

Process for the desulfurisation of CO gas

The present invention relates to a process for the
5 preparation of carbon monoxide gas (CO gas) that is free of
sulfur compounds to the greatest possible extent, to a
process for the desulfurisation of a CO gas containing
sulfur, and to the use of that gas in chemical syntheses,
for example for the synthesis of phosgene from carbon
10 monoxide and chlorine.

The availability of CO gas that is as pure as possible is
highly desirable for many chemical syntheses, because CO
gases are often contaminated with impurities, for example
15 sulfur compounds, which act as catalytic poisons or
secondary-reaction initiators or which lead in other ways
to interruptions in operation or even to the total loss of
production.

20 Many attempts have therefore been made in the past to
obtain pure forms of preparation of that gas.

For example, the method of converting organic sulfur
compounds in the presence of steam on an aluminium oxide
25 contact at temperatures of about 160°C to form hydrogen
sulfide and carbon dioxide is described on p. 3, line 6 ff
of DE-A 43 21 542, although detailed information regarding
the degree of conversion of the organic sulfur compounds is
not given.

30 DE-A 41 04 202 describes on p. 3, line 14 ff the almost
quantitative hydrolysis of carbon oxide sulfide at markedly
lower temperatures of from 20 to 150°C on aluminium oxide

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contacts which, however, have been doped very expensively with further transition metals. Column 2, line 9 ff and column 7, line 20 ff of EP-A 0 324 526 describe the use of a titanium dioxide contact for the hydrolysis of COS and CS₂ at temperatures above 300°C with a lower degree of conversion of from 90 to 96 % (based on organic sulfur compounds). However, those processes use contacts which are expensive and complex to prepare using doped aluminium oxides or titanium dioxide.

GB-A 22 48 444 is to be regarded as more remote prior art, in which there is described the use of an aluminium oxide contact for the conversion of hydrogen sulfide with carbon dioxide at from 60 to 120°C to carbon oxide sulfide and water as a reverse reaction; the resulting carbon oxide sulfide is subsequently decomposed thermally. EP-A 0 234 433 describes the use of an aluminium oxide contact doped with alkali for the absorption (not the conversion) of acidic gases, *inter alia* hydrogen sulfide. However, these processes have the disadvantage that the Al₂O₃ contacts used either have to be pretreated in a complex and expensive manner or effect too low a degree of conversion or require the use of too great an amount of energy. Those disadvantages can, surprisingly, be avoided by the process according to the invention by adhering to precisely defined process conditions with the use of inexpensive, commercially available Al₂O₃ contacts.

The process of the chemical absorption of hydrogen sulfide on iron-hydroxide-containing materials with the concomitant use of oxygen has already been mentioned in DE-A 20 06 758; the optimisation of the absorption materials in respect of the content of iron hydroxide and loosening agent is

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described therein on p. 2. DE-A 28 45 725 claims the preparation of iron-hydroxide-containing absorption materials based substantially on iron(II) sulfate and calcium oxide and their use in the chemical binding of hydrogen sulfide. DD-A 15 72 62 mentions on p. 3 the use of limonite as an iron-hydroxide-containing material for the removal of hydrogen sulfide from CO-containing gases. Such absorption materials are also used in the process according to the invention. However, by the application of defined process parameters in the process according to the invention, an improvement in the rate of absorption is, surprisingly, achieved.

US-A 6 126 911 describes the use of iron oxides (claim 3) or iron oxide hydrates (column 5, line 18) in combination with moistening agents such as glycols etc. for the absorption of hydrogen sulfide from dry gases, with only 67 % of the hydrogen sulfide contained in the gas stream being retained in the most advantageous case (column 7, line 55). WO-A 93/13184 describes the absorption of hydrogen sulfide from dry gases on iron oxides onto SiO₂-containing carrier materials in the presence of oxygen at considerably higher temperatures of about 200°C (p. 22, line 20 ff to p. 23, line 22). The hydrogen sulfide is thereby retained on the contact in the form of elemental sulfur with an efficiency of only 80 %. After catalytic hydrogenation of the gas mixture for the complete conversion of sulfur compounds into hydrogen sulfide, the residual amounts of sulfur are adsorbed on activated carbon doped with iron oxide. Column 6, lines 16-40 of EP-A 1180544 describes the use of tri-iron tetra-oxide at 400°C for the absorption of hydrogen sulfide on the contact in the form of iron sulfide; in a subsequent step, residual

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amounts of hydrogen sulfide are bonded to zinc oxide in the form of zinc sulfide. The examples of EP-A 722 774 describe the use of iron(III) oxide in combination with molybdenum oxide on an aluminium oxide carrier at at least 350°C for the absorption of hydrogen sulfide in the form of sulfide on the contact. However, all those processes either use undesirable auxiliary substances (glycol) or require the use of far too much energy, or technically complicated subsequent steps (deposition of sulfur), in order to achieve usable results. These disadvantages can, surprisingly, be avoided using the process according to the invention.

