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(54) Title: PROCESS FOR TREATING GASES OBTAINED BY COAL GASIFICATION, RESIDUE GASIFICATION, REFUSE GASIFICATION OR OIL GASIFICATION

(57) Abstract

The invention relates to a process for the treatment of synthesis gas or fuel gas obtained by coal gasification, residue gasification, waste gasification or oil gasification, in which the gas stream obtained by gasification, which contains reducing and possibly inert gases, is treated for the removal of sulfur, optionally after separation of the desired product synthesis or fuel gas, is subsequently hydrogenated, the sulfur compounds still present in the gas stream thereby being converted to hydrogen sulfide, the hydrogen sulfide is removed from the gas stream by adsorption or absorption on a solid or liquid sorbent and the loaded sorbent is supplied to the coal, residues, waste or oil to be gasified.

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Title: Process for treating gases obtained by coal gasification, residue gasification, refuse gasification or oil gasification.

The invention relates to a process for the treatment of gases obtained by coal gasification, residue gasification, waste gasification or oil gasification.

Coal gasification plants are built for the production of synthesis gas or fuel gas, which is used for generating electricity in generators which are driven by gas turbines. Coal gasification plants have advantages over directly fired coal-fired power plants, since such plants have more favorable properties with respect to emission and efficiency.

Currently, many aromatics are being produced as lead replacements in gasolines. In the production of these aromatics, a great deal of H_2 is released, which is used in the refineries again in hydrogenation and hydrogenating desulfurization processes. It is expected that the addition of aromatics to petrol will be reduced or even stopped completely because aromatics may be carcinogenic. This, however, will lead to a shortage of H_2 in refineries. Accordingly, at present residue and/or oil gasification plants are already being installed for the production of hydrogen-containing gas. For residues, gasification is most attractive, because burning this type of sulfur-rich streams is prohibited even in marine motors.

In the production of synthesis gas or fuel gas, as in coal, residue or oil gasification, many sulfur compounds are liberated, which must be removed so as to limit the emission into the atmosphere of SO_2 in particular, which is formed upon combustion of such sulfur compounds.

The synthesis or fuel gas originating from the gasification of coal, oil or residues often contains COS, CS_2, CO_2, HCN and NH_3 in addition to CO, H_2 and H_2S. Such a gas is highly reducing.

The extent to which the sulfur compounds must be removed depends on the intended application of the gas and the quality requirements to be met. If synthesis gas must satisfy the so-called "pipeline specification", the hydrogen sulfide content should be reduced to a value less than 5 mg/Nm^3. In that case, requirements with respect to the maximum content of other sulfur compounds, such as carbonyl sulfide (COS) and carbon disulfide (CS_2), are to be met as well.

In the prior art, many methods are known with which the amount of sulfur compounds in a gas, such as synthesis or fuel gas, can be reduced.

Usually, for the removal of sulfur-containing components from gases, the following process route is utilized. In a first step, the gas to be treated is purified, whereby sulfur-containing components are removed from the gas, followed by recovery of sulfur from these sulfur-containing components, followed by a residual gas sulfur purification step. In this last step, it is attempted to recover the residual percentage of sulfur before emitting the residual gas via a flue into the atmosphere.

In the gas purification step, processes are utilized in which often aqueous solvents are used. These processes are subdivided into five main groups, viz., chemical solvent processes, physical solvent processes, physical/chemical solvent processes, redox processes, in which H_2S is oxidixed directly to sulfur in aqueous solutions, and finally the group fixed bed processes, in which H_2S is absorbed or adsorbed chemically or physically, or is selectively catalytically oxidized to sulfur.

The first three groups of processes mentioned are typically used in the industry for the removal of large amounts of sulfur from typically large quantities of gas. The last two groups of processes mentioned, with the exception of fixed bed oxidation, are limited with regard to the amount of sulfur to be removed and the concentration of H_2S in the gases

to be purified and are therefore less suitable for use in large industrial gas purification plants.

The chemical solvent processes include the so-called amine processes, in which aqueous solutions of alkanolamines are used, and the so-called hot potassium carbonate processes, in which aqueous solutions or potassium carbonate are used.

In the physical solvent processes, different types of chemicals are used, for instance dimethyl ether of polyethylene glycol (DMPEG), known in this branch of the art under the name of Selexol, N-methyl-pyrrolidone (NMP), known under the name of Purisol, or methanol, known under the name of Rectisol.

Of the group of the physical/chemical processes, the Sulfinol process is very well known. This process uses a mixture of an alkanolamine with sulfolane, dissolved in a small amount of water.

In the three above-mentioned methods, an absorber and a regenerator are utilized. In the absorber, the sulfur-containing components are chemically and/or physically attached to the solvent. By lowering the pressure and raising the temperature in the regenerator, the sulfur-containing components are detached from the solvent, which can subsequently be reused.

A detailed description of these methods can be found in R.N. Maddox, "Gas and Liquid Sweetening", Campbell Petroleum Series (1977).

In these methods, the extent to which H_2S and other sulfur compounds, such as COS and CS_2, but also, for instance, carbon dioxide (CO_2), are removed, is dependent on the solvent chosen and the pressure. The higher the pressure, the more sulfur compounds are removed. For instance, from a synthesis gas or fuel gas containing 1 vol.% H_2S, approximately 99.5% of the sulfur compounds are removed at an absolute pressure of 5 bar, whereas from natural gas containing 1 vol.% H_2S, approximately 99.95% of these compounds are removed at a pressure of 80 bar. The removal of sulfur compounds, however,

is never complete and upon subsequent use of the gas, the compounds still present can give rise to some emission of SO_2.

The solvents used in these methods are recycled from the absorber to the regenerator and subsequently back to the absorber. Heat exchangers are typically used to save energy.

The sulfur compounds removed, together with the CO_2, are passed from the regenerator to a sulfur recovery plant, so as to recover sulfur from H_2S and other sulfur compounds.

A frequently used process for recovering sulfur from the thus obtained sulfur compounds, in particular H_2S, is the Claus process. This process is described in detail in H.G. Paskall, "Capability of the Modified Claus Process", Western Research Development, Calgary, Alberta, Canada (1979).

The Claus process consists of a thermal step followed by typically two or three reactor steps. In the thermal step, one-third of the H_2S is combusted to form SO_2 according to the reaction:

$$H_2S + 1^1/2\ O_2 \rightarrow SO_2 + H_2O$$

whereafter the rest, i.e., two-thirds of the H_2S react with the SO_2 formed to form sulfur according to the so-called Claus reaction

$$2\ H_2S + SO_2 \leftrightarrow 3\ S + 2\ H_2O$$

The efficiency of the Claus process depends on a number of factors. With increasing water content in the gas, the equilibrium in the Claus reaction shifts to the side of H_2S. In addition, a disturbance arises owing to the formation of COS and CS_2 in the thermal step. Further, the control of the combustion air is critical and, finally, losses occur in that in the residual gas, sulfur is entrained in the form of sulfur vapor and as sulfur particles.

