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(54) Preparation of hydrogen-containing gases

(57) In preparing hydrogen-containing gases, including ammonia synthesis gas, from hydrocarbons by desulfurization, primary and secondary reforming, shift conversion in two steps, removal of CO_2 and methanation, the first step of the shift conversion is carried out with a catalyst consisting of copper oxide, zinc oxide and chromium oxide at a steam to dry gas ratio below 0.5, preferably 0.3–0.5, at 10–50 atm. abs. and 190–400°C, preferably 200–360°C; and second step of the shift conversion with a catalyst of copper oxide, zinc oxide and aluminium oxide at an inlet temperature of 160–195°C, preferably 175–195°C, at the same time being at least the highest of the temperatures $(T_1 + 10)$°C and $(T_2 + 10)$°C where T_1 is is the dew point and T_2 the equilibrium temperature for the reaction $ZnO + CO_2 \rightleftharpoons ZnCO_3$.

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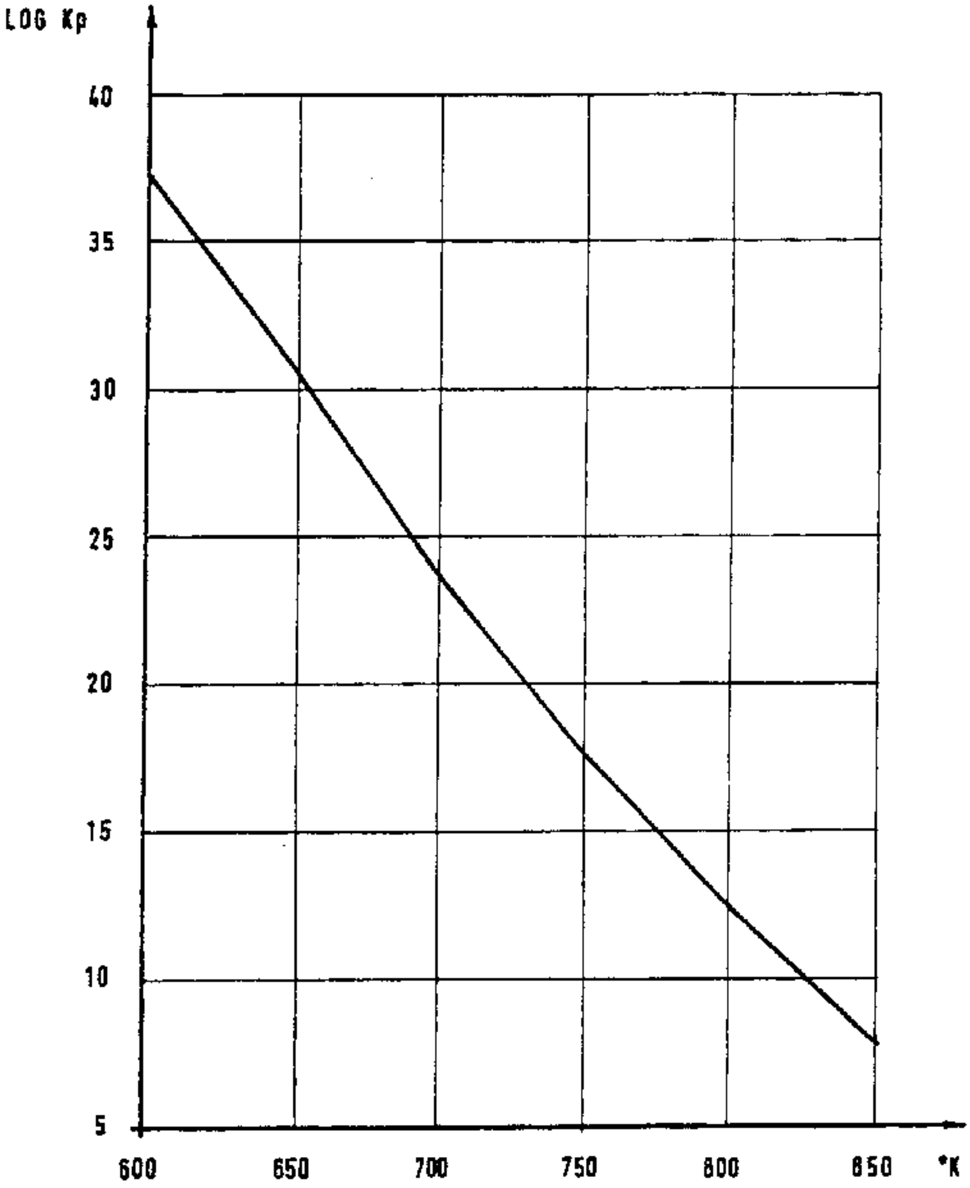

