PATENT SPECIFICATION

Date of Application and Filing Complete Specification: Sept. 8, 1953.
Application made in Germany on Sept. 15, 1952.
Complete Specification Published: May 8, 1957.

774,283

No. 24789/53

Index at Acceptance:—Class 2(3), B1(A: G).

International Classification:—C07c.

COMPLETE SPECIFICATION

Process for the Combined Purification and Methanisation of Gas Mixtures containing Oxides of Carbon and Hydrogen.

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the purification and methanisation of gas mixtures containing oxides of carbon and hydrogen.

It is known that the calorific value and the properties of commercial or industrial gases which contain oxides of carbon (CO, CO_2) and hydrogen may be improved by catalytic methanisation. Carbon monoxide and/or carbon dioxide which are contained in the gas are thereby hydrogenated with hydrogen which is also present in the gas mixture, to form methane. If the hydrogen content in gases which are rich in carbon monoxide is not sufficient, the methanisation may be preceded by a shift reaction in which, with the addition of steam, a part of the carbon monoxide present is converted into carbon dioxide with the formation of hydrogen. After having washed out a more or less large quantity of carbon dioxide, methanisation is possible.

The methanisation is used for the production of high-grade fuel gas and for the detoxication of town gas. In this way, gases having a calorific value of, for example, between 6000 and 7000 heat units/cubic metre may be obtained. A further advantage consists in that methanised gases are extremely pure thus increasing considerably the reliability of service of the equipment and apparatus fed therewith.

Commercially, nickel-containing catalysts are mainly used as methanisation catalysts. Various compositions of catalyst and various processes for the preparation of the catalysts are known. However, as high as possible a purity of the gas to be methanised is required for constant activity and long lifetime of the catalyst. Substances which have a detrimental effect on the activity of the catalysts are chiefly inorganic and organic sulphur compounds and so-called gum formers, that is, unsaturated hydrocarbons and hydrocarbon compounds which under certain circumstances may polymerize to give high molecular weight substances.

Numerous processes are known for the removal of the gaseous impurities, particularly of the inorganic and organic sulphur compounds, which are harmful to the activity of the catalyst. For example, the inorganically combined sulphur is removed by means of weakly alkalized iron oxide masses. For the removal of the organic sulphur, iron oxide masses containing about 30% of soda are, for example, used commercially and industrially at tempereatures of about 150°C. Furthermore, the use of active carbon and of scrubbing liquids (methanol, solutions of alkali metal compounds of aminocarboxylic acids) is also known. All of these processes operate at temperatures of below 200°C. and preferably at room temperatures and even lower temperatures.

It has now been found, according to the compounds for the purification of gases which contain hydrogen sulphide and organic sulphur. This method of operation has hitherto only been effected with the alkaline earth metal compounds in the form of stationary beds. Satisfactory results have not been obtained so far, mainly because the active life of the purification masses consisting of alkaline earth metal compounds has been short due to the high sulphur content and the troublesome gum formers present in industrial gases.

It has now been found, accordhing to the invention, that the purification and methanisation may be effected with particularly good commercial and economic results if the gases which contain CO, CO_2 and H_2 besides other constituents and which are preferably largely or substantially free from hydrogen sulphide are passed at a temperature in the range of 350° - 600°C., preferably in the range of 400° - 500°C., through three successive fluidized beds of fine-grained materials, the first of which contains a spent, oxidised and sulphurised nickel, magnesia and kieselguhr-containing methanisation catalyst, the second of which contains an alkaline earth metal compound, preferably calcium oxide and/or calcium carbonate, and the third of which contains an active or fresh methanisation catalyst consisting of nickel, magnesia and kieselguhr, oxygen being added to the exit gas from the first bed in an amount sufficient for the oxidisation of the hydrogen sulphide contained in that gas. It has surprisingly been found that the optimum temperature range for each of the three fluidized beds is on much the same level thus permitting particularly favourable application of the invention from the commercial, economic and operational standpoints.