Typically, the efficiency of a Claus plant is between 90 and 98%, depending on the number of reactors. In view of the environmental requirements, this sulfur recovery efficiency is presently insufficient and industrial plants are equipped with residual gas sulfur cleaning plants, known in the process

technology under the names of Tail Gas Treating Units (TGTU) or Tail Gas Clean-up Units (TGCU).

Residual gas sulfur cleaning processes are described *inter alia* in U.H.F. Sander et al., "Sulphur, Sulphur Dioxide and Sulphuric Acid", The British Sulphur Corporation Ltd, 59-95 (1984).

By the use of these residual gas sulfur cleaning processes, in which mainly residues of H_2S, SO_2, COS and CS_2 are removed, the sulfur recovery efficiency is raised to 98.5-99.95%. Known processes are for instance the Sulfreen process and the SCOT process.

One of the latest developments towards increasing the efficiency is formed by the so-called SUPERCLAUS™ process. Here, use is made of a catalyst as described in European patent applications nos. 242,920 and 242,006, and European patent application 409,353, this catalyst being deployed in a third or fourth reactor step, as described *inter alia* in "Hydrocarbon Processing", April 1989, pp. 40-42. Utilizing this method, the last residues of H_2S present in the inert gas stream are selectively oxidized to elemental sulfur according to the reaction

$$H_2S + {}^1/_2\ O_2 \quad ----> \quad S + H_2O$$

the efficiency being raised to 98.5-99.5%. The residual gases from a residual gas sulfur cleaning plant, such as, for instance, a SCOT or SUPERCLAUS plant, are after-burnt in an afterburner or incinerator before the residual gases are discharged.

In the above-mentioned process steps, the total SO_2 emission is the sum of the efficiency loss in the gas purifications step and in the sulfur recovery step. In the case where, for instance, 10,000 Nm^3/h synthesis gas containing 1 vol.% H_2S is treated in a gas purification plant having an efficiency of 99.5% and subsequently in a sulfur recovery plant having an efficiency of 95%, the total SO_2 emission is 5.475%, which corresponds to a total sulfur recovery efficiency of 94.525%.

For an equal amount of synthesis gas having the same concentration of hydrogen sulfide, the gas purification plant having an efficiency of 99.95% and the Claus plant followed by a SCOT plant having an efficiency of 99.8%, the total SO_2 emission is 0.25%, calculated on the sulfur initially present, which corresponds with a total sulfur recovery efficiency of 99.75%.

It is very difficult and costly to achieve total sulfur recovery efficiencies in excess of 99.9%.

The use of redox methods in gas purification, involving direct oxidation of H_2S to sulfur in aqueous solutions, is less suitable for the removal of large amounts of sulfur. In addition to the fact that these processes can only be used with gases of a low sulfur content, the recovered sulfur is of very poor quality owing to pollution with substances from the solvents used. Also, clogging occurs frequently, the quantity of chemicals to be used is large and there are environmental problems caused by waste chemicals, which may sometimes be very toxic, such as the arsenic compounds liberated in the known Stretford process.

A disadvantage of the use of gas purification methods in which use is made of a fixed bed is that in the majority of these processes the H_2S is absorbed, the absorbent being accordingly unsuitable for reuse. In the case of absorption on a fixed bed of absorbent that *can* be regenerated, the attendant problems are considerable. An example is the absorption on iron oxide of H_2S formed in coal gasification, the H_2S being converted into FeS (cf. H. Shirai et al, "Development of fixed bed desulfurization systems with honeycomb type iron oxide sorbents for hot coal gas"; study presented at the fourth world congress of Chemical Engineering, Karlsruhe, June 1991). As appears from this lecture, this (modern) method of gas purification using iron oxide also presents a number of problems, in particular in connection with the regeneration of partially converted absorbent.

Also in gas adsorption to activated carbon, optionally impregnated with, for instance, iodine, whereby the H_2S in the gas is directly oxidized with oxygen to form elemental sulfur below 120°C according to the reaction

$$H_2S + {}^1/_2\ O_2 \text{ ----> } S + H_2O$$

and whereby the sulfur is adsorbed into the pores of the active carbon, the active carbon is mostly used a single time, so that in this case, too, the process presents a waste problem (cf. Dechema Monographieen 64 (1970) p. 91 et seq).

The group of fixed bed processes further includes the processes for catalytic selective oxidation, which have been discussed hereinabove.

This gas purification by means of a selective oxidation catalyst, whereby the H_2S in the gas is oxidized to sulfur above the sulfur melting point of 120°C, as described, for instance, in European patent application 242,920 and in German patent application 39 03 294, has the drawback that the gas that leaves the gas purification, after condensation of the sulfur formed, still contains sulfur vapor, since, after condensation of the sulfur, the gas is still saturated with sulfur vapor. In the fuel gas line system, this sulfur vapor can give rise to serious obstruction. Another inevitable problem is that small amounts of SO_2 are formed as well when the oxidation catalyst is used. SO_2 and water vapor can, after condensation, give serious corrosion problems in the fuel gas system.

According to the invention, a process is proposed, in which the total sulfur recovery efficiency can be increased considerably, the efficiency loss being even negligibly small, for instance less than 0.1 %, so that, accordingly, no or substantially no sulfur components are discharged via the flue to the atmosphere anymore. Moreover, according to at least one of the variants of the present process, a considerable number of the operational problems enumerated can be solved. Finally, the process according to the invention is considerably cheaper than the processes known from the prior art.

Accordingly, the invention relates to a process for the treatment of synthesis gas or fuel gas obtained by coal gasification, residue gasification, waste gasification or oil gasification, in which the gas stream obtained by gasification, which contains reducing and possibly inert gases, is treated for the removal of sulfur, optionally after separation of the desired product synthesis or fuel gas, is subsequently hydrogenated, the sulfur compounds still present in the gas stream thereby being converted to hydrogen sulfide, the hydrogen sulfide is removed from the gas stream by adsorption or absorption on a solid or liquid adsorbent or absorbent and the loaded adsorption or absorption medium is supplied to the coal, residues, waste or oil to be gasified.

Suitable raw materials for gasification to form synthesis or fuel gas are the sulfur-containing raw materials conventional in the art, such as various types of coal (pit coal, brown coal and the like), oil (fuel oil and other, typically heavy petroleum fractions), waste (household waste, synthetic materials, waste treatment slurry and the like) and residues.