SPECIFICATION

A process for the preparation of hydrogen-containing gases.

Field of the Invention

The present invention relates to a process for the preparation of hydrogen-containing gases and especially an ammonia synthesis gas from hydrocarbons by desulfurization of the starting material, primary and secondary reforming, conversion of CO by the shift process in two steps mentioned below, removal of CO_2, and methanation.

The invention aims at the accomplishment of one of these part-processes, viz. the conversion of carbon monoxide by the so-called shift process:

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad (1)$$

Background of the Invention

A study of the course of the processes in an ammonia or hydrogen plant based on these processes shows that considerable savings of energy can be obtained if there is made an alteration of the operational conditions in comparison with those earlier employed. During recent years such alterations have already been carried out in certain process steps, such as the introduction of ammonia converters having radial flow and reduced synthesis pressure, by the introduction of a physical absorption process for the removal of CO_2 after the conversion of CO, and by the reduction of the steam to carbon ratio at the inlet of the primary reformer. Hereby an alteration of the steam balance in the plant takes place, and it can be shown that the utilization of the energy supplied can be improved considerably by a further reduction of the above-mentioned steam to carbon ratio. However, carrying out such reduction involves problems, especially in connection with the shift process (1).

A low steam to carbon ratio at the inlet to the primary reformer thus causes a lower steam to dry gas ratio and thereby a higher CO partial pressure in the shift section.

In the prior art the shift process is commonly carried out in two steps whereby the first step is accomplished while using an iron- and chromium-containing catalyst at a temperature of 360–500°C, a steam to dry gas ratio of 0.5–1.2 and a pressure of 10–35 atm. abs., and the second step is accomplished while using a copper-containing catalyst at 200–250°C.

The catalyst usually employed in the first step of the shift process in its active form consists of Fe_3O_4 promoted with Cr_2O_3. At a high CO partial pressure, however, Fe_3O_4 may be converted into iron carbides which may act as Fischer-Tropsch catalysts, resulting in the formation of undesired hydrocarbons.

The carbide formation may take place by various reactions while forming various iron carbides, but the main reaction will be

$$5\ Fe_3O_4 + 32\ CO \rightleftharpoons 3\ Fe_5C_2 + 26\ CO_2 \qquad (2)$$

Because of lack of or uncertain thermodynamical data for iron carbides the equation (2), however, is unsuitable for equilibrium calculations.

It has been found that a good approximation to the real facts is obtained by a calculation on the basis of the equation.

$$5\ Fe_3O_4 + 32\ CO \rightleftharpoons 15\ Fe + 6\ C + 26\ CO_2 \qquad (3)$$

The equilibrium constant K_p for this reaction (3) is expressed as follows:

$$K_p = \frac{p_{CO_2}^{26}}{p_{CO}^{32}}$$

Data for the calculation of K_p for reaction (3) may be found in thermodynamical tables (e.g. J. Barin, O. Knacke, O. Kubaschewski: Thermodynamical properties of inorganic substances, 1973, and supplement, 1977, Springer Verlag, Berlin). The drawing shows log K_p calculated on the basis of these data and plotted as a function of the temperature.

From the drawing it can be deduced whether Fe in the iron-containing catalyst at an actual set of interconnected values for temperatures and partial pressures of CO and CO_2 will be present in oxide form or carbide form. Thus, if log K_p at a given temperature is lower than shown by the curve, then the stable state is carbide. If log K_p is higher, the stable state is oxide.