The process of the physical adsorption of gases on activated carbon is general prior art. For the adsorption of hydrogen sulfide from CO gas, DE-A 4321542 claims an activated carbon that has been doped with iodine or iron compounds and permits a residual content of hydrogen sulfide in the CO gas of less than 10 mg/m³. WO-A 93/13184 describes (p. 23, line 12 ff) the use of an iron-oxide-containing activated carbon on which hydrogen sulfide is oxidised to elemental sulfur in the presence of oxygen at 50°C and adsorbed to a residual content of 2 vol.ppm hydrogen sulfide in the CO gas. However, pretreatment of the activated carbon is necessary in those processes, and in some cases excessively high absorption temperatures. The advantage of the process according to the invention is the concomitant use of an additional chemical agent (ammonia) by means of which, surprisingly, the complete absorption of all residual sulfur compounds on the activated carbon is possible in a technically simple manner.

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Accordingly, the object of the invention was to find an inexpensive and reliable process with which gaseous sulfur-containing compounds in the form of secondary constituents in the CO gas can be removed as quantitatively as possible, continuously and in justifiably short reaction times, without exhibiting the disadvantages of the prior art. The desulfurised CO gas is to be used as a material for chemical syntheses in which undesirable secondary reactions would be initiated by the presence of sulfur compounds, so that the presence of such compounds in the CO gas is additionally to be avoided at all events.

It has now been found, surprisingly, that such a process can be achieved by the combination of appropriate steps. In the process, the crude CO gas, which contains inorganic and organic sulfur compounds that are gaseous under the process conditions, is subjected in the first step to a so-called conversion stage in which the crude CO gas is continuously charged with steam and fed at elevated temperature to an aluminium oxide contact. Organic sulfur compounds are thereby converted to the greatest possible extent into carbon dioxide and hydrogen sulfide. A high degree of conversion can be achieved by adhering to defined process conditions.

In a subsequent chemical absorption stage, the CO gas, which contains predominantly hydrogen sulfide as the sulfur component, is passed continuously over reaction towers in which there is located an iron-hydroxide-containing, granular and porous material, to which hydrogen sulfide is bonded in the form of iron sulfide and elemental sulfur in the presence of defined amounts of oxygen and water. The oxygen and sulfur contents in this absorption stage can be monitored continuously at various points, in order either

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to adapt the amount of oxygen that is metered in or to change over between absorption towers in the installation in good time, before the sulfur content in the emergent CO gas becomes impermissibly high. This changeover means that

5 an absorption tower of relatively high absorption capacity, through which the gas flows later in the series and which is therefore less laden with sulfur, is connected so that it is the first absorption tower in the series of absorption towers through which the incoming CO gas flows.

10 The fully laden absorption tower is taken out of operation and the exhausted, fully laden biogas material is fed to further processing. When equipping the tower with biogas material again, either an already freshly equipped tower can be connected as a replacement into the series as the

15 last tower in the absorption stage, or the tower that has been taken out of operation is itself connected into the series again, after being re-equipped, as the last tower in the absorption stage.

20 In a third step, the CO gas so purified is passed in the so-called adsorption stage over activated carbon towers, whereby residues of organic and inorganic sulfur compounds are adsorbed almost quantitatively on the activated carbon in the presence of defined amounts of ammonia. The oxygen

25 and sulfur contents in this adsorption stage are likewise monitored continuously at various points, in order either to adapt the amount of oxygen that is metered in or to change over between activated carbon towers in the installation in good time, before the sulfur content in the

30 emergent CO gas becomes impermissibly high. This changeover means that an activated carbon tower of relatively high absorption capacity, through which the gas flows later in the series and which is therefore less laden with sulfur, is connected so that it is the first activated carbon tower

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in the series of activated carbon towers through which the incoming CO gas flows; the fully laden activated carbon tower is taken out of operation and regenerated. During the regeneration of the tower, either an already regenerated
5 tower can be connected as a replacement into the series as the last tower in the absorption stage, or the tower that has been taken out of operation is itself connected into the series again, after being regenerated, as the last tower in the absorption stage.

10

The individual process steps can all be monitored and controlled by on-line analysis in order to ensure optimal process conditions.

15

The desulfurised CO gas leaving the activated carbon has a residual content of inorganic and organic sulfur compounds of in each case less than 5 mg/Nm³, preferably less than 2 mg/Nm³.