The synthesis or fuel gas is preferably obtained from the gasification of coal, fuel oil or residues of petroleum refinement.

It has also been found possible to add waste rubber from used car tyres to the gasification. The rubber is thus gasified in a clean manner, which provides a good solution to this waste problem.

The actual implementation of the gasification occurs in a manner known in the art in a gasification unit suitable for that purpose.

The process according to the invention can be practiced in a number of ways. According to a first variant, the gas stream originating from the gasification is split into a synthesis or fuel gas stream and a gas stream which contains the sulfur compounds. This last gas stream is subsequently purified in a known manner by oxidation of the oxidizable

sulfur compounds to elemental sulfur, which is subsequently separated by condensation. Residual gaseous sulfur and sulfur compounds are hydrogenated to H_2S. Then the sulfur compounds present, optionally after oxidation, are sorbed on a solid or liquid adsorbent or absorbent (hereinafter to be referred to as sorbent). The thus loaded sorbent is finally supplied to the feed of the gasification.

Splitting the gas stream coming the gasification into a synthesis or fuel gas stream and a gas stream that contains the sulfur compounds can occur in a conventional manner, for instance in one of the manners discussed in the introduction.

According to another embodiment of the invention, the total gas stream is subjected to a selective oxidation of the H_2S, this oxidation being carried out in such a manner that the greater part of the hydrogen sulfide present is oxidized to elemental sulfur, which is subsequently separated. Then the gas stream is treated in the manner described hereinabove: hydrogenation, sorption and supply of the loaded sorbent to the feed of the gasification.

The essence of the invention resides in the manner in which the last residues of H_2S are removed from the largely purified gas. Surprisingly, it has been found that through adsorption or absorption of these last residues of H_2S using a material which, after being loaded, is supplied to the feed of the gasification, no or substantially no residual H_2S remains in the synthesis gas, fuel gas, or spent gas. The sorbent is used a single time for the removal of very small amounts of sulfur from very large gas streams. This is in contrast with the known methods, where the complete purification of the gas stream is carried out with the solid substance, whilst according to the present invention only the last residues of sulfur are removed. Owing to the inventive, specific combination of features, the environmental objections and the economic disadvantages of the known methods are avoided.

The solid or liquid sorbent may consist of any substance that does not have an adverse influence on the gasification

process. In the literature, a number of substances, including carbon, are known, which are suitable as such for the adsorption or absorption of hydrogen sulfide (Advances in Petroleum Chemistry Refining Vol 6, Chapter 7, Interscience Publishers, 1962). Taking various process conditions into consideration, such as the occurrence of slag formation, which may or may not be desired, the choice of the most suitable medium is within reach of a skilled person. The sorbent may be solid or liquid.

Liquid sorbents could for instance be oils such as 'sponge oil' or exhausted oil, but also mineral oil, vegetable oil, or an alkaline reactive aqueous solution, such as a solution of sodium, potassium and/or calcium hydroxide, or lime milk.

As a solid sorbent, advantageous use may be made of iron oxide, copper oxide, calcium oxide and/or manganese oxide, active carbon, iron oxide-impregnated active carbon, pit coal which may or may not be activated, or brown coal. When using solid sorbents, the process can be carried out in such a manner that the H_2S obtained after the hydrogenation is oxidized with oxygen at a temperature of less than 120°C to form elemental sulfur, which is deposited on the sorbent, whereafter the loaded sorbent is supplied to the feed of the gasification. This can be done in particular when using active carbon which may or may not be impregnated with iron oxide, pit coal which may or may not be activated, or brown coal. The use of iron oxide, copper oxide, calcium oxide and/or manganese oxide, will rather involve a conversion of the sorbent into the corresponding sulfide, which is supplied to the feed of the gasification.

It is observed that in European patent application 91 551 a process is described, in which hydrogen sulfide-containing gases are subjected to a direct catalytic oxidation in a tube reactor. Hydrogen sulfide is thus oxidized to elemental sulfur, which is separated in a condensation stage. The reaction gas obtained after the catalytic oxidation and the

sulfur separation still contains 5-10% of non-removed sulfur compounds.

To accomplish a further reduction of the sulfur content in the reaction gas, it is proposed in that publication *inter alia* to subject the reaction gas obtained to a catalytic Claus reaction, whereby the total hydrogen sulfide conversion can be increased to 98%. It is also proposed to add hydrogen gas to the gas and subsequently, at increased temperature, to hydrogenate the sulfur compounds to form hydrogen sulfide, using a nickel and/or cobalt and molybdenum-containing catalyst. The hydrogen sulfide can subsequently be washed from the gas using a solvent. After regeneration, this hydrogen sulfide can be returned to the tube reactor.

In that publication it is also proposed to remove the hydrogen sulfide from the gas by contacting the gas with an oxygen-containing gas and ammonia and subsequently passing it over active carbon, yielding oxidation of hydrogen sulfide to elemental sulfur, which adsorbs to the active carbon. For a complete regeneration of the sulfur, a hot gas, such as carbon dioxide or nitrogen, is passed over the active carbon, while the sulfur present on the active carbon can further be extracted with, for instance, polyammonium sulfide lye. Accordingly, no mention is made of feeding the loaded sorbent to the feed to be gasified.

In a preferred embodiment of the present invention, the process is characterized in that the sorbent is the medium to be gasified, and in particular coal. Surprisingly, it has been found that when oxidative adsorption is utilized here, i.e., when the adsorption is carried out in an oxygen-containing medium, for instance by adding an amount of air to the gas to be adsorbed, approximately one to a maximum of approximately thirty percent of the total amount of coal to be gasified is needed.

The sorbent may, in addition to the medium to be gasified, advantageously contain active carbon, dolomite, lime, iron compounds and/or siderite.

The synthesis or fuel gas coming from the gasification will, in addition to CO, H_2 and H_2S, often contain COS, CS_2, CO_2, HCN and NH_3. Such a gas is highly reducing.

According to the first embodiment of the process according to the invention, the gas stream to be treated is split into a purified synthesis or fuel gas stream and a sulfur-containing gas stream.

This occurs by removing the sulfur that is present in the synthesis or fuel gas for the greater part using a known gas purification, for instance by chemical, physical, or chemicophysical gas purification, in combination with a sulfur recovery method. The sulfur compounds are thus oxidized as much as possible to elemental sulfur, which is subsequently condensed. The residual sulfur and sulfur compounds are catalytically hydrogenated and removed from the gas stream. This last occurs according to the invention by adsorption or absorption and supplying the thus obtained loaded sorbent to the feed of the gasification. If so desired, a part of the H_2S can be removed directly after the hydrogenation, using a known method, for instance a SCOT process.