Such a calculation has been carried out for a gas the composition of which is typical in relation to the operational conditions according to the process in question, and the results are reported in Experiment 1 hereinafter.

As appears from the Experiment, the catalyst in the typical case will be present in carbide form. Moreover, it can be shown that by employing the desired low steam/dry gas ratio one cannot bring the catalyst into oxide form because this would require so high temperatures as to destroy the catalyst because of lacking thermal stability.

As the said problems of carbide formation are connected with the use of iron-containing catalysts, it has been attempted to replace them by conventional Cu-containing low temperature shift catalysts in the first step of the shift process. However, these catalysts do not possess sufficient temperature stability for use in the present process, in which there is employed temperatures up to 400°C for the sake of energy utilization.

In the second step of the two step shift process one also encounters problems when using conventional low-temperature shift catalysts.

When carrying out the second step at the usual temperatures of 200–250°C while using a feed gas having a low steam/dry gas ratio, methanol will be formed in such an amount that one will not obtain the intended advantages in the conversion as regards energy. This is due to the fact that Cu-containing low-temperature shift catalysts also catalyze the methanol synthesis.

At higher temperatures the equilibrium of the methanol synthesis, the relevant reactions of which are

$$CO + 2\,H_2 \rightleftharpoons CH_3OH \qquad (4)$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad (5)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1)$$

will be decisive for the amount of methanol formed. At lower temperatures the amount of methanol, on the other hand, depends upon kinetic conditions since the reaction rate of the methanol synthesis decreases faster with decreasing temperature than the reaction rate of the shift process.

It has therefore also been attempted to carry out the second step of the shift process at lower temperatures. However, hereby a further problem arises because the lower activity in consequence of the lower temperature calls for the use of extremely high volumes of catalyst in order to obtain the desired degree of CO-conversion. An increased content of CO in the exit gas is undesired because more hydrogen is lost thereby in the subsequent methanation process.

Summary of the Invention

It has now been found that it is possible to avoid the said problems in the first as well as the second step of the shift process by using certain conditions of operation and catalysts rendered optimum thereto.

Accordingly, the invention relates to an improved process for the preparation of hydrogen-containing gases and especially an ammonia synthesis gas from hydrocarbons as starting material by desulfurizing the starting material, subjecting the desulfurized material to primary and secondary reforming, converting the carbon monoxide contained in the reformed gas into hydrogen and carbon dioxide by the abovementioned shift process (1) in two steps, removing CO_2 from the shifted gas and methanating the gas. According to the present invention the process is characterized in that (a) the first step of the shift process is carried out in the presence of a catalyst consisting of copper oxide, zinc oxide and chromium oxide while using a feed gas having a steam to dry gas ratio below 0.5, preferably of 0.3 to 0.5, at a pressure of 10 to 50 atm. abs. and a temperature of 190 to 400°C, preferably 200 to 360°C, whereas (b) the second step of the shift process is carried out in the presence of a catalyst consisting of copper oxide, zinc oxide and aluminum oxide,, at an inlet temperature of 160 to 195°C, preferably 175 to 195°C, said inlet temperature being at the same time at least the highest of the two temperatures $(T_1 + 10)$°C and $(T_2 + 10)$°C, where T_1 is the dew point under the reaction conditions actually prevailing and T_2 the equilibrium temperature for the reaction

$$ZnO + CO_2 \rightleftharpoons ZnCO_3 \qquad (6)$$

under the reaction conditions prevailing.

The pressure during the second step of the shift process normally will be the same as that during the first step or because of a natural pressure drop of little below that, i.e. normally about 10 to 50 atm. abs.

Detailed Description of the Invention

According to the invention the catalyst employed in the first step of the shift process may have the composition

15–70, preferably 20–40 % by atoms Cu in the form of copper oxide,
20–60, preferably 30–40 % by atoms Zn in the form of zinc oxide,
15–50, preferably 20–50 % by atoms Cr in the form of chromium oxide,

wherein the percentages by atoms are calculated solely on the metal contents and the oxygen content is not taken into account.