20

The CO gas prepared in accordance with the process of the invention is additionally largely free of further impurities, such as hydrogen, oxygen, carbon dioxide, methane and water. It is used for chemical syntheses in which all the mentioned impurities would be troublesome,
25 for example especially for phosgene synthesis.

30

The desulfurisation process for CO gas according to the invention is a combination of three continuously operated process steps which, by their combination and their form, surprisingly permit particularly high efficiency of the CO gas desulfurisation from the economic point of view and lead to a particular purity of the CO gas.

The invention accordingly relates to a process for the desulfurisation of a CO gas containing as secondary constituents sulfur compounds that are gaseous under the process conditions. Such a CO gas can originate, for example, from a so-called partial oxidation installation in which carbon-rich fuels, for example hard coal coke, pitch coke, oil coke, graphite or anode residues from aluminium production, are converted to the carbon monoxide stage in the presence of pure oxygen and pure carbon dioxide using the Boudouard equilibrium. Preference is given to the use of anode residues and coke types having a sulfur content of less than 2.5 wt.%, particularly preferably less than 1.5 wt.%, very particularly preferably less than 1.0 wt.%, and an ash content of less than 10 wt.%, particularly preferably less than 3 wt.% and very particularly preferably less than 1 wt.%. Under these reducing reaction conditions, virtually no sulfur oxides but predominantly sulfur compounds such as, for example, carbon oxide sulfide, carbon disulfide, mercaptans and hydrogen sulfide are formed from the sulfur compounds contained in the fuels. The desulfurisation process according to the invention is particularly suitable for removing such compounds from the CO gas.

The process according to the invention is distinguished by high economy, efficiency and availability, which is given by the following factors:

- 1.) use of simple reaction contacts or auxiliary substances which are commercially available and are not subjected to additional treatment;
- 2.) continuous process, which is simple in terms of apparatus, on fixed-bed reactors with a high degree of

variability of the installation, in which reactors can be connected in parallel or in series, if required, thus providing reserves in the case of failure of individual reactors;

5

3.) no expensive regenerating circuits (apart from the activated carbon stage), but optimum use of reaction contacts with subsequent processing;

10 4.) energy recirculation in the conversion stage;

5.) high degree of variability in the gas throughputs throughout the installation.

15 The analytical monitoring, which takes place on-line, of the reaction processes in the process according to the invention permits the optimum use of installation capacities and accordingly also high degrees of conversion in the individual process stages.

20

Individual process steps, preferably the entire process, are carried out at pressures above normal pressure.

The process according to the invention is highly suitable especially for small and medium-sized production installations having CO gas throughputs of from 1000 to 15,000 Nm³/h CO gas with a sulfur content of up to 6000 mg/Nm³, preferably for installations having CO throughputs of from 1000 to 10,000 Nm³/h and sulfur contents of from 1000 to 5000 mg/Nm³ and particularly preferably for installations having CO throughputs of from 3000 to 8000 Nm³/h and sulfur contents of from 2000 to 5000 mg/Nm³.

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1 Nm³ here stands for "standard cubic metres", i.e. an amount which corresponds to 1 m³ at 20°C and 1.01325 bar.

5 The CO gas laden with sulfur compounds that is used in the process according to the invention should be largely free of dust before it is fed to the first stage of the sulfur conversion. Dust removal can be carried out either by a wet process or by dry dust removal. The dust-free CO gas containing the sulfur compounds is preferably heated in
10 steam heat exchangers to a temperature of at least 280°C, preferably to a temperature of 300°C, which is kept constant within a narrow range of $\pm 5^\circ\text{C}$. Before entering the conversion towers, the CO gas is charged with steam in a sufficient amount, which is dependent on the content of
15 sulfur compounds and on the moisture content of the incoming gas. The amount of steam should be so chosen that the water content in the CO gas is at least 2.5 wt.%, preferably 3.0 wt.%, based on CO gas.

20 The hot CO gas charged with steam is fed at elevated pressure, which is usually from 1.5 to 10 bar, preferably from 1.5 to 5 bar, to so-called conversion towers. These are conventional fixed-bed reactors having a sieve base, which contain an uninterrupted, compact filling of
25 aluminium oxide contact (Al_2O_3) in the form of solid grains and through which the gas flows from top to bottom. Two or more conversion towers can be connected in series or in parallel; in the case of the sulfur contents mentioned above, a single pass through a conversion tower is usually
30 sufficient.

