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(54) Title: DETECTING CONTAMINANTS IN CATALYTIC PROCESS PLANT

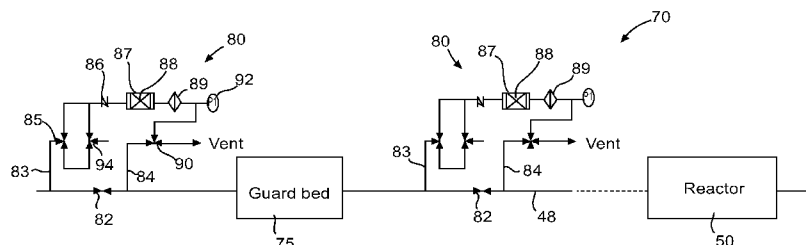


Fig.3.

(57) Abstract: A gas stream is fed (48) into the catalytic reactor (50) and wherein a contaminant removal unit (75) is provided up-
 stream of the catalytic reactor. The presence of a contaminant in the gas stream is detected by providing at least one contaminant trap
 (80) either upstream or downstream of the contaminant removal unit (75), and passing at least part of the gas stream through the or
 each contaminant trap (80) for at least some of the time. By monitoring (89, 92) the quantity of the gas that passes through each con-
 taminant trap (80), and monitoring the presence of the contaminant material trapped in the contaminant trap (80), the presence and
 concentration of the contaminant in the gas stream can be assessed.

Detecting Contaminants in Catalytic Process Plant

The present invention relates to the detection of contaminants such as poisons, for example in plant for performing a catalytic process. It is particularly but not
5 exclusively of relevance in a plant in which synthesis gas is formed or used, so for example it would be of potential relevance to a process for performing Fischer-Tropsch synthesis. It provides a method and an apparatus for detecting contaminants such as poisons. The invention may therefore be applicable in a process for treating natural gas to produce a liquid product.

10

At many oil wells natural gas is produced in relatively small quantities along with the oil. When the quantities of this associated gas are sufficiently large or the well is close to pre-existing gas transportation infrastructure, the gas can be transported to an off-site processing facility. When oil production takes place in more remote places it is
15 difficult to introduce the associated gas into existing gas transportation infrastructure. In the absence of such infrastructure, the associated gas has typically been disposed of by flaring or re-injection. However, flaring the gas is no longer an environmentally acceptable approach, while re-injection can have a negative impact on the quality of the oil production from the field.

20

Gas-to-liquids technology can be used to convert the natural gas into liquid hydrocarbons. This may follow a two-stage approach to hydrocarbon liquid production comprising syngas generation, followed by Fischer-Tropsch synthesis. In general, syngas (a mixture of hydrogen and carbon monoxide) may be generated by one or more
25 of partial oxidation, auto-thermal reforming, or steam methane reforming. Where steam methane reforming is used, the reaction is endothermic and so requires heat, and a catalyst such as platinum/rhodium. The syngas is then subjected to Fischer-Tropsch synthesis, and as regards the Fischer-Tropsch process, a suitable catalyst uses cobalt on a ceramic support.

30

Such a process is described for example in WO 01/ 51194 (AEA Technology) and WO 03/048034 (Accentus plc).

Catalysts can be detrimentally affected by the presence of certain materials in the
35 gas stream, even at very low concentrations, and such materials may be referred to as catalyst poisons or poison materials. For example mercury and sulphur may be present in the raw gas, and would act as catalyst poisons, and so the gas stream would usually be treated to remove these poison materials before it is subjected to any catalytic

treatment. This may involve passing the gas flow through a guard bed of a material which traps the poison material. Not only may poison materials be present in the gas feed, but poison materials may be formed during operation of a plant. For example if a plant contains components of steel or iron which are contacted by a gas stream

5 containing carbon monoxide (such as synthesis gas), then metal carbonyls may be formed such as nickel, iron or molybdenum carbonyl. These are vapours, and may act as catalyst poisons, so it may be appropriate to pass the gas flow through a suitable guard bed.

10 It is therefore desirable to monitor the concentration of such poison materials in the gas flow, and to monitor the performance of such guard beds. Detection of such poison materials can be difficult, as they may be present at concentrations as low as 1 ppb (part per billion, i.e. one part per thousand million).

15 More generally, the gas stream may contain a contaminant, that is to say an impurity. A contaminant may be detrimental to the operation of the catalytic reactor in a variety of different ways. For example a contaminant may cause blockages to develop, or it may lead to different chemical reactions occurring, or shift the equilibrium of the desired reactions, or it may be a catalyst poison. In the context of a catalytic chemical
20 reactor for processing a gas stream, the contaminants of greatest concern are typically those which are catalyst poisons.

According to the present invention there is provided a process for monitoring the presence of a contaminant in a gas stream being fed into a catalytic reactor including a
25 catalyst, wherein a contaminant removal unit is provided upstream of the catalytic reactor, and the gas stream is fed through the contaminant removal unit to the catalytic reactor, the process comprising providing at least one of:

- a contaminant trap upstream of the contaminant removal unit, and
- a contaminant trap between the contaminant removal unit and the catalytic reactor;

30 passing at least part of the gas stream through the or each contaminant trap for at least some of the time;
monitoring the quantity of the gas stream that passes through each contaminant trap;
and monitoring the presence of the contaminant trapped in the contaminant trap.