As to the ranges of the various components of the catalyst to use in the first step of the shift process according to the invention, it should be emphasized that catalysts having a composition within the broader ranges stated (15–70% at. Cu, 20–60% at. Zn, 15–50% at. Cr) are very well suitable for use according to the invention; whereas the preferred range of 20–40% at. Cu, 30–40% at. Zn and 20–50% at. Cr represents catalysts having particularly advantageous properties with respect to thermostability and catalytic activity.

According to the invention the catalyst employed in the second step may have the composition

25–60 % by atoms Cu in the form of copper oxide
25–45 % by atoms Zn in the form of zinc oxide
15–30 % by atoms Al in the form of aluminum oxide,

wherein the percentages by atoms are calculated in the same manner.

The catalyst employed according to the invention in the second step of the shift process is marked by a high activity and high selectivity for the shift reaction.

The lower limit stated for the inlet temperature in the second step of the shift process according to the invention accordingly is not determined out of consideration for the activity but on the contrary limited by the said two parameters, viz. the steam pressure, $p_{H_2}O$, and the carbon dioxide pressure, p_{CO_2} The reason for this is that one should avoid condensation of water in the inner parts of the catalyst bodies because it would prevent the admission of the reacting gases to the active catalyst surface; and also avoid the formation of Cu or Zn carbonates because formation of carbonates besides deactivation may involve bursting of the catalyst particles.

To ensure a reasonable safety margin it is prescribed according to the invention to use inlet temperatures at least 10°C above the dew point T_1 or equilibrium temperature T_2.

In the following the process of the invention will be illustrated by some Experiments and Examples.

Experiment 1 shows the first step of the shift process carried out in conventional manner.

Experiment 2 shows both steps of the shift process, the first step carried out in the same manner as the process of the invention and the second step in conventional manner.

Examples 1 to 4 show both of the steps of the shift process carried out by the process of the invention.

Experiment 1

Reforming of a natural gas containing 0.33% O_2, 3.91% N_2, 83.50% CH_4, 9.31% C_2H_6, 2.83% C_2H_8 and 0.12% C_4H_{10} was carried out after the addition of aqueous steam to a steam to carbon ratio of 2.5. After the primary reformer a certain amount of air is added. At the outlet from the secondary reformer, where the pressure is 31 atm. abs., the gas composition is:

H_2:	38.95 % by vol.
N_2:	17.23 % by vol.
CO:	10.89 % by vol.
CO_2:	4.38 % by vol.
Ar:	0.20 % by vol.
CH_4:	0.22 % by vol.
H_2O:	28.13 % by vol.

The gas thereafter is conveyed to the shift section where CO conversion is carried out by the shift process (1). The first step in the shift process is carried out at an inlet temperature of 360°C while using a conventional iron oxide-chromium oxide catalyst having a chromium content of about 8 % by atoms, calculated solely on the metal contents.

The adiabatic temperature increase during the passage of the first step provides an outlet temperature of 444°C corresponding to 717°K. At this temperature the shift process (1) will have gone to equilibrium.

The gas composition after the high-temperature shift reactor, where the pressure is 30 atm. abs. in the absence of other reactions will be

H_2:	46.44 % by vol.
N_2:	17.23 % by vol.
CO:	3.40 % by vol.
CO_2:	11.86 % by vol.
Ar:	0.20 % by vol.
CH_4:	0.22 % by vol.
H_2O:	20.65 % by vol.

However, the prerequisite that other reactions do not take place is erroneous. From $P_{CO_2} = 3.558$ atm. abs. and $P_{CO} = 1.020$ atm. abs. a calculation of the equilibrium constant K_p for the reaction (3) gives the result:

$$K_p = \frac{p_{CO_2}^{26}}{p_{CO}^{32}} = 1.15 . 10^{14}$$

and from this

$$\log K_p = 14.06.$$

By comparison with the drawing it is seen that the catalyst is present in carbide form. Laboratory experiments accordingly have shown that hydrocarbon formation takes place. Under the above assumptions the laboratory experiments thus show the formation of

0.5–0.7% by vol. of CH_4
0.1–0.15% by vol. of C_2H_4 and C_2H_6
0.05% by vol. of C_3H_6 and C_3H_8

and minor amounts of higher hydrocarbons, alcohols and other oxygen-containing organic compounds. It appears from this that conventional high-temperature shift catalysts are useless at the gas compositions employed according to the invention.