It is possible to use any type of sintered aluminium oxide that is suitable as contact or carrier material and

possesses adequate mechanical strength. The bulk height and the particle size of the aluminium oxide contact should be so chosen that the pressure loss in the fixed-bed reactor is less than 0.2 bar. There are suitable cylindrical

5 granules having a length of 10 mm and a diameter of 4 mm in a bulk height of less than 8 m. The specific surface area of the aluminium oxide contact should be at least 200 m²/g, preferably 230 m²/g; the pore volume should be at least 0.5 ml/g, preferably 0.7 ml/g.

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Organic sulfur compounds, especially carbon oxide sulfide and carbon disulfide, are hydrolysed on that aluminium oxide contact with water to form hydrogen sulfide and carbon dioxide (see Equations 1. and 2.):

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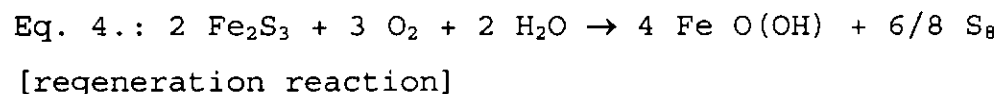
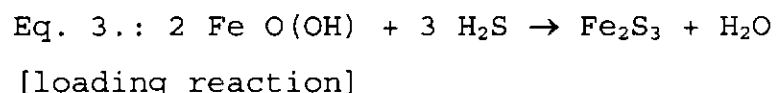
20 Under the reaction conditions according to the invention, the capacity of such conversion towers is used optimally, so that the average dwell time of the CO gas in such a conversion tower is less than 2 minutes, preferably less than 1.5 minutes. A rate of conversion of the organic

25 sulfur compounds of more than 95 %, in most cases even of more than 98 %, based on the initial amount used, is achieved. The conversion in such conversion towers is monitored by on-line analysis of the incoming and emergent CO gas stream.

30

In order to optimise the energy balance in the conversion stage, a heat exchange takes place between incoming and outgoing CO gas in a countercurrent heat exchanger.

After cooling to a temperature of below 50°C but above 20°C, preferably to 30°C, the CO gas so converted is fed to the chemical absorption stage. Before entering the absorption towers, an amount of at least 4000 mg/Nm³, optionally more than 7000 mg/Nm³, of pure oxygen is mixed with the CO gas, according to the amount of hydrogen sulfide it contains. The amount of oxygen added prior to the absorption stage is limited by the maximum permissible oxygen concentration of 0.15 vol.% at the entry to the activated carbon adsorption stage (see p. 8). The CO gas should be saturated with steam but contain at least 10,000 ppm water; steam is optionally added to the CO gas. The absorption towers are filled with an iron-hydroxide-containing, porous material, on which the conversion of hydrogen sulfide to iron sulfide and to elemental sulfur takes place in the presence of sufficient amounts of water and oxygen. In the oxidation of iron sulfide to elemental sulfur, the active form of the iron hydroxide is formed again in the presence of water and hence the capacity of the contact, based on its useful life, is increased. The chemical reactions in the loading and in the regeneration of the absorption material are shown in Equations 3 and 4:



Suitable starting materials for the iron-hydroxide-containing materials are various products occurring on an industrial scale, such as, for example, the lye residues

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from the working up of bauxite, or the so-called Béchamp residues from the reduction of organic nitro compounds with iron turnings, or so-called limonite, or synthetic materials such as are formed when iron(II) sulfate is
5 reacted with calcium hydroxide with subsequent oxidation in the air (see DE-A 28 45 725). In order to provide an adequate absorption capacity, an iron hydroxide content of at least 15 wt.% (calculated as Fe), preferably greater than 20 wt.%, based on the materials, is required. The
10 materials used in the absorption towers, which are also known as biogas materials, contain substances such as, for example, cement, lime or gypsum as binders for increasing the mechanical strength. For increasing the capacity of such materials there are used loosening agents, which
15 increase the diffusion of the gas into the material, so that not only the surface of the granular, porous materials but also the layers located more deeply take part in the chemical absorption. An example of a suitable loosening agent is sawdust (see DE-A 28 45 725, DE-A 20 06 758); care
20 must be taken to ensure that such loosening agents do not contain acids, which may react with the binders in the materials.

When operating the absorption towers with such so-called
25 biogas materials, it is important that the pressure loss of the CO gas in the absorption zone does not become inadmissibly high, i.e. does not exceed a pressure difference of 0.5 bar, preferably 0.4 bar, even with the series connection of absorption towers. That is achieved
30 substantially by suitably selecting the biogas material and by measures relating to the apparatus.

Suitable biogas materials are distinguished by the fact that they ensure sufficiently high permeability of the

granular material even in the laden state, taking into account the elemental sulfur that is deposited, which can lead in places to considerable solidification of the biogas material laden with sulfur. Sufficient permeability of the biogas material, even in the laden state, is achieved by optimum particle size distribution, the particle size being not more than 10 mm and not less than 3 mm and the proportion of particle sizes between 5 mm and 8 mm being at least 45 wt.%.