35 The contaminant trap captures at least a proportion of the contaminant in the gas stream that passes through it, so the contaminant in the contaminant trap is that accumulated from all the gas that has passed through the contaminant trap. Hence the concentration of the contaminant may be sufficiently high to be monitored more readily.

The contaminant trap upstream of the contaminant removal unit enables the concentration of the contaminant to be monitored in the gas flow that flows into the contaminant removal unit. This monitored concentration will enable the operational life of the contaminant removal unit to be predicted; when the capacity of contaminant removal unit has been reached, it may be necessary to replace at least parts of the contaminant removal unit. The gas stream may be passed through this upstream contaminant trap either continuously, or at intervals.

The contaminant trap downstream of the contaminant removal unit, between the contaminant removal unit and the catalytic reactor, provides a check on the effectiveness of the contaminant removal unit. The downstream contaminant trap may have a gas stream passed through it continuously.

In another aspect the present invention provides an apparatus for monitoring the presence of a contaminant in a gas stream being fed into a catalytic reactor including a catalyst, wherein a contaminant removal unit is provided upstream of the catalytic reactor, and the gas stream is fed through the contaminant removal unit to the catalytic reactor, the apparatus comprising at least one contaminant trap, and means to connect the contaminant trap to carry at least part of the gas stream either upstream of the contaminant removal unit, or between the contaminant removal unit and the catalytic reactor, and means to monitor the quantity of the gas stream that passes through each contaminant trap.

The means to connect the contaminant trap preferably includes valves such that the contaminant trap can be disconnected, or fed with the gas stream, without any significant effect on the flow of the gas to the reactor. The contaminant trap is therefore typically arranged within a bypass, so it can carry a portion of the flow of gas to the reactor, and this portion can be varied. The apparatus may also include valves to enable a flushing gas to be passed through the contaminant trap.

The contaminant removal unit clearly must be suited to the contaminant that is to be removed, and in some cases it may comprise a guard bed, which may comprise a bed of particulate material which reacts with and absorbs the contaminant. Alternatively it might comprise a monolith defining flow channels within which the contaminant is selectively trapped. The contaminant removal unit may make use of other processes, as the contaminant may be subjected to a chemical change before it can be absorbed and so removed.

A potential contaminant is sulphur. Sulphur may be present in natural gas as compounds such as hydrogen sulphide (H_2S), carbonyl sulphide (COS), mercaptans and thiophenes. Where the sulphur compound is primarily hydrogen sulphide, this may be removed alongside CO_2 using a suitable membrane or an acid gas wash using a solvent
5 such as refrigerated methanol, glycol or propylene carbonate or an aqueous amine. Hydrogen sulphide may alternatively be absorbed using one or more beds of an absorbent such as a metal-promoted, e.g. Cu-promoted ZnO/alumina composition or ZnO composition. Soda lime may also be used to absorb hydrogen sulphide. Where sulphur compounds other than hydrogen sulphide are present in high concentrations it
10 may be desirable to include a first step of hydrodesulphurisation followed hydrogen sulphide absorption. In this case the contaminant removal unit may comprise a bed of hydrodesulphurisation catalyst located upstream of a bed of hydrogen sulphide absorbent.

15 The contaminant trap comprises a trapping material to trap the contaminant material. The trapping material is selected in accordance with the nature of the contaminant that is to be trapped; it may be the same material as is used in a guard bed to remove that contaminant. For example, a material suitable for trapping mercury vapour would be spherical granules of a pre-sulphided mixed oxide, with which the
20 mercury reacts to form mercury sulphide, so the mercury is absorbed and removed from the gas stream, such as Puraspec 1163 (trade mark) from Johnson Matthey.

In the case of hydrogen sulphide as the contaminant material, a material suitable for trapping the hydrogen sulphide would be a metal-promoted ZnO/alumina
25 composition, or a ZnO composition, or soda-lime (as mentioned above in relation to the poison material removal unit).

For trapping iron carbonyl it has surprisingly been found that alumina is an effective trapping material at ambient temperature. Alternatively metal carbonyls
30 may be trapped on a material such as a zeolite at an elevated temperature at which the carbonyls decompose, for example above 200°C .

The contaminant trap may contain the contaminant-trapping material in a transparent container. This is advantageous if the material changes colour when the
35 contaminant is trapped. For example it has been found that alumina becomes brown as it absorbs iron-based compounds such as iron carbonyl. Consequently the extent to which contaminant has been trapped can be estimated merely from the colour of the material. This is particularly useful for a contaminant trap which is downstream of the

contaminant removal unit, between the contaminant removal unit and the catalytic reactor, as it will provide a visible indication that the contaminant material removal unit is no longer functioning adequately.

5 Whether or not there is a discernible colour change, it may be appropriate to remove or inspect the contaminant trap at intervals, to monitor the concentration of contaminant that has been trapped in it. This may be performed using a sensitive measurement technique such as ICP-MS (inductively coupled plasma mass spectrometry).

10

 The removal of contaminants is of particular concern where the contaminant may act as a poison to a catalyst. So, in that case, the contaminant may be referred to as a catalyst poison.

15 In some situations the contaminant is formed from the material of which a plant is made. For example carbon monoxide can react with metals to form metal carbonyls, which are catalyst poisons. Other mechanisms such as metal dusting also lead to degradation of the structural material of which the plant is made. The resulting metal – based dust may also be perceived as a contaminant, whether or not it is also a catalyst
20 poison. It will be appreciated that when designing and building a chemical plant, the materials are selected to minimise such degradation, and the materials may also be treated to enhance their stability.