The treatment of the gas may be effected at atmospheric pressure, but the use of elevated pressure such for example, as 1 - 35 kg./sq. cm. advantageously 5 - 25 kg./cm.², is preferered. Corresponding to the operational pressure, the gas load or throughput must be adapted to maintain a substantially uniform fluidized bed. To fluidize the methanisation catalyst containing nickel, magnesia and kieselguhr, an effective linear gas velocity of 2 - 15 cm./second and preferably of 4 - 8 cm./second is required. The particle size of the catalyst should range between 500 and 5000 mesh/cm². Small proportions of smaller or larger catalyst particles will cause no trouble.

The process in accordance with the invention may be carried out in such a manner that the gas, after the removal of hydrogen sulphide, is with its content of organic sulphur compounds and gum formers and having a carbon monoxide:hydrogen ratio of from 1:10 to 1:0.5, first contacted with a fluidized oxidised and sulphurised nickel methanisation catalyst. The reaction temperature will be between 350°C. and 600°C. and preferably between 400°C. and 500°C. Under these conditions a practically quantitative conversion of the organic sulphide occurs within the fluidized bed while the gum formers are hydrogenated to give saturated compounds.

The next fluidized bed is used for the removal of the hydrogen sulphide formed in the first fluidized bed. For the removal of the hydrogen sulphide by oxidation to sulphur or to oxygen-containing sulphur compounds such as sulphates and the like, and subsequent absorption of these compounds, there are used in accordance with the invention fluidized alkaline earth metal compounds, particularly quicklime or limestone $(CaCO_3)$ of suitable particle size, which for example, pass through sieves of 750 and 10,000 mesh/sq. cm. Small amounts of activators which may consist of oxygen-containing compounds of iron, aluminium, titanium, or silicon are suitably added to these alkaline earth metal compounds. Catalysts of this type effect at the same time an oxidation of the hydrogen sulphide and the absorption of the sulphur oxides formed.

Small amounts of oxygen must be present for this removal of hydrogen sulphide. The oxygen required is introduced in the form, for example of relatively pure oxygen or in the form of air into the gas mixture to be purified. The quantity of oxygen present should preferably be in excess of that required to convert the hydrogen sulphide into the sulphate form according to the equation $H_2S + 5O = SO_4 + H_2O$. Advantageously, from 3 to 30 mols, preferably from 12 to 20 mols, of oxygen are added per mol of H_2S.

With the use of alkaline earth metal compounds, the removal of hydrogen sulphide is effected at practically the same temperature as that required for the conversion of the organic sulphur compounds into hydrogen sulphide. In contrast to other processes which effect a conversion of the organic sulphur at high temperature in the first stage, and thereafter a removal of the hydrogen sulphide with, for example, alkaline iron oxide at a low temperature, the process according to the invention operates in both stages at temperature levels which are much closer to each other. Thus no gas cooling is required between the two stages; this results in a considerable simplification of the process and a reduction in cost of the gas treatment.

In view of the higher specific gravity of the alkaline earth metal compounds, a corresponding increase in gas velocity is required to develop an efficiently operating fluidized bed. Suitably effective gas velocities are such as lie between 8 and 60, and preferably between 12 and 50 cm./second.

By means of alkaline earth metal compounds and small amounts of oxygen added to the gas, the hydrogen sulphide present in the gas is mainly converted into sulphate. In addition, sulphite and thiosulphate in more or less large amounts and small amounts of sulphide are formed.

Even after only a partial loading the alkaline earth metal compounds show no complete absorption for the oxidised sulphur compounds present in the gas. For this reason, it is preferable to use two or more reactors in series. In the first reactor, a considerable absorption of sulphur-oxygen compounds still occurs even after the breaking through of the sulphur compounds. With this manner of operation, the utilization of a catalyst mass which, for example, consists of quicklime or limestone may be carried on, for example, in three stages to a limit of about 70 - 80% of the theoretical absorptive capacity.

After the second purification stage operating in the form of a fluidized bed, the gas, which is now practically free from sulphur, is passed to the methanisation zone proper. This zone is also operated with a fluidized bed of the methanisation catalyst. With hydrogen-rich gases which contain sufficient quantities of hydrogen for the conversion of the carbon monoxide and carbon dioxide present in the gas mixture, the operating conditions, that is to say the gas flow rate and the quantity of gas put through per unit time, correspond practically to the operating conditions used in the first stage, since in both cases a catalyst of the same or similar composition is involved.