Suitable apparatuses are, for example, absorption towers in which the biogas materials are accommodated in a plurality of mesh baskets each of limited but equal bulk height. Such mesh baskets are in principle so constructed that the CO gas to be desulfurised is able to flow freely over the surface of the biogas material, and the biogas material is separated mechanically from the side on which the desulfurised CO gas is discharged by means of a sufficiently fine-meshed grid, so that it is not possible for larger amounts of biogas material particles to be carried away together with the gas stream. Fine-grained, inert solids (e.g. fine-grained crushed coke) can optionally be used as a filter layer between the biogas material and the grid construction. The intake and discharge sides are separated from one another by solid walls. Furthermore, the mesh baskets are separated from one another by means of bases or cover plates, so that each mesh basket forms its own separate gas chamber, but all the mesh baskets are preferably coupled to common supply and discharge pipes. In mesh baskets that are preferably used, the CO gas to be desulfurised flows in from above, so that the CO gas flows through a loose filling of biogas material that is from 120 to 180 cm high, preferably about 150 cm high, and exits through a horizontally arranged grid plate

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located in the base region of the basket. Between the grid plate and the base plate of the basket, the emergent CO gas is diverted to a centrally arranged discharge pipe, via which it leaves the absorption tower. The mesh baskets that
5 are preferably used can be stacked one above the other in the absorption tower so that the CO gas can enter the baskets from the side through defined spaces along the outside walls of the baskets and can flow into the biogas material from above. In the middle of each basket there is
10 a vertically arranged tube segment which contains inlet openings between the grid plate and the base plate, so that a central discharge pipe for the CO gas is formed when all the baskets are in the stacked state. At the bottom and top of the absorption tower, the discharge pipe is sealed with
15 respect to the other gas chamber (CO gas to be desulfurised) of the absorption tower.

Because the reactions taking place on the biogas material are slightly exothermic, it may under certain circumstances
20 be advantageous to cool the CO gas down again between the absorber towers in a heat exchanger.

The CO gas to be desulfurised can flow through the absorption towers either in series or in parallel,
25 depending on the operational conditions, such as throughput and sulfur content. The reduction in the absorptive capacity of an absorption tower can be monitored by on-line analytical measurements of the sulfur content in the incoming CO gas stream and in the emergent CO gas stream,
30 so that such an apparatus can be taken out of operation in good time in a targeted manner in order to avoid inadmissibly high sulfur contents in the emergent CO gas. When the installation is operating in the optimum manner, the CO gas leaves the chemical absorption stage with a

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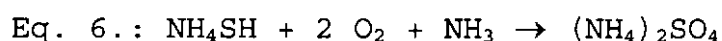
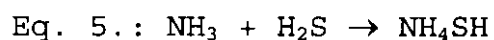
content of organic and inorganic sulfur compounds in the range of in each case approximately from 50 to 100 mg/Nm³ CO gas. This corresponds to a rate of absorption of more than 98 %, based on the ingoing amount of inorganic sulfur compounds.

The CO gas so desulfurised is then passed to the activated carbon adsorption stage. The temperature in the heat exchanger is so adjusted that the temperature of the CO gas on entering this stage is below 50°C, preferably not more than 35°C. Before the CO gas enters the activated carbon adsorption towers, an amount of at least 150 mg/Nm³ but not more than 310 mg/Nm³ of gaseous ammonia is mixed homogeneously with the CO gas. The oxygen content in the CO gas, which is present as an excess from the oxidation reaction in the preceding chemical absorption stage, should be not more than 0.15 vol.%.

A plurality of activated carbon adsorption towers are present, and the CO gas can flow through them either in series or in parallel, depending on the operational requirements. The activated carbon towers are fixed-bed reactors and are in the form of cylindrical apparatuses having a sieve base; they contain an uninterrupted packing of granular activated carbon, through which the gas flows from top to bottom. Suitable granular activated carbons have sufficient strength to avoid inadmissibly large amounts of fine abraded material, which can be formed especially in regeneration procedures. The particle size distribution should be so chosen that the pressure loss of the CO gas in the adsorption stage as a whole is not more than 0.4 bar. Suitable activated carbons have a specific surface area of from 1000 to 1200 m²/g and a pore volume, at

pore sizes of less than 20 nm, of from 0.5 to 0.7 ml/g, e.g. the activated carbon "D 47-4" from "VFT".