 In another aspect, the present invention hence provides a process for monitoring
25 for degradation of structural components of a chemical plant, where the degradation forms a contaminant in a gas stream being fed into a catalytic reactor, the process comprising providing a contaminant trap upstream of the catalytic reactor, and upstream of any contaminant removal unit associated with the catalytic reactor;
passing at least part of the gas stream through the or each contaminant trap for at least
30 some of the time;
monitoring the quantity of the gas stream that passes through each contaminant trap;
and monitoring the presence of the contaminant trapped in the contaminant trap.

 The invention also provides an apparatus for monitoring for degradation of
35 structural components of a chemical plant, by such a method.

 The invention will now be further and more particularly described, by way of example only, and with reference to the accompanying drawings, in which:

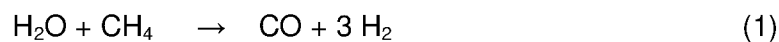
Figure 1 shows a schematic flow diagram of a gas-to-liquid plant and associated equipment, including a Fischer-Tropsch reactor;

Figure 2 shows a flow diagram of a contaminant removal apparatus suitable for use in the plant of figure 1; and

- 5 Figure 3 shows a flow diagram of a modification to part of the apparatus of figure 2 in accordance with the present invention.

1. Gas-to-Liquid Plant Overview

- 10 The invention is applicable in a chemical plant and process for converting natural gas (primarily methane) to longer chain hydrocarbons. The plant is suitable for treating associated gas, which is natural gas that is produced along with crude oil, and is then separated from the crude oil. The first stage of the chemical process involves the formation of synthesis gas. This may be achieved for example by steam reforming, by a
15 reaction of the type:



- This reaction is endothermic, and may be catalysed by a rhodium or platinum/rhodium
20 catalyst in a first gas flow channel. The heat required to cause this reaction may be provided by catalytic combustion of a gas such as methane or hydrogen, which is exothermic, in an adjacent channel, or by heat exchange with exhaust gases from a separate combustion reactor. The combustion may be catalysed by a palladium catalyst, and the catalyst may be on a stabilised-alumina support which forms a coating
25 typically less than 100 μm thick on a metallic substrate. Alternatively, the catalyst may be applied to the walls of the flow channels or may be provided as pellets within the flow channel. The heat generated by the combustion would be conducted through the metal sheet separating the adjacent channels. As shown in equation (1) the resulting syngas H_2/CO ratio is 3.0, although the exact value depends on reactor conditions, and on the
30 ratio of steam to methane provided to the reactor, and for example the ratio may be 3.5 if a higher proportion of steam is provided.

- The gas mixture produced by the steam/methane reforming is then, in this example, used to perform a Fischer-Tropsch synthesis to generate a longer chain
35 hydrocarbon, that is to say:



which is an exothermic reaction, occurring at an elevated temperature, typically between 190°C and 280°C, for example 230°C, and an elevated pressure typically between 1.8 MPa and 2.7 MPa (absolute values), in the presence of a catalyst. Whilst Fe based catalysts can be used, metallic Co promoted with precious metals such as Pd, Pt, Ru or Re doped to 1 wt% are preferred when operating at lower temperatures as they have enhanced stability to oxidation. The active metals are impregnated to 10-40 wt% into refractory support materials such as TiO₂, Al₂O₃ or SiO₂ which may be doped with rare earth and transition metal oxides to improve their hydrothermal stability.

It will be appreciated from the equations above that, if steam/methane reforming is used to produce the synthesis gas, there is an excess of hydrogen. A hydrogen-rich gas stream can therefore be separated either from the synthesis gas stream before performing Fischer-Tropsch synthesis, or from the tail gases that remain after performing Fischer-Tropsch synthesis. Such a separation may use a membrane separator.

Referring to figure 1, there is shown a gas-to-liquid plant 10 which may include the invention. A natural gas feed 5 consists primarily of methane, but with small proportions of other gaseous hydrocarbons, hydrocarbon vapours, and water vapour. The gas feed 5 may for example be at a pressure of 4.0 MPa (40 atmospheres) and 35°C, following sea water cooling from an initial temperature of 90°C, and may constitute associated gas from a well that produces crude oil.

The natural gas feed 5 is supplied to a pretreatment system 25, in which it is subjected to treatment which may comprise one or more of the following: changing its pressure; changing its temperature; and removing impurities such as sulphur or mercury. It is then mixed with steam in a mixer 26.

2. Making Synthesis Gas

The gas/steam mixture, preferably at a temperature of about 450°C, is then fed into a catalytic reactor 28. The first section of the reactor 28 is a pre-reformer 29 in which any ethane or higher hydrocarbons are converted to methane, while the second section is a steam/methane reformer 30. The catalytic reactor 28 consists of a compact catalytic reactor formed from a stack of plates defining two sets of channels arranged alternately. One set of channels are for the pre-reforming or reforming reaction, and contain a suitable catalyst, which may be on removable corrugated metal foil supports, while the other set of channels are for the provision of heat. In a modification the pre-reformer and the reformer are separate reactors. In this example the heat is provided by combustion,

over a platinum/palladium catalyst, in the channels for the provision of heat.