If the gas to be treated contains sufficient quantities of hydrogen for the hydrogenation of the carbon monoxide and carbon dioxide, the methanisation zone operates without the addition of steam. If the quantity of hydrogen is insufficient, steam must be injected during the methanisation. Corresponding to the quantity of steam injected, a decrease in gas load is required to keep the effective gas velocity constant for a steadily operating fluidized bed. With gases which are very rich in carbon monoxide, a relatively large quantity of steam must be added. With a lower content of carbon monoxide, the quantity of steam is correspondingly reduced. If, for example, the gas to be processed contains 1 volume of hydrogen per volume of carbon monoxide, then about 100 - 150 volumes of steam per 100 volumes of carbon monoxide will be approximately sufficient to obtain a shift reaction of about 50% of the carbon monoxide and perhaps a 50% methanisation of the gas. It is advantageous to add 0.2 - 3 mols, preferably 0.5 - 1.5 mols, of steam per mol of the excess carbon monoxide. A practically quantitative conversion of carbon monoxide takes place. The treated gas contains only small amounts of hydrogen which is extremely important for the production of methane-rich gases. If the carbon dioxide formed by the process in accordance with the invention is removed in known manner by scrubbing or washing, it is possible to obtain gases which contain more than 90% of methane.

Due to the use of fluidized catalyst beds, the operating temperature in the methanisation process according to the invention is considerably higher than with the use of fixed bed catalysts. The best results are obtained, particularly when processing gases rich in carbon monoxide and with the addition of steam, at temperatures above 400°C.

In the third stage, that is to say, in the methanisation proper, cooling elements must be located within the fluidized bed of the methanisation catalyst to permit an efficient removal of the reaction heat. In the first two stages cooling is not required since no heat is evolved in these stages.

The gas load of all stages, which is dependent on the operating pressure, may be varied within wide limits and may amount, for example, to about 300 or to more than 5000 volumes of gas per volume of catalyst per hour. While the first and also the second stage are practically without exception operated with a single pass of the gas, gas recycling, that is, recirculation of a more or less large quantity of tail gas, may be advantageous in the third stage in which the methanisation proper takes place. The recycle ratio ranges between about 0.5 and 5 and is preferably between 1 and 2.

The process which, in accordance with the invention, operates with three successive fluidized beds, has the advantage that the three stages of the gas methanisation, that is, the conversion of the organic sulphur, the removal of the hydrogen sulphide thereby formed, and the methanisation proper, may be effected at temperature levels which do not differ very much from each other. Cooling and re-heating of the gas between the individual stages is thus practically eliminated, it being generally sufficient to heat the gas once to 400° - 500°C. before the first stage of the gas treatment. In this way, the commercial methanisation may be effected with substantially reduced operating costs and initial investment in a much more advantageous manner than by the conventional processes. The three fluidized beds required for effecting the process may be disposed in superposition in one common casing or in juxtaposition in separate apparatus.

A specific advantage of the manner of operation described above consists in that a completely continuous operation of all stages is now possible in the methanisation. The replacement of spent catalyst has hitherto been attended by a shut-down of the operation; this may be avoided when using the process in accordance with the invention.

If small amounts of catalyst are carried along by the gases leaving the methanisation stage, these losses may be readily replaced without interrupting the operation. It is not necessary continuously to replace the catalyst losses. It is sufficient for the quantities of catalyst carried out by the gases to be replaced at intervals of, for example, 2 or 3 weeks. The replacement is effected by charging the quantity of catalyst required into the tube space by means of a lock which is filled with fresh reduced catalyst and inert gases.

If during normal operation the methanised gases do not remove any of the catalyst from the methanisation zone, it is possible by increasing the linear gas velocity for a short time to discharge the desired quantity of catalyst, thus permitting the replacement of spent catalyst by fresh catalyst without interruption of continuous operation.

The increase in the flow velocity of the gas required for this purpose may be achieved, if several reactors connected in parallel are present, in a most simple manner by shutting down some of the catalyst units or reactors. The increased gas flow velocity which will then prevail in the catalyst units kept in operation will enforce the discharge of the desired quantity of catalyst.

The replacement of the catalyst in the desulphurisation and hydrogenation units which are operated by the fluidized process may be effected in a similar manner.

The process of the invention is illustrated in the following example.

EXAMPLE.

