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⑤④ **Process for the preparation of synthesis gas from a hydrocarbon-containing feed.**

⑤⑦ A process for the preparation of synthesis gas from a hydrocarbon-containing feed (e.g. methane) comprising the following steps:

a) at least part of the hydrocarbon-containing feed is partially converted at elevated temperature and pressure with steam into a product containing H₂ and CO;

b) product from step a) and any remaining part of the feed is subjected to catalytic partial oxidation with an oxygen-comprising gas; and

c) CO₂ is removed from the product obtained from step b).

EP 0 212 758 A2

PROCESS FOR THE PREPARATION OF SYNTHESIS GAS FROM A HYDROCARBON-CONTAINING FEED

The present invention relates to a process for the preparation of synthesis gas from a hydrocarbon-containing feed which comprises the following steps:

a) the hydrocarbon-containing feed is partially converted at elevated temperature and pressure with steam into a product containing H₂ and CO;

b) product from step a) and any remaining part of the feed is subjected to catalytic partial oxidation with an oxygen-comprising gas; and

c) CO₂ is removed from the product obtained from step b).

The hydrocarbon-containing feed employed in step a) may furthermore contain organic compounds containing oxygen. Preferably, gaseous and liquid hydrocarbons, and in particular normally gaseous hydrocarbons, are employed as feed components. The process according to the present invention is particularly suited for the preparation of synthesis gas from methane or natural gas.

Step a) is preferably carried out at a temperature from 400 to 1500 °C, and most preferably from 500 to 900 °C, and at a pressure from 3 to 50 bar and most preferably from 15 to 30 bar.

Step a) can be performed with or without a catalyst. If no catalyst is employed, the temperature will preferably lie between 1000 and 1500 °C. However, preferably a catalyst is employed, in which case the temperature applied will preferably lie between 500 and 1000 °C. Suitable catalysts preferably contain nickel, optionally applied to a carrier such as alumina.

Tubular reactors are preferably used for carrying out steps a) and b).

The various steps of the process according to the invention be carried out either discontinuously, semi-continuously or continuously. Preferably, the whole process is carried out continuously, with a solid-, moving-, or fluidized bed of catalyst particles being used in step a); a solid bed being preferred.

The space velocity of the hydrocarbon-containing feed and steam is preferably from 600 -1200 and from 3500 -4500 l (S.T.P.)/1 catalyst/hour, respectively, and is preferably from 700 - 1000 and from 3800 -4200 l (S.T.P.)/1 catalyst/hour, respectively. "S.T.P." means Standard Temperature of 0 °C and Pressure of 1 bar abs. throughout the specification.

The quantity of hydrocarbons which in step a) are converted into the product containing H₂ and CO is preferably between 50 and 99%v of the total quantity of hydrocarbons present in the feed for step a).

The product obtained from step a), which contains, besides unconverted hydrocarbons, H₂ and CO, can also contain CO₂ and H₂O, and is passed to step b) where it is partially oxidized with the aid of an oxygen-comprising gas in the presence of a catalyst. The quantity of H₂ and CO in the product obtained from step a) generally lies between 80 and 90%v on the basis of dry gas.

Hydrocarbons remaining unconverted in step a) are converted in step b) at least partially into CO and H₂. This reaction is exothermic.

Air or an oxygen-comprising gas with an oxygen content greater than that of air can be applied in step b). Preferably, an oxygen-comprising gas with an oxygen content of 90-100%v is employed. Most preference is given to substantially pure oxygen, which is understood to mean a gas that, besides oxygen, contains no more than 0.5%v of other components, such as N₂ or Ar.

In step b), the space velocity relating to the reaction product of said step is advantageously from 5000 -10000 l (S.T.P.)/1 catalyst/hour and most preferably from 7000-9000 l (S.T.P.)/1 catalyst/hour.