The reaction channels of the reactor 28 may contain a nickel catalyst in an initial part of the channel, of length between 100 and 200 mm, for example 150 mm, out of a total reaction channel length of 600 mm. In the first part of the channel, where the nickel catalyst is present, pre-reforming takes place, so any higher hydrocarbons will react with steam to produce methane. This section is therefore called the pre-reformer 29. The remainder of the length of the reaction channels contains a reformer catalyst, for example a platinum/rhodium catalyst, where the steam and methane react to form carbon monoxide and hydrogen.

The heat for the steam/methane reforming reaction in the reformer 30 is provided by combustion of a fuel gas in a stream of combustion air. The fuel gas is primarily hydrogen, but it may also include methane and other flammable compounds. The combustion air may be preheated in a heat exchanger (not shown) taking heat from the hot exhaust gases from the combustion after they have passed through the reformer 30. The exhaust gases may then be vented through a stack.

A mixture of carbon monoxide and hydrogen at above 800 °C emerges from the reformer 30, and is quenched to below 400 °C by passing it through a steam-raising heat exchanger 36 which may be a thermosiphon, arranged to generate steam. The resulting steam is supplied to the mixer 26.

The gas mixture, which is a form of synthesis gas, is then subjected to further cooling in a heat exchanger 38. It is then subjected to compression using two successive compressors 40 (only one is shown) preferably with cooling and liquid-separation stages (not shown) after each compressor 40. The compressors 40 raise the pressure to about 2.6 MPa (26 atm) (absolute).

It will be appreciated from equation (1) above that the ratio of hydrogen to CO produced in this way is about 3:1, whereas the stoichiometric requirement is about 2:1, as is evident from equation (2). The high-pressure synthesis gas is therefore passed by a hydrogen-permeable membrane 42 to remove excess hydrogen. This hydrogen may be used as the principal fuel gas for the combustion step.

3. Fischer-Tropsch Synthesis

The stream of high pressure carbon monoxide and hydrogen is then fed through

a duct 48 to a catalytic Fischer-Tropsch reactor 50, the duct 48 including a poison-removing guard bed 44 and a heat exchanger 46 through which the carbon monoxide and hydrogen flow. The Fischer-Tropsch reactor 50 is a compact catalytic reactor formed from a stack of plates as described above, with channels for a coolant fluid alternating with channels for the Fischer-Tropsch synthesis. Within each of the channels for Fischer-Tropsch synthesis is a catalyst, which may be provided as a removable catalytic insert (not shown) consisting of a corrugated 50 μm thick foil (typically of thickness in the range from 20-200 μm) with a ceramic coating acting as a support for the catalytic material; instead of a single foil, the insert may consist of a stack of shaped foils.

The reactant mixture flows through the reaction channels of the reactor 50, while a coolant flows through the other channels. The coolant is circulated through a heat exchanger 52. Initially, when the catalyst is new, the Fischer-Tropsch reaction takes place at about 210°C, and the coolant is circulated at such a rate that the temperature varies by less than 10 K on passage through the reactor 50.

The reaction products from the Fischer-Tropsch synthesis, predominantly water and hydrocarbons such as paraffins, are cooled in a heat exchanger 60 and fed to a separating chamber 62 in which the three phases water, hydrocarbons and tail gases separate. The aqueous phase contains water with about 1-2% oxygenates such as ethanol and methanol which are formed by the Fischer-Tropsch synthesis. At least some of the aqueous phase is fed as process water through the heat exchanger 52, and hence through a pressure-drop valve 64, so it can be used to provide the steam to the mixer 26.

It will be appreciated that the arrangement for separating the reaction products may be more complex than shown in figure 1. In particular the vapour and gas phase from the separating chamber 62 may be fed through successive cooling heat exchangers to a lower temperature, so as to condense more of the hydrocarbon product.

The remaining vapour phase, which is at the same pressure as the Fischer-Tropsch reactor 50, may be passed through a throttle valve (not shown) to expand adiabatically into a lower pressure region, with no significant heat input from the surroundings, so as to cool the gas further, and then fed into a phase separating vessel. This may increase the amount of water and light hydrocarbon product that is obtained.

4. Catalyst Protection

The above description is of the normal operation of the plant 10. A commercial

plant may include several steam/methane reformers 30 operating in parallel, and may also include several Fischer-Tropsch reactors 50 operating in parallel.

5 The feed gas 5 may include impurities such as sulphur or mercury which would act as catalyst poisons to the catalysts in the pre-reformer 29 and the reformer 30. The feed gas 5 is therefore passed through a pretreatment system 25, in which such impurities are removed. As discussed above, this may include a guard bed, or other chemical processes, which would be dependent on the nature of the contaminant.

10 Since the synthesis gas contains carbon monoxide, then if the pipework or other plant components are of steel or stainless steel, there is a risk of formation of certain metal carbonyls, which would be in the vapour form and would have a detrimental effect on the catalyst in the Fischer-Tropsch reactor 50, as the metal carbonyls would also constitute a catalyst poison to the catalyst in the Fischer-Tropsch reactor 50.

15 It will thus be appreciated that contaminants which may act as catalyst poisons may be present in the feed gas 5, or may be formed as the gases flow through the plant 10. Appropriate contaminant removal apparatus, which may be referred to as poison removal apparatus, should therefore be provided upstream of each catalytic reactor, to
20 remove whatever contaminant is likely to be present. In the plant 10 this is exemplified by the provision of the guard bed 44.

