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⑤④ **Desulphurisation.**

⑤⑦ The absorption capacity of a desulphurising absorbent bed is increased by temporarily increasing the temperature of the absorbent bed by at least 50°C from the normal operating temperature to a maximum temperature not in excess of 500°C.

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Desulphurisation

This invention relates to desulphurisation of feedstocks such as natural gas, or gases derived therefrom, and liquids or gases derived from oil or solid hydrocarbonaceous materials such as coal. Liquid feedstocks include LPG, naphthas, and kerosene.

Desulphurisation of such feedstocks can be effected by passing the gas through a suitable absorbent which is commonly zinc oxide and/or copper oxide and is typically in the form of granules or pellets.

When a feedstock containing absorbable sulphur compounds such as hydrogen sulphide is passed through a bed absorbent, break-through of the sulphur compounds into the effluent occurs long before the bed has reached its theoretical absorption capacity, i.e. where all of the absorbent in the bed is fully saturated, because, while the absorbent near to the bed inlet may become fully, or nearly fully, saturated with the sulphur compounds, break-through occurs well before the absorbent at the bed outlet becomes saturated.

This early break-through is particularly noticeable where the absorption temperature is low. Recently absorbents having a high surface area, typically above 20, and particularly in the range 50 to 200, m^2g^{-1} have become available and are of particular use for low temperature desulphurisation, e.g. at temperatures between -10°C and 200°C . Even so premature break-through is a problem.

We have found that the absorption capacity of a bed of a desulphurisation absorbent can usefully be increased by a temporary increase in bed temperature.

Accordingly the present invention provides a method of desulphurising a liquid or gaseous feedstock wherein the feedstock is passed through a bed of a desulphurising absorbent characterised by temporarily increasing the temperature of the absorbent bed from the normal operating temperature by at least 50°C to a temperature not in an excess of 500°C , preferably not in an excess of 400°C .

The increase in temperature is preferably to a temperature in the range 150 to 350°C and is preferably for a period of at least 1 hour. While benefits are obtained by the use of extended periods, e.g. 1 or more days, at the increased
5 temperature, at increased temperatures above about 280°C, the higher the temperature, the shorter should be the time at that temperature, in order to avoid undue loss of surface area of the absorbent. For the aforesaid high surface area absorbents the maximum temperature is preferably below 300°C.

10 The maximum normal operating temperature, at which there is a noticeable benefit by temporary increase of the temperature, is about 300°C: with the aforesaid high surface area absorbents the normal operating temperature is preferably below 250°C and is preferably in the range 0 to 150°C.

15 The absorbent bed may be subjected to the temperature increase while on-line if the resultant increase in temperature of the desulphurised product is acceptable: however such a process also involves heating of the feedstock during at least part of the period of the increased temperature and economic considerations
20 may render this an unacceptable mode of operation. Alternatively, and preferably, the absorbent bed is heated while the bed is off-line. Thus in a continuous process, two or more absorbent beds may be provided and while one or more beds remain on absorption duty one or more other beds are subjected to the temperature
25 increase. Because of the heat capacity of the bed, in many cases it is not necessary to pass a fluid through the bed throughout the period for which the bed is to be subjected to an increased temperature: thus the bed may be heated via an external jacket, or by passing hot gas or liquid through the bed, until the desired
30 maximum temperature has been achieved for a sufficient period and then the bed left static to cool down to the normal operating temperature.

In one particular form of the invention desulphurisation follows treatment of the feedstock with a molecular sieve to
35 adsorb other impurities e.g. moisture. In such a case the

molecular sieve adsorbent and the desulphurisation absorbent may be in the same vessel. Where regeneration of the molecular sieve adsorbent is effected by heating, the temporary heating of the desulphurisation absorbent may be effected at the same time as
5 regeneration of the molecular sieve adsorbent. In a preferred form of the invention wherein a molecular sieve and an absorbent bed are employed in series, the regeneration of the molecular sieve and the temporary increase in temperature of the absorbent bed are effected by passage of a heated gas stream containing a
10 combustible gas through the absorbent bed and through the molecular sieve. After leaving the absorbent bed and molecular sieve, the gas stream is combusted and the combustion products thereof are passed through a heat exchanger wherein heat is transferred to the gas stream employed for the regeneration
15 step.

The time interval before the temporary heating of the desulphurisation absorbent becomes necessary will depend on the rate at which the absorbent becomes saturated, i.e. upon the absorbable sulphur compound content of the feedstock and the space
20 velocity at which the feedstock is fed through the bed. Where the rate of sulphur pick up is very low, e.g. where the absorbable sulphur compounds content of the feedstock, and the space velocity, are low, little benefit may be obtained by the present invention. However such conditions are not normally encountered
25 in commercial operations. The heating step should normally be effected before the sulphur break-through becomes significant.