In principle, any catalyst known in the art for the conversion of hydrocarbons (and optionally oxygen-containing organic compounds) and O₂ into CO and H₂ can be used in step b). Preferred catalysts contain nickel, optionally applied to a carrier such as alumina. In step b) as well, as solid-, moving-or fluidized catalyst bed can be employed. A solid bed is preferred.

The reactor used for step b) is preferably of the same type as used for step a).

The main advantage of performing the catalytic partial oxidation after step a) is that extreme conditions in step a) can be avoided. Much of the hydrocarbons can be converted in step a) at relatively low temperature and pressure into a product comprising H₂ and CO. At least some of the unconverted hydrocarbons is converted in step b) into H₂ and CO. As a result of side reactions, H₂O and CO₂ may also be formed. Step b) is carried out autothermally at a temperature from 600 °C to 1100 °C. The pressure during this step will advantageously lie between 10 and 50 bar.

If the quantity of unconverted hydrocarbons from step a) is insufficient for a full employment of the capacity of the reactor used in step b), a remaining part of the hydrocarbon-containing feed is preferably led directly to step b). Preferably, step b) is also carried out in the presence of additional steam. Due to the preferably higher temperature at which step b) is carried out, relatively more of the additional hydrocarbons with steam will be con-

verted into H₂ and CO than was the case in step a). Moreover, the endothermic reaction of hydrocarbons and steam enables the temperature, which the exothermic reaction of hydrocarbons and oxygen causes to rise, and which preferably lies between 850 and 950 °C, to be optimally controlled.

The amount of additional hydrocarbons and steam preferably added to step b) is between 50 and 100%v and between 0 and 50%v, respectively, of the product from step a) added to step b).

The product from step b) generally comprises, besides H₂ and CO also CO₂ and H₂O and small amounts of unconverted hydrocarbons oxygen, nitrogen and argon. Nitrogen and argon originate from the oxygen-comprising gas and/or from a natural gas feed. The amount of H₂ and CO in the product from step b) is preferably between 80 and 90%v on the basis of dry gas.

Subsequently, CO₂ is removed in step c) from the product obtained from step b). This can be done by a method known per se, such as membrane-or preferably adsorption-techniques e.g. carried out with the aid of molecular sieves or liquid organic amino compounds and/or aqueous alkali carbonate solutions.

A solution containing adsorbed CO₂ can subsequently be regenerated by, for example, raising its temperature or by passing an inert gas, such as nitrogen, through it.

The thus obtained synthesis gas can, optionally after removing H₂O therefrom, be used for the preparation of, for example, methanol or hydrocarbons.

Preferably at least a part, and in particular substantially all of the CO₂ removed in step c) is led to step a) and/or b) in order to attain optimal use of carbon sources in the process according to the invention.

Preferably, beside the CO₂ removed in step c), also CO₂ will be led to at least one of steps a) and b) which is obtained by partially converting a hydrocarbon-containing feed in an additional step d) at elevated temperature and pressure with steam into a product containing H₂ and CO, catalytic partial oxidation of product thus obtained in an additional step e) with an oxygen-comprising gas, and removing CO₂ from the product obtained from step e) in an additional step f).

When the feed contains substantially methane, the molar H₂/CO ratio of the synthesis gas obtained in step c) will be about 2.7:1 or more if no CO₂ is added to step a) and/or b). If CO₂ is added to step a) and/or b), said ratio can be reduced, depending on the amount of added CO₂. Lowering this molar ratio is important, since the synthesis gas, if employed as starting material for the preparation of methanol or hydrocarbons, preferably has a ratio from 1.5:1 to 2.5:1 and in particular from 1.75:1 to

2.25:1. If in addition to the CO₂ obtained from step c) also extra CO₂ e.g. obtained from step f) is led to step a) and/or b), it has been found that synthesis gas can be economically obtained with a molar H₂/CO ratio from 1.5:1 to 2.5:1 or lower. Such a lowering will not in general be achieved by adding just a part or even all the CO₂ obtained in step c). The synthesis gas obtained from step f) has a ratio of about 1.7:1 or more. If the synthesis gas from step c) has a ratio which is lower than that desired, then the desired ratio can be simply obtained by mixing with it a part of the synthesis gas obtained in step f). Accordingly, the process according to the invention shows a great flexibility since all or a large part of the synthesis gas can thus be obtained economically in the desired ratio, so that the ratio of just a relatively small part, if any, of the synthesis gas needs to be brought to the desired level by, gas separation or by another known method.