According to a second embodiment of the process according to the invention, first the greater part of the sulfur compounds that are present in the synthesis or fuel gas are converted by selective oxidation to elemental sulfur, which is subsequently condensed. The residual sulfur and sulfur compounds are catalytically hydrogenated and removed from the gas stream. The last occurs according to the invention by adsorption or absorption and supplying the thus obtained loaded sorbent to the feed of the gasification. If so desired, a part of the H_2S can be removed directly after the hydrogenation, using a known method, for instance a SCOT process.

In the selective oxidation step, which is optionally carried out after separation of the synthesis or fuel gas, H_2S is converted over a suitable selective oxidation catalyst to form elemental sulfur according to the reaction

$$H_2S + {}^1/_2\ O_2 \rightarrow S + H_2O.$$

Preferably, the selective oxidation catalysts are used as described in European patent applications 242,920 and 242,006 and in European patent application 409,353, because these yield a conversion efficiency in excess of 80% geven. The contents of these patent applications is incorporated herein by reference. It is surprising that the conversion percentages attained are achieved with these catalysts during oxidation in the presence of highly reducing gases as in the present case.

The catalyst according to European patent applications 242,920 and 242,006 contains a support, of which the surface that can come into contact with the gaseous phase exhibits no alkaline properties under the reaction conditions, whilst on this surface a catalytically active material has been provided. Further, the specific surface area of this catalyst is less than 20 m^2/g, and less than 10% of the total pore volume in this catalyst has a pore radius of between 5 and 500 Å.

The catalyst according to European patent application 409,353 has a specific surface area of more than 20 m^2/g and an average pore radius of at least 25 Å, whilst this catalyst exhibits substantially no activity for the Claus reaction under the reaction conditions.

The process according to the invention, however, can also be carried out using other oxidation catalysts, such as for instance the Rhône Poulenc CRS-31-catalyst, a TiO_2 catalyst described in European patent applications 38741 and 60741; the so-called Selectox catalyst, described in U.S. Patent Nos. 4,123,507, 4,243,647 and 4,311,683; the catalyst described in U.S. Patent No. 4,197,277; the catalyst described in U.S. Patent No. 4,519,992; the catalyst described in European patent application 91,551; and the catalyst described in European patent application 84200720.5.

These catalysts, however, have a lower conversion efficiency because they are sensitive to water, so that,

depending on the water concentration in the gas, the reverse Claus reaction occurs, viz.,

$$\frac{3}{n}S_n + 2\ H_2O \rightarrow SO_2 + 2\ H_2S.$$

The SO_2 thus formed will, upon hydrogenation, use more H_2, which is economically unattractive. Moreover, in the last step much more hydrogen sulfide must be removed, so that the required amount of sorbent increases and thus the process becomes more expensive.

The selective oxidation reaction occurs best in the temperature range of between 180°C and 300°C with a minor excess of air oxygen. The molar ratio oxygen/hydrogen sulfide is preferably set between 0.5 and 2.0, and in particular between 0.5 and 1.0. It is practically inevitable that through side-reactions a small amount of SO_2 is formed, for instance by gaseous phase oxidation of sulfur vapor. Important is that the temperature in the selective oxidation bed is maintained above the dew point of sulfur so as to prevent the sulfur formed from condensing in the catalyst bed.

The selective oxidation of hydrogen sulfide occurs with the aid of a catalyst suitable for that purpose. In this selective oxidation, the greater part of the hydrogen sulfide, preferably more than 50%, which is present in the gas stream, is converted and recovered as elemental sulfur. Subsequently all sulfur compounds and oxygen residues formed by side-reactions in the extraction are converted to hydrogen sulfide and water through hydrogenation.

Preferably, the selective oxidation of hydrogen sulfide is carried out with a slight stoichiometric excess of oxygen with regard to the hydrogen sulfide.

The gas mixture from the selective oxidation reactor is cooled to 125-160°C, the sulfur thereby being condensed. After condensation of the sulfur, the gas mixture consists of sulfur components in the form of H_2S, SO_2, sulfur vapor and sulfur mist and a small amount of oxygen.

In the process according to the invention, these sulfur components are converted using a catalyst with hydrogenating properties. SO_2 and elemental sulfur in the form of vapor and of entrained small drops of mist are converted with hydrogen to form hydrogen sulfide, and oxygen is converted with hydrogen to water according to the reactions

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O + \text{heat}$$

$$S_8 + 8H_2 \rightarrow 8H_2S$$

$$1/2\ O_2 + H_2 \rightarrow H_2O + \text{heat}$$

In the embodiment of the process according to the invention where the sulfur compounds are not primarily separated, the hydrogen needed is already present in the gas mixture. In the other embodiment of the process according to the invention, where the sulfur compounds are already separated from the synthesis or fuel gas at the outset, preferably a small amount of the purified synthesis or fuel gas is supplied to the feed of the catalytic hydrogenation reactor.

In carrying out this hydrogenation, the gas stream is heated from the condensation temperature of 125-160°C to a temperature level of approx. 200°C of higher, depending on the properties of the hydrogenation catalyst chosen. Preferably, the gas stream is heated to 250-300°C. Catalysts which have the desired hydrogenating properties and moreover are sulfur-resistant, are known to the skilled worker and are typically catalysts having aluminium oxide as a support, which contain Co-Mo, as described in Catal. Rev.-Sci.Eng. 21, (2), 275-318 (1980).

When the gas stream contains CO_2 in addition to H_2S, the CO_2 will not interfere with the selective oxidation, hydrogenation and absorption or adsorption.

When the gas stream also contains COS and/or CS_2, it is preferred to hydrolyze COS and/or CS_2 in or after the hydrogenation reactor, because the gas stream is already at the desired temperature level there and the H_2S concentration is lowest there.

When the gas stream contains HCN and NH_3, the gas is preferably washed or HCN and NH_3 are reacted to remove these components completely. Removal through washing of the gas or conversion will preferably occur before the selective oxidation step.

If the gas stream contains much CO, the water content will have to be regulated so as to control the reaction

$$CO + H_2O \rightarrow CO_2 + H_2 + \text{heat}$$

in the hydrogenation step. This process is described in European patent application 324.526, the contents of which are incorporated herein by reference.

It may also be desirable to completely convert the CO present in the gas, which is preferably done using a CO shift reaction in which CO reacts with water to form H_2 and CO_2. For such a shift reaction, preferably a cobalt-molybdenum on alumina catalyst is used. In practice, this will typically occur in at least two reactors with intermittent heat removal.

In the process according to the invention, such a complete conversion of CO will for instance be practiced if a synthesis gas is to be obtained having a highest possible H_2 content, which is very convenient for H_2 of NH_3 production. It may also be desirable to keep the CO content as low as possible so as to avoid COS formation in the selective oxidation.

