C, more preferably from 200 to 300°C. In order to obtain an acceptable level of conversion, the process is preferably operated  
20 at elevated pressures. Suitable pressures are in the range of from 25 to 200 bar, more preferably from 50 to 150 bar.

Suitable absorbents are also well known in the art. Examples of suitable methanol absorbents include  
25 alcohols, paraffinic oils, olefinic oils, hydroxylated aromatic solvents and xylenes. In particular, the absorbent may be selected from alcohols having from 3 to 16 carbon atoms, more preferably from 3 to 10 carbon atoms, paraffins and olefins having from 7 to 16 carbon  
30 atoms, more preferably from 7 to 10 carbon atoms and hydroxylated aromatic compounds having from 6 to 10 carbons atoms, more preferably 6 to 8 carbon atoms. Especially preferred solvents are tetraethylene glycol dimethyl ether (TEGME), sulfolane and the crown ethers.  
35 TEGME is an especially preferred absorbent.

The operating conditions of the desorber 22 will depend upon the specific absorbent selected for use in the process. Typically, the methanol product may be recovered from the absorbent by flashing the liquid stream to a lower pressure, by heating the liquid to a temperature at which the methanol desorbs, or a combination of these, for example by flash distillation. The desorption may be carried out in a single or a multi-stage operation. If the latter is employed, the desorber 22 shown in the Figure can be taken as representing a series of separate desorption stages or vessels. Apparatus for carrying out the desorption stage is well known in the art.

The carbon monoxide and hydrogen used as feed to the methanol synthesis process may be obtained by any of the synthesis gas manufacturing techniques well known in the art. Examples of suitable process include the partial oxidation (combustion), steam reforming and carbon dioxide reforming of a hydrocarbon feed stock. Methane or natural gas is a most suitable and convenient hydrocarbon feed stock. Carbon monoxide and hydrogen are preferably present in the feed at a ratio of hydrogen to carbon monoxide of about 2.

Employing the process scheme as shown in the Figure, a typical process scenario is as follows:

The reactor 2 comprises a first and a second fixed bed of catalyst 4 and 6 each comprised of a copper/zinc/alumina catalyst containing 60% wt copper, 25% wt zinc and 15% wt alumina and having an average particle size of 2.0 mm. A mixture of carbon monoxide and hydrogen, having a hydrogen to carbon monoxide ratio of 2.0, is introduced via the line 8 into the reactor 2 at a pressure of 80 bar and a gas hourly space velocity of 3000 Nl gas/l catalyst/hour. The reactor 2 is operated at a temperature of 280°C. The first stage

fixed bed of catalyst has a space time yield of methanol (STY) of  $4.6 \text{ kg/m}^3/\text{s}$  at its inlet and an STY of  $1.5 \text{ kg/m}^3/\text{s}$  at its outlet.

5 The effluent from the first stage fixed bed of catalyst is mixed with TEGME supplied to the liquid inlet of the reactor 2 at a flowrate sufficient to absorb substantially all the methanol produced in the second stage and fed via the distributor 16 to the upper portion of the second stage fixed bed of catalyst 6. The second  
10 stage fixed bed of catalyst 6 has a constant STY of  $1.5 \text{ kg/m}^3/\text{s}$  throughout its length. The two catalyst beds combined exhibit an overall STY of  $2 \text{ kg/m}^3/\text{s}$ .

C L A I M S

1. A process for carrying out a chemical equilibrium reaction in which, in a first stage, one or more reactants are contacted with a fixed arrangement of a catalyst under conditions such that the reactants and the products of the reaction are gaseous, the unconverted reactants and products of the first stage being passed to a second stage, in which they are contacted with a fixed arrangement of a catalyst and the reaction allowed to proceed in the presence of an absorbent capable of absorbing a product of the reaction.
2. A process according to claim 1, characterised in that the first stage consists of a single reaction stage.
3. A process according to either of claims 1 or 2, characterised in that the second stage consists of a single reaction stage.
4. A process according to any preceding claim, characterised in that the first and second stages are operated such that the yield, in terms of the mass of product per unit volume of catalyst per hour, at the outlet of the first stage is substantially equal to the yield at the inlet of the second stage.
5. A process according to any preceding claim, characterised in that the reaction is selected from the etherification or hydration of olefins, a dehydrogenation reaction, the water gas shift reaction and the synthesis of methanol.
6. A process according to any preceding claim for the synthesis of methanol from carbon monoxide and hydrogen, in which, in a first stage, carbon monoxide and hydrogen are contacted with a fixed arrangement of a catalyst active in catalysing the synthesis of methanol under



conditions such that the methanol formed is present as a gas under the prevailing reaction conditions, the unconverted carbon monoxide and hydrogen and methanol produced in the first stage being passed to a second stage, in which they are contacted with a fixed arrangement of a catalyst active in catalysing the synthesis of methanol and the reaction allowed to proceed in the presence of an absorbent capable of absorbing methanol.

5  
10 7. A process according to claim 6, characterised in that the absorbent used in the second stage is a liquid, preferably tetraethylene glycol dimethyl ether, sulfolane or a crown ether, more preferably tetraethylene glycol dimethyl ether.

15 8. A product obtained by a process according to any preceding claim.

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**Patents Act 1977**  
**Examiner's report to the Comptroller under Section 17**  
**(The Search report)**

Application number  
 GB 9519489.0

**Relevant Technical Fields**

- (i) UK Cl (Ed.N)      B1F  
 (ii) Int Cl (Ed.6)      B01J 8/04, C07C 29/151, C07C  
    29/152

Search Examiner  
 J H WARREN

Date of completion of Search  
 13 DECEMBER 1995

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-  
 1-8

(ii) ONLINE DATABASE (WPI)

**Categories of documents**

- |  |   |
|--|---|
| <p><b>X:</b> Document indicating lack of novelty or of inventive step.</p> <p><b>Y:</b> Document indicating lack of inventive step if combined with one or more other documents of the same category.</p> <p><b>A:</b> Document indicating technological background and/or state of the art.</p> | <p><b>P:</b> Document published on or after the declared priority date but before the filing date of the present application.</p> <p><b>E:</b> Patent document published on or after, but with priority date earlier than, the filing date of the present application.</p> <p><b>&amp;:</b> Member of the same patent family; corresponding document.</p> |
|--|---|

Category	Identity of document and relevant passages	Relevant to claim(s)
Y	GB 2255516 A (SHELL) page 7 line 16 - page 8 line 2	1, 2, 3, 5, 6, 7
X	GB 0589342 (STANDARD OIL) page 2 line 33 - page 3 line 21	1, 2, 3
Y	EP 0430699 A2 (CSIR) page 3 lines 15-36	1, 2, 3, 5, 6, 7
		-

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