In the plant of figure 1, considering the gas supplied to the Fischer-Tropsch reactor 50, there may be a number of different contaminants or catalyst poisons that
25 should be removed. Consequently it may be appropriate to provide a number of different guard beds through which the gas flows in series. Referring now to figure 2, there may in practice be a number of different guard beds arranged in succession. In this example the first guard bed 44 operates at ambient temperature, and it contains soda lime (a mixture of sodium hydroxide, calcium hydroxide and calcium carbonate) to remove acid
30 gases such as hydrogen sulphide. This removal process generates some water vapour, so the next guard bed is a dehydrating guard bed 75 containing particulate alumina. The gas stream then passes through the heat exchanger 46 so it is at a temperature above 200 °C. The gas then passes through a third guard bed 76 containing zeolite, and at this elevated temperature metal carbonyls undergo decomposition and are trapped by the
35 zeolite. Thus these three guard beds 44, 75 and 76 successively remove hydrogen sulphide, water vapour, and metal carbonyls from the gas stream, so that substantially clean synthesis gas is supplied to the Fischer-Tropsch reactor 50.

It has been found that the guard bed 75 absorbs not only water vapour but also iron carried in the gas or vapour phase, for example as iron carbonyl, even though it is at ambient temperature; iron carbonyl from the vapour phase may form a different iron-based compound when it is absorbed. In accordance with the present invention the guard bed 75 is provided with additional features, this combination being referred to as a poison removal apparatus 70. This is shown in more detail in figure 3, to which reference is now made. The poison removal apparatus 70 is upstream of the Fischer-Tropsch reactor 50, although it will be appreciated from figure 2 that there may be other components between the poison removal apparatus 70 and the Fischer-Tropsch reactor 50. Although this poison removal apparatus 70 is described in relation to the guard bed 75 which precedes the Fischer-Tropsch reactor 50, it will be appreciated that a similar poison removal apparatus might be provided in association with a guard bed which precedes the catalytic reactor 28.

The poison removal apparatus 70 is upstream of the Fischer-Tropsch reactor 50 in the duct 48 carrying the synthesis gas to the reactor 50, and includes the guard bed 75 which contains a packed bed of alumina. This may be alumina in the form of calcined pellets, extrudates or spheres, primarily intended for use as an absorbent for water vapour; such a material is commercially available from Catal International Ltd under the brand CT 540. This packed bed captures and absorbs iron-based contaminants, until the capacity of the guard bed is substantially exhausted, at which time there will be a breakthrough of the iron-based contaminant. It is therefore necessary to regenerate or replace the guard bed 75 at intervals before any such breakthrough occurs. For this reason it would be beneficial to know the concentration of iron in the gas stream which is supplied through the guard bed 75 to the Fischer-Tropsch reactor 50.

The apparatus 70 includes two poison traps 80, one upstream and one downstream of the guard bed 75. Each poison trap 80 is associated with a valve 82 in the duct 48. Upstream of each valve 82 a pipe 83 branches off from the duct 48, and downstream of each valve 82 a return pipe 84 joins the duct 48. The pipe 83 leads via a three-way valve 85 and a check valve 86 to a borosilicate glass tube 87 packed with particulate absorber material 88 of alumina, which at ambient temperature acts as an absorber for iron-based contaminant in the gas or vapour phase, for example in the form of iron carbonyl. After the borosilicate glass tube 87 the gas passes through a flow meter 89 and a three-way valve 90 to communicate with the return pipe 84. A pressure sensor 92 is arranged to monitor the gas pressure adjacent to the flow meter 89. The iron-based contaminant forms a brown or yellow colouration, and is primarily on the surfaces of the particles of absorber material 88, although the colour is throughout the particles of

absorber material 88. It appears that the iron is then in the form of an iron oxide, and so the iron-based contaminant has undergone a chemical reaction.

5 A three-way valve 94 communicates with the pipe 83 just downstream of the check valve 86, and communicates also with one of the inlets to the three-way valve 85. An inlet to the three-way valve 94 may be supplied with a flushing gas such as high-pressure nitrogen, which may be fed through the borosilicate glass tube 87 directly through the check valve 86 or via the three-way valve 85. An outlet from the three-way valve 90 enables the flushing gas to be discharged to a vent.

10

The valves 82, 85 and 90 enable the flow of gas through the borosilicate glass tube 87 to be controlled, that is to say the flow can be turned on or off, and can be adjusted. The flow meter 89 and the pressure sensor 92 enable the quantity of gas which that has flowed through the borosilicate glass tube 87 to be determined. The
15 particulate absorber material 88 absorbs the iron-based contaminant from the gas that has passed through the borosilicate glass tube 87. At intervals the quantity of iron-based contaminant absorbed in the particulate absorber material 88 is monitored. This may be achieved, in some cases, merely by observing the colour of the particulate absorber material 88. In other cases it may be necessary to switch off the flow of gas through the
20 borosilicate glass tube 87, and remove at least some of the particulate absorber material 88 for chemical analysis. In practice it may be more convenient to remove all the particulate absorber material 88, and to replace it with fresh particulate absorber material 88. This can be achieved without interrupting the flow of gas through the duct 48 to the reactor 56.