In the process according to the invention, the gas stream is subsequently purified of the residual H_2S by adsorbing or absorbing it preferably to the pit coal to be gasified or to the oil residues and subsequently supplying it to the gasification in adsorbed or absorbed form.

When the gas stream to be purified is the synthesis or fuel gas and has an increased pressure, for instance 20 bar, the solid or liquid sorbent must also be adjusted to that pressure. Systems for pressurized supply of solid substances are known. In coal gasification so-called lockhoppers are used. These are parallel lock vessels which operate discontinuously; when one vessel is unloaded, the other is

filled. The solid substance is fed into the lock vessel at atmospheric pressure, whereafter the vessel is closed. Subsequently, the vessel is adjusted to a pressure of at least 20 bar with a suitable gas, for instance nitrogen. Subsequently, the contents are introduced via a metering device, for instance a cell wheel lock, into a line for pneumatic transport, or directly into the adsorber or absorber. The pneumatic transport can be effected with an inert gas, such as nitrogen, but also with the synthesis or fuel gas to be gasified.

In the absorber, an intensive contact between the gas to be purified and the sorbent is effected. Optionally, and preferably, air is added to the gas so as to promote oxidative adsorption.

In general, the duration of contact between the gas to be purified and the sorbent is not critical, although, depending on the type of sorbent and the nature and the amount of hydrogen sulfide to be removed from the gas, in principle for each sorbent an optimum contact time is given. This can be determined experimentally in a simple manner. Depending on the type of sorbent, in each case a different, but maximum load will apply, so that it loses its activity after a certain residence time. It is therefore preferred to pass the sorbent through the adsorber in such a manner that the spread in residence time is limited.

The contact of the gas with the sorbent can occur in co-current, countercurrent, cross-current flow or a combination of these flow patterns. Cross-current flow has been found to be most suitable for the activation of the sorbent with hydrogen sulfide-containing gas, because this ensures a relatively long contact between the sorbent and the gas with the highest hydrogen sulfide-concentration. In this case, the absorber or adsorber comprises an activation section and an absorption or adsorption section. In the activation section, the unactivated sorbent is contacted with the unpurified gas, whereafter, in the absorption or adsorption

section, the gas that flows from the activation section is purified in countercurrent flow with activated sorbent to the desired level. It is also possible to design the absorber or adsorber as a cascade of contact devices, so as to limit the spread of residence of the solids and to realize the desired contact pattern of gas and solids.

In the process according to the invention, the choice of a suitable contact device is not critical. The optimal choice will be determined depending *inter alia* on the size of the sorbent particles.

When the sorbent consists of a fine powder, for instance pulverized coal such as is supplied to the gasifier, the use of a fluidized or circulating bed is most suitable. These beds are known per se, for instance in catalytic cracking and whirling bed combustion. On account of the spread in particle size, a part of the solids may be entrained with the gas stream. A gas-solids separator passes the solids back to the bed. For that purpose, in principle, cyclones, which may or may not be combined with a filter, have been found suitable. To keep the adsorber compact and yet to create a large area, this in connection with limitations with regard to the gas velocity, the use of a tray column has been found to be suitable. Thus, at the same time a stepped flow of the sorbent is obtained.

When the sorbent is coarser in structure, a packed bed can be conveniently used. Preferably, this bed is refreshed continuously (moving bed), for instance by using a transport lock in the bottom. Such a principle is known in a so-called shelf furnace. A packed bed with coarse sorbent has an advantage over the fluidized bed in that the gas velocity calculated on the diameter of the adsorber or absorber may be greater without the solids being blown away or too large a pressure drop arising.

For the separation of entrained sorbent from the purified gas stream, the use of a cyclone, optionally together with cloth, ceramic or electrostatic filters has been found

suitable. A cyclone with a ceramic candle filter behind it is known per se.

After the sorbent has been loaded, it is passed to the gasifier. A suitable method for this purpose is to introduce the loaded sorbent, for instance using a cell wheel lock, into a pneumatic transport system and subsequently to pass it directly into the gasifier. When a coarse sorbent is used, it is preferred to grind it first. In the case of coal gasification, it can then be mixed with the coals in the transport section to the lockhoppers which supply the gasifier.

To obtain a good hydrogen sulfide-adsorption to pit coal, some types of pit coal must undergo a thermal pretreatment.

It is also possible to use liquid sorbents. Well known is 'sponge oil', whereby H_2S is absorbed from the gas stream to be purified by absorption into the oil. Exhausted oil can be used for this purpose too.

The oil can be contacted with the oil in co-current or countercurrent flow in a column provided with gas/liquid contact trays or a with a packing material. For obtaining a more complete absorption, optionally air, and/or a solid sorbent such as active carbon, pulverized coal or brown coal can be added to the oil.

In addition to pit coal and/or oil residues, other sorbents can be used, such as active carbon, dolomite or lime (CaO), iron oxide, iron ore, siderite and the like. If H_2S is absorbed to dolomite or iron oxide, respectively CaS and FeS are formed. Upon return to the gasification plant, during combustion, H_2S, COS and CS_2 are formed again, which, in the process according to the invention, are converted again to elemental sulfur. Because the amount of the sorbent is relatively small, this does not have any influence on the quality or any slag formed.

The use of coal, oil, waste and residue gasification is economically eligible over a directly fired plant if the emission is lower and the efficiency is higher.

The process according to the invention will make a contribution to this, because the addition of sulfur-loaded sorbent to the medium to be gasified yields a total sulfur recovery efficiency of more than 99.9%.

Figuur 1 gives a schematic overview of a process according to the invention.

An amount of pit coal or oil residue to be gasified is passed through line 1 to the gasification plant 2. The synthesis or fuel gas produced is passed via line 3 to the selective oxidation reactor 5. The slag formed is removed from the gasification plant via line 4.

The gas is brought to the desired temperature in the line 3. The amount of oxygen or air needed for the oxidation is supplied via line 6. The elemental sulfur produced in reactor 5 is removed, after condensation, via line 7.

In line 8, the gas is brought to the desired hydrogenation temperature before being passed into the hydrogenation reactor 9. All SO_2, residual O_2, and sulfur vapor and drops of sulfur mist are converted to H_2S and H_2O. The gas from the hydrogenation reactor 9 is passed, after cooling, via line 10 to an absorber or adsorber 11.

The H_2S still present in the main stream 10 is absorbed or adsorbed in the adsorber or absorber 11.

The loaded sorbent is returned to the gasification plant 2 via line 12. The desulfurized synthesis or fuel gas leaves the plant via line 13.