1000 standard litres of water gas which had been freed in known manner from H_2S and which contained about 12 grams of organic sulphur compounds per 100 cubic metres, were passed under a pressure of 10 kg./sq. cm. through a vertical reaction tube of 1.5 metre length and 56 mm. inside diameter which contained 1 litre (thickness of the bed 50 cm.) of a spent, oxidised and sulphurised nickel catalyst which had a particle size of between 0.05 and 0.25 mm. The composition by volume of the water gas was 6.0% CO_2, 40.3% CO, 50% H_2, 0.3% CH_4 and 3.4% N_2. The reactor was maintained at a temperature of about 450°C. by means of a diphenyl-diphenyl oxide mixture. Thereby, the organic sulphur was practically completely converted into hydrogen sulphide.

Immediately thereafter, the gas leaving the reactor streamed without cooling through another reactor which contained lime ($CaCO_3$) which had been prepared by crushing and sieving to a particle size of about 0.02 - 0.15 mm. and which still contained small amounts of SiO_2, Fe_2O_3 and Al_2O_3. The reactor was maintained at 450°C. by means of diphenyl-diphenyl oxide. It had a diameter of 26 mm. and contained 500 cc. of catalyst. Three of such reactors were connected in series. Before the first lime purifier, air was added to the water gas in an amount of 10 standard litres per 1000 standard litres of water gas. When starting the operation, more than 90% of the sulphur was combined or retained in the first reactor as sulphate, sulphide, thiosulphate, and the like. The remaining quantity was removed in the second reactor before which about 1/10 of the quantity of air added prior to the first lime purifier, was injected into the gas stream. After the first purifier was loaded with about 40% of the stoichiometrical quantity, the third lime reactor was brought into operation at 450°C. After being loaded with about 80% of the theoretically possible quantity, the first purifier was discharged. refilled and operated as the third stage while the original second stage was now operated as the first stage and the original third stage was now operated as the second stage.

The water gas which was now freed from hydrogen sulphide and organic sulphur to a residual content of 0.2 grams/100 cubic metres, was passed to the methanisation stage proper. The reactor which consisted of a tube of 56 mm. diameter contained 1 litre of a catalyst which had been prepared by precipitation from a hot nickel and magnesium nitrate solution by means of a hot sodium carbonate solution at a pH of 9.0, subsequent stirring-in of kieselguhr (Ni : MgO : kieselguhr = 100 : 12 : 50), careful washing of the mass, drying of the washed mass at 110°C. and sieving in such a manner that after the reduction which was carried out at 380°C. with hydrogen for 60 minutes (reduction value - 80%), a catalyst having particle size of between 0.25 and 0.05 mm. was obtained.

The methanisation reactor was provided in the interior with a double tube of 12 mm. outside diameter through which steam was passed for the removal of the heat reaction. The water gas was charged at the rate of 1000 standard litres/hour to which 400 cc. of water in the form of steam were added hourly. (Thus, the ratio of CO : H_2O was 1 : 1.25). The reaction temperature ranged between about 380°C. and 420°C. and the pressure was 11 kg./sq. cm.

The gas leaving the reactor had the following composition by volume: 45.5% CO_2, 0.3% CO, 1.1% H_2, 46.0% CH, and 7.1% N_2, so that, based on carbon monoxide charged, about 60% had been converted into methane and about 40% had been converted into CO_2. After having washed out about 90% of the carbon dioxide in the conventional manner, the gas contained about 77% CH_4 and 11.8% N_2, the remainder being CO in addition to a little CO and N_2.

The catalysts and solid constituents in all of the five reactors, formed fluidized beds with the gases passed through.

What we claim is :—

1. A process for the combined purification and methanisation of a gas mixture containing oxides of carbon and hydrogen in addition to other constituents, which comprises passing the gas at a temperature within the range 350°C. - 600°C. successively through three zones containing fluidized beds of fine-grained materials, the fluidized bed or beds in the first zone being formed by a spent oxidised and sulphurised nickel, magnesia and kieselguhr-containing methanisa-

tion catalyst, the fluidized bed or beds in the second zone being formed by an alkaline earth metal compound or compounds and the fluidized bed or beds in the third zone being formed by a nickel, magnesia and kieselguhr-containing methanisation catalyst, oxygen being added to the exit gas from the first zone in an amount sufficient for the oxidation of the hydrogen sulphide contained in that exit gas.