25

The removed particulate absorber material 88 may be subjected to quantitative analysis to determine the amount of trapped metals such as iron, nickel or molybdenum. Such metals had originally formed part of the steel components of the plant 10, and had been carried in the gas stream as metal carbonyls (or possibly in another form). The
30 chemical analysis may utilise techniques such as ICP-MS to detect low levels of absorbed metal. Since the quantity of gas that has passed through the borosilicate glass tube 87 is known, it is hence possible to deduce the concentration of iron-based contaminant in the gas stream.

35

Considering the poison trap 80 upstream of the guard bed 75, this enables the concentration of iron-based contaminant such as iron carbonyl in the gas stream supplied to the guard bed 75 to be monitored. Hence the operational life of the guard bed 75 can be more accurately predicted, and the guard bed 75 can be regenerated or

replaced before breakthrough of iron-based contaminant through the guard bed 75 occurs.

5 The poison trap 80 downstream of the guard bed 75 serves a somewhat different purpose. It enables the effectiveness of the guard bed 75 to be monitored, and enables any breakthrough of iron-based contaminant such as iron carbonyl to be detected.

10 The poison trap 80 upstream of the guard bed 75 will trap not only iron-based contaminants in the gas or vapour phase (such as iron carbonyl) but also any metal-containing contaminants arising from degradation of structural materials of the plant 10 by the process referred to as metal dusting, if this degradation occurs. Indeed the guard bed 75 would also trap the contaminants arising from such metal dusting. By monitoring the contaminant loading of the poison trap 80 as described above, an indication may also be provided about the degree of degradation of the structural materials of the plant 15 10 upstream of the poison trap 80.

The poison trap 80 upstream of the guard bed 75 would typically be used only at intervals, that is to say the gas would be passed through the borosilicate glass tube 87 of this poison trap 80 only at intervals. It may be appropriate to pass gas through this 20 borosilicate glass tube 87 for example for between 5 min and 60 min, for example 15 min, every day. Since the level of contaminants in the gas stream does not change rapidly, this would be sufficient to monitor the average concentration of the contaminants over a period of months. On the other hand, particularly where the level of contaminants is very low, it may be satisfactory to pass gas through this borosilicate glass tube 87 25 continuously.

In a slightly different mode of operation, the poison trap 80 upstream of the guard bed 75 may be used less frequently, but for a longer time period which is sufficient to trap a measurable quantity of contaminant. For example gas might be passed through 30 the borosilicate glass tube 87 of the upstream poison trap 80 for three hours, once a week; and the particulate material 88 would then be analysed. Hence this would enable the concentration of the contaminant or poison in the gas stream to be measured on a weekly basis.

35 The poison trap 80 downstream of the guard bed 75 would typically be used continuously, that is to say the gas would be passed through the borosilicate glass tube 87 of this poison trap 80 continuously, as the level of contaminants should be very low as a result of passage through the guard bed 75. In this case the gas flow through the

borosilicate glass tube 87 would be stopped at intervals, so the particulate absorber material 88 can be removed for analysis, and replaced with fresh absorber material 88. For example this may be performed once a week.

5 It will hence be appreciated that the two poison traps 80 serve somewhat different purposes, and may be used independently. There nevertheless is a benefit in using both the poison traps 80, as shown in figure 2.

10 It will also be appreciated that the poison traps 80 are shown only by way of example. Various modifications may be made to the design. For example the use of the borosilicate glass tubes 87 is particularly appropriate where a colour change occurs to the particulate absorber material 88, and if no such colour change occurs then the borosilicate glass tubes 87 might be replaced by tubes of a non-transparent material such as stainless steel or titanium.

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Claims

1. A process for monitoring the presence of a contaminant in a gas stream being fed into a catalytic reactor including a catalyst, wherein a contaminant removal unit is provided upstream of the catalytic reactor, and the gas stream is fed through the contaminant removal unit to the catalytic reactor, the process comprising providing at least one of:
- a contaminant trap upstream of the contaminant removal unit, and
 - a contaminant trap between the contaminant removal unit and the catalytic reactor;
- passing at least part of the gas stream through the or each contaminant trap; monitoring the quantity of the gas stream that passes through each contaminant trap; and monitoring the presence of the contaminant trapped in the contaminant trap.
2. A process as claimed in claim 1 wherein the presence of the contaminant trapped in the contaminant trap is detected from a change of colour.
3. A process as claimed in claim 1 wherein presence of the contaminant trapped in the contaminant trap is detected by removing and analysing material from the contaminant trap.
4. A process as claimed in any one of the preceding claims wherein the contaminant trap comprises a particulate absorbent or adsorbent material, and the contaminant is trapped in or on the absorbent/adsorbent material by absorption or adsorption or by a chemical reaction.
5. A process as claimed in any one of the preceding claims using a contaminant trap upstream of the contaminant removal unit, wherein the gas stream is passed through the contaminant trap upstream of the contaminant removal unit only at intervals.
6. A process as claimed in any one of the preceding claims using a contaminant trap downstream of the contaminant removal unit, wherein the gas stream is passed through the contaminant trap downstream of the contaminant removal unit continuously.
7. An apparatus for monitoring the presence of a contaminant in a gas stream being fed into a catalytic reactor including a catalyst, wherein a contaminant removal unit is provided upstream of the catalytic reactor, and the gas stream is fed through the contaminant removal unit to the catalytic reactor, the apparatus comprising at least one contaminant trap, and means to connect the contaminant trap to carry at least part of the

gas stream either upstream of the contaminant removal unit, or between the contaminant removal unit and the catalytic reactor, and means to monitor the quantity of the gas stream that passes through each contaminant trap.