The number of heating steps that can be employed before the bed needs recharging will depend on how saturated the bed is before each heating step and the severity, i.e. duration and
30 temperature of the heat treatment. After a number of heat treatments, which may be as few as one, economic considerations may indicate that recharging is preferable to a further temporary temperature increase.

The sulphur compounds initially present usually include
35 one or more of the following: H_2S , COS , and possibly CS_2 , CH_3SH

and others such as diethyl sulphide or tetramethylene sulphide. The total initial concentration thereof is typically in the range 1 - 1000 ppm V/v calculated as sulphur-equivalent H_2S . The outlet The outlet sulphur compounds concentration is typically under 1
5 ppm, for example under 0.5 ppm, but this is a matter of design depending on the product user's requirement.

The absorbent material preferably comprises at least 60, especially at least 80, % W/w of ZnO , calculated on its constituents non-volatile at 900°C . As used in the process, the zinc
10 oxide may be, at least initially, wholly or partly hydrated or in the form of a salt of a weak acid. Typically the surface area of the solid material is at least 20, preferably in the range 50 to 200, m^2g^{-1} ; and its pore volume is typically at least 0.2. A preferred solid material for the process is characterised further
15 by an H_2S -adsorption capacity of at least 20, especially 35 - 80%, of the theoretical, at temperatures up to 120°C , as determined in a standard test in which a mixture of H_2S (2000 ppm V/v), CO_2 (4% V/v) and methane (balance) is passed over the solid material as 1 bar abs. pressure and a volume hourly space velocity of 1000.

20 The absorbent bed can be in the form of a fixed, lift-able or fluidised bed.

The invention is illustrated by the following example:

In this example the absorbent comprised a bed of 60 ml of granules (of 3-5 mm diameter) of zinc oxide of surface area of 79
25 m^2g^{-1} inside a tube of 25 mm internal diameter and a mixture of natural gas, to which 5% V/v of hydrogen sulphide had been added, was used as the feedstock.

The feedstock was passed through the bed at 20°C and at a space velocity of 700 hr^{-1} at atmospheric pressure. Break-
30 through of H_2S occurred 93 minutes after commencing the gas flow. Calculation showed that at this stage the average sulphur content of bed was 8.6% W/w . Analysis confirmed this figure.

The gas flow was then stopped and, while still under a static atmosphere of the gas, the bed was heated to 200°C for 6
35 hours and then allowed to cool to 20°C .

The gas flow was recommenced: break-through occurred 29 minutes later. The calculated average sulphur content of the bed was then 11.3% ^w/w.

5 The gas flow was stopped and residual gas flushed out with nitrogen. The bed was then heated to 200°C under a static nitrogen atmosphere for 16 hours and then allowed to cool to 20°C.

10 The gas flow was recommenced: break-through occurred 16 minutes later. The calculated average sulphur content of the bed was then 12.8%, while analysis gave a value of 12.3% ^w/w.

It is seen that the two heat treatments enabled the absorption capacity of the bed to be increased by nearly 50%.

1. A method of desulphurising a liquid or gaseous feedstock wherein the feedstock is passed through a bed of a desulphurising absorbant

characterised by temporarily increasing the temperature of the absorbent bed from the normal operating temperature by at least 50°C to a temperature not in an excess of 500°C.

2. A method according to claim 1 wherein the increase in temperature is to a temperature in the range 150 to 350°C for a period of at least one hour.

3. A method according to claim 1 or claim 2 wherein the absorbent comprises zinc oxide and/or copper oxide and has a surface area above 20 m².g⁻¹, the normal operating temperature is in the range -10 to +200°C, and the maximum temperature is below 300°C.

4. A method according to any one of claims 1 to 3 wherein the absorbent comprises zinc oxide and/or copper oxide and has a surface area above 20 m².g⁻¹ and the normal operating temperature is in the range 0 to 150°C.

5. A method according to any one of claims 1 to 4 wherein at least two absorbent beds are employed and, while at least one bed is on absorption duty, at least one other of the beds is subjected to the increase in temperature and then said at least one bed that has been subjected to the temperature increase is returned to absorption duty.

6. A method according to any one of claims 1 to 5 wherein the feedstock is also treated with a molecular sieve and regeneration of the molecular sieve is effected by heating, and the regeneration of the molecular sieve is effected at the same time as the temporary increase in temperature of the absorbent bed.

7. A method according to claim 6 wherein the molecular sieve and the absorbent bed are in the same vessel.