Depending on the use of the synthesis gas produced, it may be desirable to convert all CO with water in a shift reactor reaction to form CO_2 and H_2. Such a CO shift is preferably arranged between the gasification plant 2 and the selective oxidation 5. Water is supplied to line 3.

Figure 2 gives a schematic view of another process according to the invention.

An amount of pit coal or oil residue to be gasified is passed via line 1 to the gasification plant 2. The synthesis gas or fuel gas produced is passed via line 3 to a gas

purification 14. The slag formed is removed from the gasification plant via line 4. The desulfurized synthesis or fuel gas leaves the plant via line 13.

The sulfur-containing inert gas stream is passed via line 15 to the Claus plant 16, in which the greater part of the sulfur compounds is converted to elemental sulfur, which is removed via line 17. Via line 18, the gas is supplied to a selective oxidation reactor 5.

The gas is brought to the desired temperature in line 18. The amount of oxygen or air needed for the oxidation is supplied via line 6. The elemental sulfur produced in reactor 5 is removed, after condensation, via line 7.

In line 8, the gas is brought to the desired hydrogenation temperature before being passed into the hydrogenation reactor 9. All SO_2, residual O_2, and sulfur vapor and drops of sulfur mist are converted to H_2S and H_2O. The gas from the hydrogenation reactor 9 is passed, after cooling, via line 10 to an absorber or adsorber 11.

The H_2S still present in the main stream 10 is absorbed or adsorbed in the adsorber or absorber 11.

The loaded sorbent is supplied to the gasification plant 2 via line 12. The desulfurized synthesis or fuel gas leaves the plant via line 19.

The invention will be further explained in and by the following Examples.

Example 1

In a coal gasification plant, 2940 t/d Drayton coal with 2.30% sulfur, corresponding to 68.6 t/d sulfur, was mixed with 60 t/d active carbon impregnated with iron oxide, originating from a sulfur adsorption step with a total of 17.1 t/d sulfur. This total amount of 3000 t/d coal with 85.7 t/d sulfur was fed to the gasifier together with 3000 t/d oxygen and 400 t/d steam.

The coal was ground to powdered coal and gasified at a temperature of 1500°C and an absolute pressure of 25 bar. The coal gas was cooled to 250°C by cooling with recirculation gas and a synthesis or fuel gas cooler, whereafter the gas was purified of dust by means of dry gas filters and a wet dust collector. Thus an acid slurry was formed, which was passed to a stripper. In the wet dust collector, the gas cooled further to 120°C. Subsequently, the gas was heated to 180°C and passed over a reactor filled with a titanium oxide catalyst for conversion of HCN to NH_3 and CO_2.

Subsequently, an amount of water was supplied to the gas to allow the CO shift reaction to occur. For this shift reaction, the gas was heated to 230°C and subsequently passed through two reactors, each filled with a supported cobalt-molybdenum catalyst. The reaction heat developed was removed while forming steam and through heat exchange with other gas streams in the process. In total, 2860 t/d water was used for the shift reaction. The COS present in the gas was simultaneously hydrolyzed.

Then the gas was cooled to 40°C. The water vapor thereby condensing was removed to an acid water stripper. The thus obtained amount of gas of 8590 t/d (400,000 Nm^3/h) had the following composition at a temperature of 40°C and an absolute pressure of 23 bar.

0.63 vol.% H_2S	1.15 vol.% CH_4
41.8 vol.% CO_2	0.02 vol.% COS
55.7 vol.% H_2	traces of CS_2
0.30 vol.% CO	0.4 vol.% H_2O

Subsequently, the gas was heated to 200°C with the aid of a heat exchanger. 1500 Nm^3/h oxygen was supplied to the gas mixture. The molar oxygen/H_2S ratio was set at 0.6. Then the gas mixture was passed through a selective oxidation reactor which contained a catalyst based on iron oxide, provided on silicon dioxide.

More than 80% of the H_2S present in the gas was converted to elemental sulfur. The outlet temperature of the selective oxidation reactor was 240°C. The gas was subsequently passed to the sulfur condensor, where 68.6 t/d sulfur was condensed at a temperature of 130°C. The gas was then heated to 285°C to convert all sulfur components and residual O_2 to H_2S and H_2O in a hydrogenation reactor containing a Co-Mo on alumina catalyst, using the H_2 present in the gas. The outlet temperature of the hydrogenation reactor was 325°C. Subsequently, the gas was cooled to 50°C.

To the gas mixture 350 Nm^3/h oxygen was added, resulting in a molar oxygen/H_2S ratio of 0.7. Then this total gas mixture was contacted in an adsorber with 2500 kg/h (60 t/d) active carbon which had been impregnated with iron oxide. The 0.13 vol.% H_2S still present in the gas was oxidized to sulfur and adsorbed to the carbon.

A load of 30 wt.% sulfur on the active carbon was achieved. Then the carbon loaded with 17.1 t/d sulfur was ground and mixed with the 2940 t/d powdered coal which was used as feed of the coal gasification plant.

The product gas contained 2 ppm volume H_2S, so that the desulfurization efficiency was 99.97%.

Example 2

In a refinery, an amount of 150 t/d fuel oil (Bunker C quality) containing 1.3 t/d sulfur was gasified in an oil gasification plant with 177 t/d O_2 and 69.1 t/d steam. In an intensive mixer, the fuel oil was mixed with 3 t/d carbon black from a carbon black separator and 9 t/d brown coal loaded with 0.54 t/d sulfur. Carbon black and brown coal were ground fine and added to the fuel oil in dispersed form.

This mixture was passed to the burner of the gasifier and atomized. At 1550°C and an absolute pressure of 20 bar, this mixture was gasified.

In a waste heat boiler, the gas was cooled to 300°C, generating 455 t/d high-pressure steam of an absolute pressure of 40 bar.

The partially cooled gas was passed through a carbon black separator, where the carbon black formed in the gasifier was separated with water. The product gas was subsequently washed in a water washer to remove the last traces of carbon black.

The carbon black slurry was treated with naphtha, with water and carbon black separating. The carbon black was, as specified, mixed with the fuel oil.

Subsequently, an amount of water was supplied to the gas to allow the CO shift reaction to occur. For this shift reaction, the gas was heated to 250°C and subsequently passed through two reactors, each filled with a supported cobalt-molybdenum catalyst. The reaction heat developed was removed while forming steam and through heat exchange with other gas streams in the process. In total, 185 t/d water was used for the shift reaction.