5 The residual sulfur compounds, e.g. unconverted organic sulfur compounds, elemental sulfur and hydrogen sulfide, are retained on the activated carbon. In the presence of ammonia and traces of oxygen there is formed *inter alia* ammonium sulfate, which can be removed from the activated carbon during the regeneration with steam. The chemical
10 reactions are shown in Equations 5 and 6:



15

The oxygen, ammonia and sulfur contents are monitored continuously at various points in the adsorption stage in order to correct the amounts of material metered in, where appropriate, or in order to change over between activated
20 carbon towers in the installation in good time, before the sulfur content in the emergent CO gas can exceed the permissible value.

If an activated carbon adsorption tower has reached the
25 limit of loading with sulfur, it is disconnected from the other towers and regenerated separately. Regeneration of the activated carbon adsorption towers is carried out in two steps. For that purpose, apparatuses from different process stages can be connected together. In the first
30 step, about 1000 Nm³/h of desulfurised CO gas, which is removed at the end of the preparation process and heated in a heat exchanger to at least 280°C, preferably 300°C, flow through the laden activated carbon from top to bottom. The

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emergent CO gas is fed back to the CO stream entering the sulfur conversion step upstream of the countercurrent heat exchanger. This "flushing process" is continued until the sulfur content in the emergent CO gas is below 100 mg/Nm³.

5 In the second step, steam, preferably steam at 5 bar, is passed through the activated carbon tower from top to bottom, the sulfur-containing condensed steam being discharged at the base of the tower.

10 When the activated carbon adsorption stage is operating in the optimum manner in accordance with the specifications, the CO gas leaves the installation with a content of organic and inorganic sulfur compounds of in each case less than 5 mg/Nm³, preferably less than 2 mg/Nm³. This
15 corresponds to a rate of adsorption of the sulfur compounds of more than 95 %.

The CO gas so purified is brought to a pressure of 3.5 bar, and water is removed therefrom to a residual content of
20 less than 10 ppm in a subsequent conventional drying stage in accordance with known prior art by preliminary condensation in a brine heat exchanger at a temperature of 3°C and by subsequent drying in towers filled with silica gel.

25 The pure CO gas leaving this desulfurisation installation contains in each case less than 5 mg/Nm³, preferably less than 2 mg/Nm³, of organic and inorganic sulfur compounds, less than 1.5 vol.% hydrogen, less than 0.15 vol.% oxygen,
30 less than 50 ppm methane and less than 10 ppm water.

The individual stages are preferably present at least in duplicate in terms of apparatus, CO gas flowing through the

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apparatuses in parallel or in series, as required, and it being possible for individual apparatuses of different process stages to be connected together in a targeted manner if required. As a result, for example, the entire process can be carried out continuously, because the apparatuses can be operated and regenerated in turn.

The process sequence as a whole is subjected to continuous analytical monitoring at various points in the entire process, so that any violations of limiting values in respect of substance concentrations in the CO gas can be recognised sufficiently rapidly and acted upon. In the process according to the invention, the following substances in the CO gas are monitored continuously by so-called on-line analytical methods:

- organic sulfur compounds
(calibration of the equipment having been carried out with the following chemical compounds: carbon disulfide, carbon oxide sulfide, methylmercaptan, ethylmercaptan)
- inorganic sulfur compounds (hydrogen sulfide, sulfur dioxide)
- oxygen
- ammonia
- (in addition: residual water content and purity)

The inorganic and organic sulfur compounds are determined, for example, by means of on-line gas chromatographs from Siemens, using devices of the type: Sicromat RGC 202 R 219 where the sulfur contents in the CO gas are high, and using Sicromat RGC 202 R 220 where the sulfur content in the CO gas is low. The measured values in each case relate to the

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sulfur content of the chemical compounds and mean mg [S]/Nm³ CO gas.

5 Ammonia in the CO gas is determined photometrically using the "BINOS" device from Endress und Hauser. Oxygen in the CO gas is determined by a paramagnetic measuring process using the "OXIMAT" device from Siemens.

10 In the case of the sulfur determinations, sampling points are provided in the inlet stream and in the outlet stream of the CO gas in the sections of the process that are to be monitored, in order to allow the efficiency of a part of the process to be assessed. Because individual towers of the installation are periodically taken out of operation
15 because their capacity has been exhausted and they require regeneration, the sampling points are moved accordingly; the conversion towers constitute an exception, because regular regeneration thereof is not required.

20 The analytical data are recorded and registered in evaluatable form. If given limiting values are exceeded, alarms are sounded and in critical cases, as in the case of oxygen and ammonia, these are associated with the shutting down of the installation for safety reasons.