2. A process according to Claim 1, in which the gas mixture fed to the first zone is substantially free from hydrogen sulphide.

3. A process according to Claim 1 or Claim 2, in which the temperature in each of the three zones is maintained in the range 400°-500°C.

4. A process according to any one of the preceding claims, in which the fluidized bed or beds in the second zone consist of calcium oxide and/or calcium carbonate.

5. A process according to any one of the preceding claims, in which the alkaline earth metal compound or compounds in the second zone are activated by oxygen-containing compounds of one or more of the following elements: iron, aluminium, titanium and silicon.

6. A process according to any one of the preceding claims, in which the gas throughput and the pressure in the three zones are adapted to one another to maintain under the existing conditions of temperature and pressure, a linear gas velocity of 2 - 15 cm. per second in the first and third zones, and of 8 - 60 cm. per second in the second zone.

7. A process according to any one of the preceding claims, in which the linear gas velocity, under the existing conditions of temperature and pressure, in the first and third zones lies between 4 and 8 cm. per second, whilst that in the second zone lies between 12 and 50 cm. per second.

8. A process according to any one of the preceding claims, in which the mechanisation of a gas mixture rich in carbon monoxide the effective gas velocity under the existing conditions of temperature and pressure is 2 - 15 cm./second, preferably 4 - 8 cm/second calculated for the gas mixture being converted plus steam, the quantity of the gas mixture being reduced and the quantity of steam being increased with increase in the content of carbon monoxide in the gas mixture.

9. A process according to any one of the preceding claims, in which the gas mixture contains less hydrogen than corresponds to the stoichiometrical amount required to convert all of the carbon monoxide into methane, steam being injected into the gas mixture for the conversion of the excess quantity of carbon monoxide.

10. A process according to Claim 9, in which 0.2 to 3 mols of steam are added per mol of the excess carbon monoxide.

11. A process according to Claim 10, in which 0.5 - 1.5 mols. of steam are added per mol of the excess carbon monoxide.

12. A process according to any one of the preceding claims, in which the quantity of oxygen added to the exit gas from the first zone lies within the range 3 - 30 mols per mol of H_2S.

13. A process according to Claim 12, in which the quantity of oxygen added lies within the range 12 - 20 mols per mol of H_2S.

14. A process according to any one of the preceding claims, in which the pressure in each of the three zones is within the range from atmospheric pressure to a pressure of 35 kg./sq. cm.

15. A process according to Claim 14, in which the pressure in each of the three zones is within the range 5 - 25 kg./sq. cm.

16. A process according to any one of the preceding claims, in which the space velocity through the fluidized beds lies in the range 300 - 5000, depending upon the reaction pressure.

17. A process for the purification and methanisation of a gas mixture containing hydrogen and oxides of carbon together with organic sulphur compounds as substantially the sole sulphur-containing impurities, which comprises passing the gas mixture successively through three zones at a temperature within the range 350°-600°C., at a pressure within the range from normal atmospheric pressure to a pressure of 35 kg./sq. cm., the first zone containing a fluidized bed of a spent, oxidised and sulphurised nickel-magnesia-kieselguhr methanisation catalyst, effective for the conversion of the organic sulphur compounds into hydrogen sulphide, the second zone containing a fluidized bed of an alkaline earth compound and the third zone containing a nickel-magnesia-kieselguhr catalyst effective for the methanisation of the gas mixture, oxygen being added to the exit gas from the first zone prior to its entry into the second zone, the quantity of oxygen so added being adequate for the oxidation of the whole of the hydrogen sulphide contained in the exit gas from the first zone.

18. A process for the purification and methanisation of a gas mixture containing hydrogen and oxides of carbon together with organic sulphur compounds as impurities, substantially as hereinbefore described.

19. A process for the purification and methanisation of a gas mixture containing hydrogen and oxides of carbon together with organic sulphur compounds as impurities, substantially as hereinbefore described in the Example.

20. A gas containing methane whenever produced according to the process claimed in any one of the preceding claims.

EDWARD EVANS & CO.,
14-18, High Holborn, London, W.C.1.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by Kingston Printers Ltd., Portsmouth. 335/3.—1956.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.