5 8. An apparatus as claimed in claim 7 wherein the means to connect the contaminant trap includes valves such that the contaminant trap can be disconnected, or fed with the gas stream, without any significant effect on the flow of the gas to the reactor.

9. An apparatus as claimed in claim 8 also comprising valves to enable a flushing gas to
10 be passed through the contaminant trap.

10. An apparatus as claimed in any one of claims 7 to 9 wherein the contaminant trap comprises a particulate absorbent or adsorbent material.

15 11. An apparatus as claimed in claim 10 wherein the particulate absorbent or adsorbent material is alumina.

12. An apparatus as claimed in claim 10 wherein the particulate absorbent or adsorbent material is a pre-sulphided mixed oxide, suitable for absorbing mercury.

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13. An apparatus as claimed in claim 10 wherein the particulate absorbent or adsorbent material is a metal-promoted zinc oxide/alumina composition or a zinc oxide composition, suitable for absorbing or adsorbing hydrogen sulphide.

25 14. An apparatus as claimed in any one of claims 7 to 13 wherein a contaminant-trapping material is contained within a transparent container.

15. Use of an apparatus as claimed in any one of claims 7 to 14 incorporating a contaminant trap upstream of the contaminant removal unit, for monitoring for
30 degradation of structural components of a chemical plant, wherein the contaminants are generated by degradation of structural components of a chemical plant.

16. A process for monitoring for degradation of structural components of a chemical plant, where the degradation forms a contaminant in a gas stream being fed into a
35 catalytic reactor, the process comprising providing a contaminant trap upstream of the catalytic reactor, and upstream of any contaminant removal unit associated with the catalytic reactor;
passing at least part of the gas stream through the or each contaminant trap;

monitoring the quantity of the gas stream that passes through each contaminant trap;
and monitoring the presence of the contaminant trapped in the contaminant trap.