25 The Examples which follow are intended to illustrate the process according to the invention, but without limiting it.

ExamplesExample 1:

5 A CO gas from a crude CO gas producing source, containing less than 1.5 vol.% hydrogen, less than 0.15 vol.% oxygen and less than 50 ppm methane and having a content of organic sulfur compounds of 3300 mg/Nm³ and a content of inorganic sulfur compounds of 200 mg/Nm³, is fed
10 continuously in amounts of 8400 Nm³/h to a steam heat exchanger of the conversion stage. A portion of the gas stream, having a temperature of 50°C, comes from a wet dust-removing operation and is fed to a heat exchanger by way of a precompression stage and a countercurrent heat exchanger.
15 Another portion of the gas stream, having a temperature of about 200°C, comes from a dry dust-removing operation for the crude CO gas and is fed directly to the heat exchanger. The crude CO gas is there heated to about 300°C and fed to the towers of the conversion stage, which are filled with
20 aluminium oxide contact (BASF D 10-10). Before entering the conversion towers, an amount of 100 kg/h of steam is added continuously to the CO gas. The CO gas is at a pressure of 2.8 bar in this stage. The CO gas leaving the conversion stage is cooled over countercurrent heat exchangers, in
25 which a portion of the heat of the emergent gas is given up to the gas entering the conversion stage, to about 30°C over water heat exchangers. Continuous analytical monitoring of the emergent CO gas by so-called "on-line gas chromatography" gives a value of 50 mg/Nm³ for the content
30 of organic sulfur compounds and a value of 3450 mg/Nm³ for the content of inorganic sulfur compounds, which corresponds to a rate of conversion of the organic sulfur compounds of 98.5 %.

An amount of oxygen of 25 Nm³/h (or 4250 mg/Nm³ CO) is added to the cooled CO gas so converted, and the CO gas is passed continuously to the absorption towers of the chemical
5 absorption stage at a pressure of 2.6 bar. In those towers, absorption of sulfur compounds and conversion into elemental sulfur takes place on the iron-hydroxide-containing porous material (product: BIOGASMASSE from RAG) in the presence of oxygen and water. The CO gas passes
10 through four absorption towers in series. The heat of reaction that forms is dissipated by intermediate water heat exchangers to such an extent that a CO gas temperature of about 30°C is still maintained after leaving the absorption stage. The CO gas leaves the chemical absorption
15 stage with a content of organic and inorganic sulfur compounds of in each case 50 mg/Nm³. This corresponds to a rate of absorption of inorganic sulfur compounds of 98.6 %.

An amount of 1.7 Nm³/h (or 154 mg/Nm³ CO gas) of ammonia is
20 added to the CO gas so desulfurised, and the CO gas is fed continuously at a pressure of 2.2 bar to the towers of the activated carbon adsorption stage, which are filled with granular activated carbon (VFT, type D 47-4). The CO gas passes through four adsorption towers in series. In those
25 towers, the residual sulfur compounds from the CO gas are retained in the presence of not more than 0.15 vol.% oxygen and at a temperature of 30°C and a pressure of 2.0 bar. The CO gas leaves the activated carbon adsorption stage with a content of organic and inorganic sulfur compounds of in
30 each case less than 2 mg/Nm³. This corresponds to a rate of adsorption of inorganic and organic sulfur compounds of in each case more than 96 %.

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The CO gas so purified is brought to a pressure of 3.5 bar in a final compression step, and water is removed therefrom to a residual content of less than 10 ppm in a subsequent conventional drying stage in accordance with known prior art by preliminary condensation in a brine heat exchanger at a temperature of 3°C and by subsequent drying in towers filled with silica gel.

The pure CO gas leaving this desulfurisation installation contains in each case less than 2 mg/Nm³ of organic and inorganic sulfur compounds, less than 1.5 vol.% hydrogen, less than 0.15 vol.% oxygen, less than 50 ppm methane and less than 10 ppm water.

Example 2:

The crude CO gas production source, the apparatuses used and the physical conditions of pressure and temperature are identical with Example 1. The sulfur content of the CO gas is substantially increased compared with Example 1, the gas throughput is reduced.

In the same manner as described in Example 1, a CO gas containing less than 1.5 vol.% hydrogen, less than 0.15 vol.% oxygen and less than 50 ppm methane and having a content of organic sulfur compounds of 5650 mg/Nm³ and a content of inorganic sulfur compounds of 350 mg/Nm³ is fed continuously in amounts of 7000 Nm³/h to the heat exchanger of the conversion stage. Before entering the conversion towers, an amount of 200 kg/h of steam is added continuously to the CO gas. The CO gas leaving the conversion stage has, according to continuous analytical monitoring, a content of organic sulfur compounds of

100 mg/Nm³ and a content of inorganic sulfur compounds of 5900 mg/Nm³, which corresponds to a rate of conversion of the organic sulfur compounds of 98.3 %.