The above statements relating to steps a), b) and c) also apply to steps d), e) and f), respectively.

The CO₂ removed in steps c) and f) is preferably, before being added to step a) and/or b), jointly separated from any liquid absorbent. The amount of CO₂ obtained from steps c) and f) is preferably approximately equal. The total amount of CO₂ which is preferably added to step a) and/or b) is 35 to 65%v of the quantity of methane or natural gas used in step a). Most preferably, the CO₂ is added to step a).

In another preferred embodiment of the process according to the invention, in addition to the hydrocarbons and steam to be added to step a), at least a part of a light fraction, preferably a C₅-fraction, is also led to step a), which light fraction is obtained by converting at least some of the synthesis gas obtained in step c) and possibly in step f) into hydrocarbons in the presence of a catalyst and separating the light fraction from a heavy fraction, preferably the C₅+ fraction, and employing any remaining part of the light fraction as fuel gas in order to generate at least some of the heat needed in step a). In particular, at least a part of a C₄-fraction is led to step a), which C₄-fraction is obtained by converting at least some of the synthesis gas obtained in step c) and optionally in step f) into hydrocarbons in the presence of a catalyst and separating the C₄-fraction from the C₅+ fraction, and employing any remaining part of the C₄-fraction as fuel gas.

The conversion of synthesis gas obtained in step c) into hydrocarbons can, as is known, be carried out with Fischer-Tropsch catalysts, which contain Fe, Co, Ni and/or Ru. Preferably, the light fraction and in particular the C₄-fraction, obtained in the process of preparing middle distillates from

synthesis gas from step c), is used as described above. In this context, "middle distillates" is understood to mean hydrocarbon mixtures having a boiling range corresponding substantially to that of the kerosine-and gas oil fractions obtained by atmospheric distillation of crude oil. The middle distillate boiling range is mainly between about 150 and 360 °C.

Middle distillates can be prepared in one or two stages. They are prepared in one stage by passing the synthesis gas obtained from step c) over a Fischer-Tropsch catalyst containing one or more promoters and a carrier material. The products which can be prepared with these catalysts generally have a very wide molecular weight distribution and often comprise, in addition to branched and unbranched paraffins, considerable quantities of olefins and oxygen-comprising organic compounds. Often, only a small part of the obtained products consists of middle distillates. Besides the yield, the cetane number of the gas oil often leaves much to be desired on account of the presence of the above-mentioned olefins and oxygen-comprising organic compounds. For this reason, a two-stage preparation process is preferably employed in which in a first stage a class of Fischer-Tropsch catalysts is employed, which catalysts have the property that they produce a product containing only very small amounts of oxygen-comprising organic compounds, which product consists almost entirely of unbranched paraffins, many of which boil above the middle distillate range, and in which in a second stage the high-boiling part of the product obtained in the first stage is converted by hydrocracking into middle distillates. The feedstock chosen for the hydrocracking is at least that part of the product whose initial boiling point lies above the final boiling point of the heaviest middle distillate wanted as end product. The hydrocracking, which is characterized by a very low hydrogen consumption, produces middle distillates with a considerably better pour point than those obtained by direct conversion of an H₂O/CO mixture according to the Fischer-Tropsch method.

The Fischer-Tropsch catalysts used in the first stage of the two-stage process contain silica, alumina or silica/alumina as carrier and cobalt together with zirconium, titanium and/or chromium as catalytically active metals in such quantities that 3-60 parts by weight of cobalt and 0.1-100 parts by weight of zirconium, titanium and/or chromium per 100 parts by weight of carrier are present. The catalysts are prepared by applying the appropriate metals to the carrier by kneading and/or impregnating. Before being used, the cobalt catalysts are

preferably activated. This activating can suitably be carried out by contacting the catalyst at a temperature of between 200 and 350 °C with hydrogen or a hydrogen-comprising gas.