Experiment 2

One proceeds as in Experiment 1 with the exception that there is used an inlet temperature of 209°C in the first step of the first process and a catalyst in accordance with the invention containing 20 % by atoms Cu, 30 % by atoms Zn and 50 % by atoms Cr, all as oxides, the atomic percentages calculated solely on the metal contents. The adiabatic temperature increase during the passage of first step gives an outlet temperature of 321°C. At a pressure of 30 atm. abs. there is hereby obtained an exit gas having the following composition:

H_2: 48.60 % by vol.
N_2: 17.23 % by vol.
CO: 1.24 % by vol.
CO_2: 14.03 % by vol.
Ar: 0.20 % by vol.
CH_4: 0.22 % by vol.
H_2O: 18.4 % by vol.

As there are no carbide problems in this process, one proceeds to the second step of the shift process.

This step is carried out while using the gas obtained above at an inlet temperature of 200°C and while using a conventional low-temperature shift catalyst consisting of 30 % by atoms Cu, 50 % by atoms Zn and 20 % by atoms Al in the form of oxides, the percentages stated being calculated solely on the metal contents. The adiabatic temperature increase during the passage of second step is about 12°C. At a pressure of 30 atm. abs. there is hereby obtained an exit gas having the following composition:

H_2: 49.17 % by vol.
N_2: 17.30 % by vol.
CO: 0.24 % by vol.
CO_2: 14.88 % by vol.
Ar: 0.20 % by vol.
CH_4: 0.22 % by vol.
H_2O: 17.77 % by vol.
CH_3OH: 0.22 % by vol.

Under these conditions there is thus formed methanol in undesired amounts. In an ammonia plant where 1000 tons of ammonia are produced per day, there will at the same time be produced about 13 tons of methanol per day, which represents an unacceptable energy loss.

Example 1

In the first step of the shift process there is used as in Experiment 2 an inlet temperature of 209°C and a catalyst in accordance with the invention, consisting of copper oxide, zinc oxide and chromium oxide having the same contents of the metals as in Experiment 2, i.e. 20% by atoms Cu, 30% by atoms Zn and 50% by atoms Cr, all calculated solely on the metal contents. The adiabatic temperature increase during the first step as in Experiment 2 is to an outlet temperature of 321°C and at the pressure of 30 atm. abs. there is obtained an exit gas having the same composition as stated in Experiment 2, i.e. 48.60% by vol. of H_2, 17.23% of N_2, 1.24% of CO, 14.03% of CO_2, 0.20% of Ar, 0.22% of CH_4 and 18.48% of H_2O.

This gas is conducted to the second step of the shift process where the inlet temperature is 175°C and the catalyst is in accordance with the invention, having the composition 60 % by atoms Cu, 25 % by atoms Zn and 15 % by atoms Al, all calculated solely on the metal contents. The adiabatic temperature increase by the passage of the second shift step is about 13°C and at a pressure of 30 atm. abs. there is obtained an exit gas having the following composition:

H_2: 49.61 % by vol.
N_2: 17.25 % by vol.
CO: 0.15 % by vol.
CO_2 15.08 % by vol.
Ar: 0.20 % by vol.
CH_4: 0.22 % by vol.
H_2O: 17.45 % by vol.
CH_3OH: 0.04 % by vol.

At these conditions, which are in accordance with the invention, the formation of methanol thus is extremely limited and per 1000 tons of ammonia a day only corresponds to about 2 tons of methanol a day, which is acceptable. Moreover, the CO content in the exit gas is almost halved compared to the content according to Experiment 2.

Example 2

The two steps of the shift process are carried out in the manner explained in Example 1, with the only exception that the catalyst used in the first step of the shift process has the composition 15% by atoms of Cu, 35% by atoms of Zn and 50% by atoms of Cr, all in the form of oxides, the percentages being calculated solely on the metal contents. The exit gas obtained has practically the same composition as that in Example 1.