Then the gas was cooled to 40°C. The water vapor thereby condensing was removed to an acid water stripper. The amount of synthesis gas was 710,000 Nm^3/d and had the following composition at an absolute pressure of 17 bar and 40°C:

0.18 vol.% H_2S	0.13 vol.% CH_4
0.2 vol.% CO	0.48 vol.% N_2
63.3 vol.% H_2	0.45 vol.% H_2O
35.26 vol.% CO_2	

This gas was heated to 240°C using a gas-fired indirect heater. To the gas, 760 Nm^3/d (1.08 t/d) O_2 was supplied, which resulted in a molar oxygen/H_2S ratio of 0.6.

The gas mixture was passed to a selective oxidation reactor, which contained a titanium-containing catalyst. More than 70% of the H_2S present in the gas was converted to elemental sulfur. The outlet temperature of the reactor was

265°C. The gas was then passed to a sulfur condensor where 1.3 t/d sulfur was condensed at a temperature of 135°c.

The gas was then heated to 285°C to convert all sulfur components to H_2S and H_2O in a hydrogenation reactor, using the H_2 present in the gas. The hydrogenation reactor contained a Co-Mo catalyst whose support material was alumina.

Subsequently, the gas was cooled to 50°C. To the gas mixture 260 Nm^3/d (0.37 t/d) oxygen was added (molar oxygen/H_2S ratio 0.7).

In an adsorber this gas mixture was contacted with 9 t/d brown coal. The 0.05 vol.% H_2S still present in the gas was oxidized to sulfur and adsorbed to the coal.

A load of 6 wt.% was achieved. Then the brown coal loaded with 0.54 t/d sulfur was ground and mixed with the fuel oil.

The product gas contained 1 ppm volume H_2S, so that the desulfurization efficiency was 99.94%.

Example 3

In a coal gasification plant 2000 t/d pit coal with 1% sulfur was gasified.

The amount of fuel gas which was available after cooling by means of steam generation, after dust removal and after hydrolysis of HCN and COS was 160,000 Nm^3/h. The gas had an absolute pressure of 25 bar, a temperature of 40°C and had the following composition:

0.4 vol.% H_2S	0.2 vol.% CH_4
2.5 vol.% CO_2	0.01 vol.% COS
31 vol.% H_2	3.59 vol.% N_2 + Ar
62 vol.% CO	0.3 vol.% H_2O

This gas was subsequently contacted in an absorber of a gas purification plant with a monodiethanolamine solution, the H_2S and a part of the CO_2 being absorbed.

The product gas contained 4 ppm H_2S. After desorption in a regenerator, the acid H_2S/CO_2 gas mixture was passed to a sulfur recovery plant.

The sulfur recovery plant consisted of a thermal stage, two Claus reactor stages and a selective oxidation reactor stage.

The amount of acid gas was 2410 Nm^3/h and had the following composition at 40°C and an absolute pressure of 1.8 bar

26.6 vol.% H_2S
66.4 vol.% CO_2
1.0 vol.% H_2
1.8 vol.% CO
4.2 vol.% H_2O

To the burner of the thermal stage, 321 Nm^3/h oxygen was supplied, so that after the second Claus reactor stage 1.1 vol.% H_2S and 0.05 vol.% SO_2 was present in the process gas. To this gas, 95 Nm^3/h of air was supplied.

The molar oxygen/H_2S ratio was set at 0.8. The inlet temperature of the selective oxidation reactor was 210°C and the outlet temperature was 270°C. The selective oxidation reactor was filled with an iron/chromium catalyst on α-alumina.

The sulfur formed in the sulfur recovery plant was condensed after each stage and removed. The amount was 935 kg/h. To the remaining inert gas, whose composition was as follows:

0.01 vol.% H_2S
0.15 vol.% SO_2
0.22 vol.% COS/CS_2
0.05 vol.% S
1.3 vol.% CO
60.9 vol.% CO_2

0.11 vol.% O_2
0.46 vol.% H_2
6.3 vol.% N_2
30.5 vol.% H_2O

185 Nm^3/h purified fuel gas was added, needed for the next step, the hydrogenation of all remaining sulfur components and oxygen to form H_2S and water. The inert gas was then heated to 285°C and passed to the hydrogenation reactor which contained a Co-Mo catalyst.

The temperature of the egressing gas was 325°C. At this temperature, the inert gas was subsequently passed directly over an absorber containing dehydrated bog ore. The residual 0.8 vol.% H_2S was absorbed in the form of iron sulfide. The egressing inert gas contained less than 100 ppm volume H_2S. Via an after-burning stage, the inert gas was passed to the flue.

The iron oxide was loaded with sulfur to 8%. The amount of iron oxide needed was 425 kg/h.

The sorbent loaded with sulfur was ground and mixed with the pit coal and, together, introduced into the gasifier.

In the gasifier the iron sulfide decomposed completely. The iron oxide added finally left the gasifier with the slag. The total desulfurization was 99.86%.

Example 4

In a residue gasification, 100 t/d residue was gasified, containing 4.83 t/d sulfur together with 1.7 t/d active carbon which had been loaded with 0.084 t/d sulfur, and 2 t/d carbon black originating from a carbon black separator.

The synthesis gas obtained in the gasification had an absolute pressure of 15 bar and a temperature of 35°C. The amount was 260,000 Nm^3/d and had the following composition:

1.3 vol.% H_2S 0.3 vol.% CH_4

51.0 vol.% CO
41.0 vol.% H_2
5.5 vol.% CO_2
0.4 vol.% N_2
0.1 vol.% COS
0.4 vol.% H_2O

This gas was contacted in a gas purification plant with a physical solvent, the H_2S, the COS being absorbed completely and the CO_2 being absorbed partially. The purified gas contained 10 ppm (vol) H_2S.

The absorbed H_2S, COS and CO_2 gas were passed, after desorption, to a sulfur recovery plant (as described in Example 3) where H_2S and COS were converted to elemental sulfur.

To the inert gas of this plant, the amount of which was 13,965 Nm^3/d of the following composition:

0.01 vol.% H_2S
0.15 vol.% SO_2
0.21 vol.% COS/CS_2
0.05 vol.% S
1.2 vol.% CO
61.28 vol.% CO_2
0.1 vol.% O_2
0.4 vol.% H_2
6.6 vol.% N_2
30.0 vol.% H_2O

610 Nm^3/d purified synthesis gas was added for hydrogenation of sulfur components and oxygen to form H_2S and water. The inert gas was then heated to 290°C and passed over a hydrogenation reactor containing a Co-Mo catalyst.

The temperature of the egressing gas was 320°C. The inert gas was then cooled to 40°C, with condensation of 2.8 t/d water, which was removed from the system.

To the inert gas, 210 Nm^3/d air was supplied. This gas mixture containing 0.53 vol.% H_2S was contacted with 1.7 t/d active carbon in an absorber. The H_2S was converted by the

oxygen to 0.084 t/d elemental sulfur, which deposited on the active carbon.