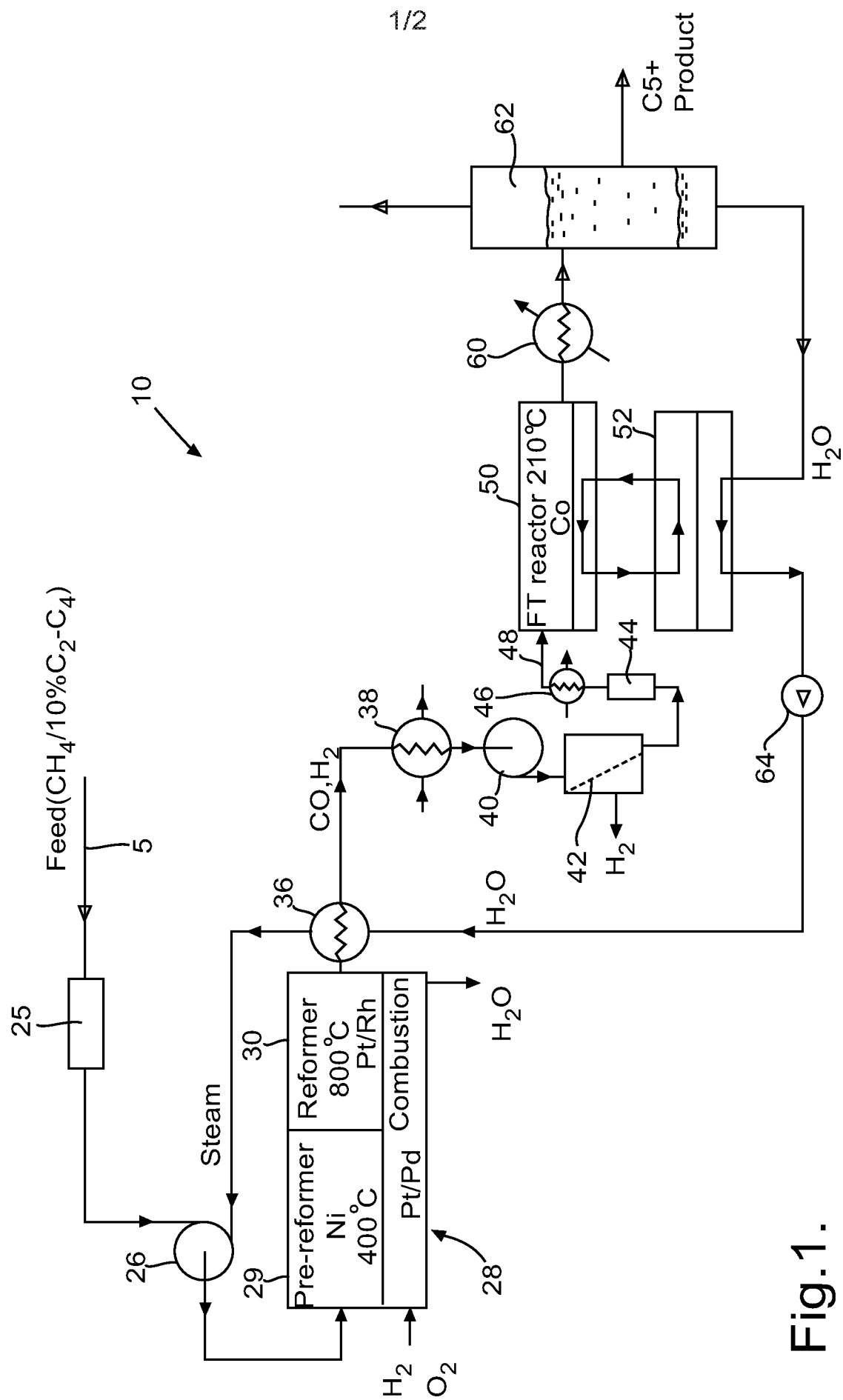
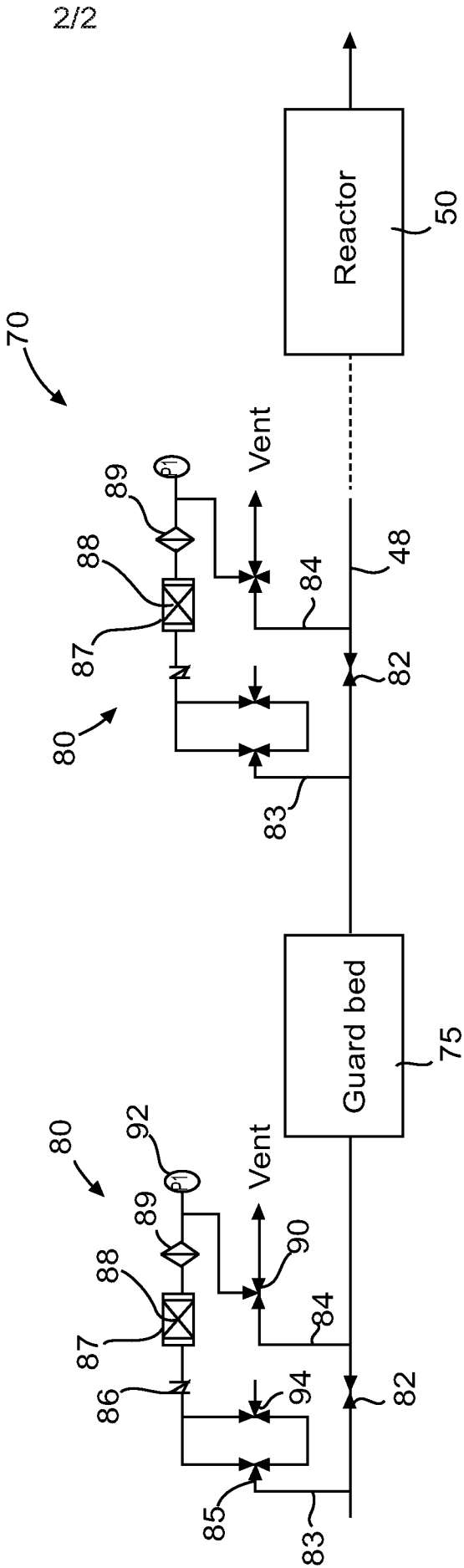
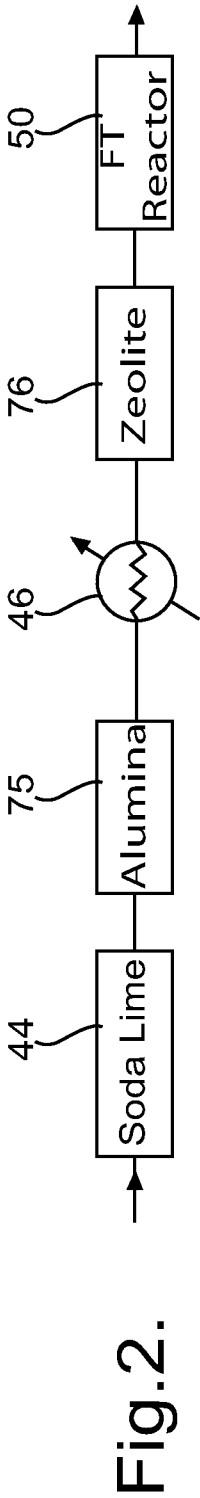


Fig. 1.



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2013/051559

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D53/30 B01D53/34 B01D53/86 G01N1/00 C10K1/00
C10K1/32

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D G01N C10K

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 239 111 A2 (UNION CARBIDE CORP [US]) 30 September 1987 (1987-09-30)	1,7,15, 16
Y	page 2, line 12 - line 20 page 3, line 5 - line 9 page 4, line 15 - line 18 page 8, line 51 - line 52; table 1 -----	15,16
Y	WO 2005/094972 A1 (VOLVO TECHNOLOGY CORP [SE]; LINDSTROEM BAARD [SE]; EKDUNGE PER [SE]) 13 October 2005 (2005-10-13) figure 1 page 3, line 15 - line 29 page 4, line 31 - line 33 ----- -/-	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

13 September 2013

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2013/051559

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	figure 1 column 2, lines 59-63 column 5, line 21 - line 35 column 6, line 32 - line 33 -----	1-16
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Y	figure 1 page 2, line 16 - page 3, line 2 -----	1-16
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Y	figure 1 paragraph [0036] paragraph [0046] -----	1-16
A	US 4 108 552 A (AUSTIN TERRY MARSHALL ET AL) 22 August 1978 (1978-08-22) the whole document -----	1-16

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Information on patent family members

International application No

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