Example 3

The two steps of the shift process are carried out in the manner explained in Example 1, with the only exception that the catalyst used in the first step of the shift process has the composition 25% by atoms of Cu, 60% by atoms of Zn and 15% by atoms of Cr, all in the form of oxides, the percentages being calculated solely on the metal contents. The exit gas obtained has practically the same composition as that in Example 1.

Example 4

The two steps of the shift process are carried out in the manner explained in Example 1, with the only exception that the catalyst used in the first step of the shift process has the composition 62% by atoms of Cu, 20% by atoms of Zn and 18% by atoms of Cr, all in the form of oxides, the percentages being calculated solely on the metal contents. The exit gas obtained has practically the same composition as that in Example 1.

The inlet temperature in the second step of the Examples is within the temperature range prescribed according to the invention. As one can calculate a CO_2 partial pressure of 4.209 atm. abs. for the gas employed, corresponding to an equilibrium temperature in reaction (6) of 164°C, and a steam partial pressure of 5.544 atm. abs., corresponding to a dew point of 155°C, the lowest usable inlet temperature according to the invention is 174°C. Moreover, the temperature is below 195°C which is stated hereinbefore as the highest temperature in the second step of the shift process.

Beyond the advantages appeararing from what has been said herein, it should be added that by the process of the invention one removes a source of sulfur poisoning of the catalyst in the second step because the use of sulfur-containing iron catalysts is avoided.

CLAIMS

1. An improved process for the preparation of hydrogen-containing gases, especially an ammonia synthesis gas, from hydrocarbons by desulfurization of the starting material, primary and secondary reforming, conversion of carbon monoxide by carrying out the shift process

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad (1)$$

in two steps, removal of CO_2 and methanation, in which (a) the first step of the shift process is carried out in the presence of a catalyst consisting of copper oxide, zinc oxide and chromium oxide while using a feed gas having a steam to dry gas ratio below 0.5, at a pressure of 10 to 50 atm. abs. and a temperature of 190 to 400°C, and (b) the second step of the shift process in the presence of a catalyst consisting of copper oxide, zinc oxide and aluminum oxide, at an inlet temperature of 160 to 195°C which at the same time fulfils the condition of being at least the highest of the two temperatures $(T_1 + 10)$°C and $(T_2 + 10)$°C, where T_1 is the dew point and T_2 the equilibrium temperature for the reaction

$$ZnO + CO_2 \rightleftharpoons ZnCO_3 \qquad (6),$$

both under the reaction conditions actually prevailing.

2. A process as claimed in claim, in which the gas mixture used in the first step of the shift process has a steam to dry gas ratio of 0.3 to 0.5.

3. A process as claimed in claim 1 or claim 2, in which the first step of the shift process is carried out at a temperature of 200–360°C.

4. A process as claimed in anyone of claims 1 to 3, in which the second step of the shift process is carried out at an inlet temperature of 175 to 195°C.

5. A process as claimed in anyone of claims 1–4, in which the catalyst used in the first step of the shift process has the composition 15–70 % by atoms of Cu as copper oxide, 20–60 % by atoms of Zn as zinc oxide and 15–50 % by atoms of Cr as chromium oxide, the percentages by atoms being calculated solely on the metal contents of the catalyst.

6. A process according to claim 5, in which the catalyst used in the first step of the shift process has the composition 20–40 % by atoms of Cu as copper oxide, 30–40 % by atoms of Zn as zinc oxide and 20–50 % by atoms of Cr as chromium oxide, the percentages by atoms being calculated solely on the metal contents of the catalyst.

7. A process according to anyone of claims 1–6, in which the catalyst used in the second step of the shift process has the composition 25–60 % by atoms of Cu as A7855Rcopper oxide, 25–45 % by atoms of Zn as zinc oxide and 15–30 % by atoms of Al as aluminum oxide, the percentages by atoms being calculated solely on the metal contents of the catalyst.

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