The conversion of the synthesis gas obtained in step c) into middle distillates is preferably carried out at a temperature of 125-350 °C and in particular 175-275 °C and at a pressure of 5-100 bar and in particular 10-75 bar.

The H₂ and CO-comprising feedstock, which is converted into middle distillates with the aid of the above-mentioned type of catalysts, preferably has a H₂/CO molar ratio of 1.0-2.5 and in particular 1.25-2.25.

From the thus obtained hydrocarbon mixture a light fraction can be separated preferably the C₈-fraction and in particular the C₄-fraction. If the C₈-or C₄-fraction is separated, then at least a part of the C₉+ fraction and preferably at least a part of the C₅+ fraction will then be subjected to hydrocracking in order to convert the high boiling part into middle distillates. The feedstock chosen for the hydrocracking is at least that part of the product whose initial boiling point lies above the final boiling point of the heaviest middle distillate wanted as end product.

Although in the preparation of middle distillates from the product obtained over the cobalt catalyst a feedstock can be used consisting of that part of the product whose initial boiling point lies above the final boiling point of the heaviest middle distillate wanted as end product, preferably the total C₉+ fraction is used for this purpose, and in particular the total C₅+ fraction of the product prepared over the cobalt catalyst, since it has been found that the quality of the benzine, kerosine and gas oil fractions contained therein is improved by the catalytic hydrogen treatment.

The hydrocracking is carried out by contacting the fraction to be treated at elevated temperature and pressure and in the presence of hydrogen with a catalyst containing one or more noble metals from group VIII on a carrier. A preferred hydrocracking catalyst is one which contains 0.1-2wt.% and in particular 0.2-1 wt.% of one or more noble metals from Group VIII on a carrier. Preferred catalysts are those which comprise platinum or palladium as noble metal from Group VIII and comprise silica/alumina as carrier. The hydrocracking is preferably carried out at a temperature of 200-400 °C and in particular 250-350 °C and at a pressure of 5-100 bar and in particular 10-75 bar. If steps d), e) and f) are employed, the hydrogen can suitably be obtained from the product from step f), that usually has an H₂/CO molar ratio greater than 3:1, by separating a part of the H₂ e.g. with the aid of an alternating-pressure adsorption apparatus.

If the product prepared over the cobalt catalyst still contains sufficient unconverted hydrogen for performing the hydrocracking, both steps can be carried out in "series flow". In that case, the light fraction, preferably the C_2 -fraction and in particular the C_4 -fraction is not separated after the first step but only after the second step. As is known, carrying out a multi-stage process in series flow means that the entire product from a given stage, without any components being removed from it or added to it, is employed as feedstock for the following stage, which is carried out at substantially the same pressure as the preceding one.

The C_2 - or C_4 -fraction contains, besides hydrocarbons with 1-8 or 1-4 carbon atoms respectively, H_2O , N_2 , Ar and possibly unconverted H_2 and CO.

It is attractive to recycle this fraction as a whole back to step a) in order to make the carbon atoms material balance as favourable as possible. However, the drawback of this is that after a time the quantity of N_2 and Ar in the system rises to such an extent that the yield of -ultimately -middle distillates starts falling considerably.

It has been found that the wishes concerning the carbon atoms balance can be accommodated to some extent, without detriment to the yield, by adding a part of the C_2 -fraction and in particular the C_4 -fraction to step a) and by burning the other part thereof in order to generate the heat required for step a).

Preferably, between 40 and 90%v and in particular between 50 and 80%v of the C_2 -fraction or C_4 -fraction respectively is passed to step a).

Passing the afore mentioned part of the C_2 - or C_4 -fraction to step a) can advantageously be combined with the passing to step a) of CO_2 removed in step c), either partly, wholly or together with extra CO_2 from step f), as described above.