The active carbon loaded with sulfur was added to the feed of the gasifier.

The egressing amount of inert gas was 11190 Nm^3/d and contained 3 ppm H_2S and was subsequently passed to a flue. The total desulfurization efficiency was 99.92 %.

CLAIMS

1. A process for the treatment of synthesis gas or fuel gas obtained by coal gasification, residue gasification, waste gasification or oil gasification, in which the gas stream obtained by gasification, which contains reducing and possibly inert gases, is treated for the removal of sulfur, optionally after separation of the desired product synthesis gas or fuel gas, is subsequently hydrogenated, the sulfur compounds still present in the gas stream thereby being converted to hydrogen sulfide, the hydrogen sulfide is removed from the gas stream by adsorption or absorption on a solid or liquid sorbent and the loaded sorbent is supplied to the coal, residues, waste or oil to be gasified.

2. A process as claimed in claim 1, characterized in that the sorbent consists in part or in whole of the medium to be gasified.

3. A process as claimed in claim 1 of 2, wherein, as sorbent, active carbon, which may or may not have been impregnated with iron oxide, pit coal which may or may not be activated, or brown coal is used.

4. A process as claimed in claims 1-3, wherein the H_2S obtained after the hydrogenation is oxidized with oxygen at a temperature of less than 120°C to form elemental sulfur, which is deposited on the sorbent.

5. A process as claimed in claim 1, wherein as sorbent a petroleum fraction, such as residue, is used.

6. A process as claimed in claim 1, wherein, as sorbent, use is made of iron oxide, copper oxide, calcium oxide and/or manganese oxide.

7. A process as claimed in claim 1, wherein a liquid sorbent is used, selected from the group consisting of mineral oil, vegetable oil and an alkaline reactive aqueous solution, such as a solution of sodium hydroxide, potassium hydroxide and/or calcium hydroxide, or lime milk.

8. A process as claimed in claims 1-7, wherein said treatment for the removal of sulfur at least comprises a selective oxidation, which is carried out in such a manner that the greater part of the hydrogen sulfide present is oxidized to elemental sulfur, which is separated.

9. A process as claimed in claims 1-7, wherein the sulfur compounds are separated from the synthesis gas, whereafter these sulfur compounds are converted to elemental sulfur in a conventional manner.

10. A process as claimed in claim 9, wherein the majority of the sulfur compounds are first converted to elemental sulfur in a Claus plant and subsequently the remaining sulfur compounds are subjected to a selective oxidation to elemental sulfur.

11. A process as claimed in claim 8 or 10, characterized in that the selective oxidation of the hydrogen sulfide is carried out using a catalyst as described in European patent application 242,920, 242,006 and/or 409,353.

12. A process as claimed in claims 8-11, characterized in that the selective oxidation of hydrogen sulfide is carried out using a small stoichiometric excess of oxygen relative to the hydrogen sulfide.

13. A process as claimed in claims 1-12, characterized in that when appreciable amounts of HCN and/or NH_3 are present in the synthesis gas, these are washed out and/or converted prior to the selective oxidation.

14. A process as claimed in claims 1-13, characterized in that when appreciable amounts of COS and/or CO_2 are present in the synthesis gas, these are hydrolyzed prior to and/or subsequent to the hydrogenation.

15. A process as claimed in claims 4-14, characterized in that CO is converted with water to H_2 and CO_2 prior to the selective oxidation.

16. Synthesis gas or fuel gas obtained utilizing the process according to one or more of claims 1-15.

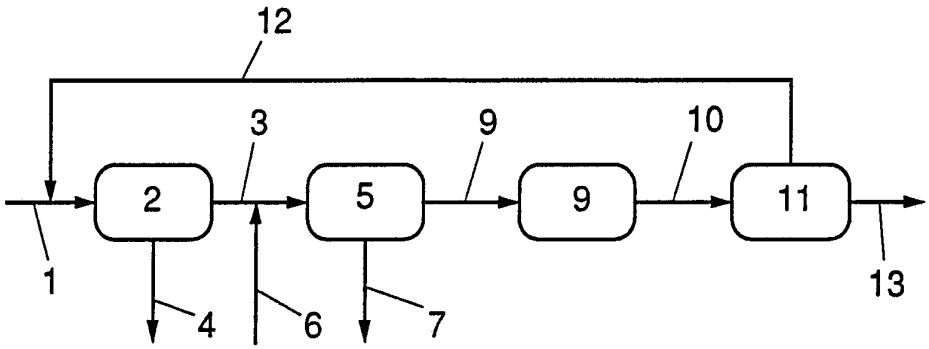


FIG. 1

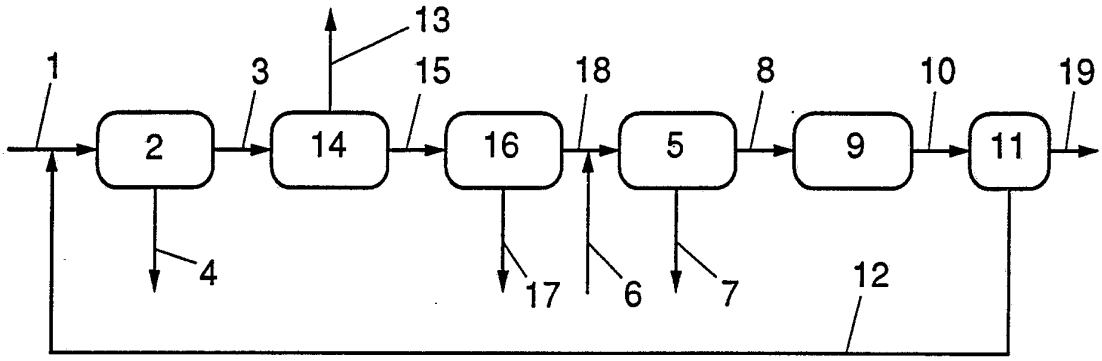


FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 92/00240

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C10K1/34; B01D53/36

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C10K ; B01D ; C01B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	US,A,4 085 199 (ALAN H. SINGLETON ET AL,) 18 April 1978 see column 15 - column 16; claim 1; figure 2	1
A	FR,A,2 300 126 (HOLTER HEINZ) 3 September 1976 see page 13; claims 1-3	1
A	US,A,4 206 186 (HEINZ HÖLTER) 3 June 1980 see page 9; claim 7	1
A	BE,A,562 928 (RIENLUFT G.M.B.H.) 31 December 1957 see page 8 - page 10; claims 1,2	1

° Special categories of cited documents :[10]

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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"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

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
01 MARCH 1993	15. 03. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	PYFFEROEN K.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

NL 9200240
SA 69208

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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		SE-A- 7711608	22-04-78
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