5 An amount of oxygen of 35 Nm³/h (or 7140 mg/Nm³ CO) is added to the cooled CO gas so converted, and the CO gas is passed continuously to the absorption towers of the chemical absorption stage at a pressure of 2.6 bar. The CO gas passes through four absorption towers in series. When the
10 installation is operating in the optimum manner (see Example 1), the CO gas leaves the chemical absorption stage with a content of organic and inorganic sulfur compounds of in each case 100 mg/Nm³. This corresponds to a rate of absorption of inorganic sulfur compounds of 98.3 %.

15 An amount of 2.8 Nm³/h (or 308 mg/Nm³ CO) of ammonia (substance C) is added to the CO gas so desulfurised, and the CO gas is fed continuously at a pressure of 2.2 bar to the towers of the activated carbon adsorption stage, which
20 are filled with granular activated carbon (VFT, type D 47-4). The CO gas passes through four adsorption towers in series. The CO gas leaves the activated carbon adsorption stage with a content of organic and inorganic sulfur compounds of in each case less than 5 mg/Nm³. This
25 corresponds to a rate of adsorption of inorganic and organic sulfur compounds of in each case more than 95 %.

In the case of this procedure, the pure CO gas leaving the desulfurisation installation contains, after additional
30 drying as described in Example 1, in each case less than 5 mg/Nm³ of organic and inorganic sulfur compounds, less than 1.5 vol.% hydrogen, less than 0.15 vol.% oxygen, less than 50 ppm methane and less than 10 ppm water.

Patent claims

1. Process for the preparation of a CO gas that is low in sulfur, characterised in that a CO gas containing
5 sulfur compounds that are gaseous under the process conditions

a) is fed continuously to a conversion stage at elevated temperature and with a defined steam
10 content, organic sulfur compounds contained in the CO gas being converted on an aluminium oxide contact to hydrogen sulfide and carbon dioxide,

b) the CO gas containing the sulfur compounds so converted is then fed continuously to a chemical
15 absorption stage, in which the hydrogen sulfide contained in the CO gas is converted on an iron-hydroxide-containing, porous material, in the presence of oxygen and water, into iron sulfide
20 and elemental sulfur and is absorbed,

c) the CO gas so desulfurised is then fed continuously to an activated carbon adsorption stage for the removal of traces of hydrogen
25 sulfide and optionally other sulfur compounds, some of the sulfur compounds still contained in the CO gas being converted in the presence of ammonia and traces of oxygen into water-soluble ammonium compounds.

30 2. Process for the preparation of a CO gas according to claim 1, characterised in that the aluminium oxide contact has a specific surface area of more than 200 m²/g and a pore volume of at least 0.5 ml/g.

3. Process for the preparation of a CO gas according to claim 1, characterised in that the conversion of the organic sulfur compounds is carried out at
5 temperatures of more than 280°C and with a steam content of at least 2.5 wt.% (based on CO gas).
4. Process for the preparation of a CO gas according to claim 1, characterised in that the iron-hydroxide-
10 containing, porous material used in the chemical absorption stage b) contains at least 15 wt.% (calculated as Fe) active iron(III) oxide hydrate (based on material).
- 15 5. Process for the preparation of a CO gas according to claim 1, characterised in that the temperature of the CO gas is not more than 35°C in the activated carbon adsorption stage c).
- 20 6. Process for the preparation of a CO gas according to claim 1, characterised in that, in the activated carbon adsorption stage c), ammonia is present in the CO gas in an amount of not less than 150 and not more than 310 mg/m³ and oxygen is present in an amount of
25 not more than 0.15 %.
7. Apparatus for the desulfurisation of CO gas, characterised in that iron-hydroxide-containing, porous material is accommodated in a cylindrical
30 apparatus in a plurality of gas-permeable mesh baskets arranged vertically one above the other, in a bulk height of in each case not more than 150 cm.

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8. Apparatus for the desulfurisation of CO gas according to claim 7, characterised in that the CO gas to be desulfurised flows into all the mesh baskets simultaneously from above through appropriate spaces between the individual mesh baskets, and in that the desulfurised CO gas is discharged in each case between a mesh grid and a separating plate at the base of each mesh basket into a central discharge pipe.
- 5
- 10 9. Desulfurised CO gas having a residual content of total sulfur compounds of less than 5 mg/m³, having a residual methane content of less than 50 ppm, having a residual oxygen content of less than 0.15 vol.%, having a residual hydrogen content of less than
- 15 1.5 vol.% and having a residual water content of less than 10 ppm.
10. Use of desulfurised CO gas according to claim 9 for chemical syntheses, especially for the preparation of phosgene.
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