If in addition CO_2 from step f) is passed to step a), the light fraction, preferably the C_2 -fraction and in particular the C_4 -fraction of a middle distillate synthesis process based on the synthesis gas from step f), can be used for step a) or step d). Preferably, the synthesis gas from step f) is combined with the synthesis gas from step c) after having been brought to the desired H_2/CO molar ratio. The thus combined synthesis gas is then used for the middle distillate synthesis process. The light fraction, preferably the C_2 -fraction and in particular the C_4 -fraction thus obtained is then used for step a) as described above.

The process according to the invention will be illustrated with reference to the embodiments represented schematically in Figures 1-7, which do not however, in any way restrict the scope of the present invention.

According to Figure 1 a hydrocarbon-containing feed, preferably methane or natural gas, is led via line 2 and steam via line 3 to reactor 1 wherein step a) is carried out. The product obtained from step a) is led via line 4 to reactor 5 wherein step b) is carried out with the addition of an oxygen-comprising gas via line 6 and preferably with the addition of a remaining part of the hydrocarbon-containing feed (not indicated in Fig. 1). The product obtained from step b) is led via line 7 to separator 8 wherein step c) is carried out. CO_2 leaves the separator via a line 9. The synthesis gas is discharged via line 10.

In Figures 2-7 the reference numerals 1-10, in as far as used, refer to the same as in Figure 1.

According to Figure 2, a part of the CO_2 from step c) is led via line 11 to step a) after having been purified in a suitable apparatus (not shown in Fig. 2).

According to Figure 3, all of the CO_2 obtained from step c) is led via line 11 to step a). According to Figure 4, in addition to the CO_2 obtained from step c), an additional quantity of CO_2 supplied via line 12 is led via 11 to step a).

In Figure 5 the reference numerals 1'-8' and 10' refer to the same as the reference numerals 1-8 and 10, except that step d) is carried out in reactor 1', step e) in reactor 5' and step f) in separator 8'. All of the CO_2 separated in step f) is led via lines 12 and 11 to step a) together with the CO_2 separated in step c).

According to Figure 6, the synthesis gas obtained in step c) is led via line 10 to an apparatus 13 for the preparation of middle distillates. The C_2 + fraction leaves this apparatus via line 14; the C_4 -fraction is discharged via line 15 and split into a first part that is led via line 17 to step a) and a second part that is led via line 16 to a combustion unit, not shown, where it is burned to generate at least some of the heat required for step a). The flue gas formed in the combustion unit is discharged via line 18.

The embodiment represented in Figure 6 can be expanded with the modification shown in Figures 2-5 in which the CO_2 from step c) is led partly, wholly or together with extra CO_2 from step f) to step a).

In Figure 7 the previously used reference numerals refer to the same as before. Reference numerals 13'-18' refer to the same as 13-18, except that the C_4 -fraction, as described above, is used for step d). It is also possible -and this is preferable -instead of using apparatus 13' and lines 14'-18', to connect line 10' to line 10 and to lead the synthesis gas from step f), possibly after modifying the molar H_2/CO ratio, to apparatus 13.

The invention will be further illustrated with the aid of the following Examples, without this limiting the scope of the invention in any way.

EXAMPLE 1

Synthesis gas is prepared according to the embodiment shown schematically in Figure 1. Natural gas (space velocity 800 1(S.T.P.)/1 catalyst/hour) and steam (space velocity 4000 1-(S.T.P.)/1 catalyst/hour) are contacted with each other in reactor 1 (step a) at 500-850 °C and 38 bar in the presence of a supported nickel catalyst. 90%v of the natural gas is thus converted (step a)).

The product obtained from step a) which contains 85%v H₂ + CO is contained continuously in reactor 5 (step b)) with oxygen containing 0.5%v Ar and N₂ combined in the presence of a supported nickel catalyst. The space velocity is 8500 1-(S.T.P.)/1 catalyst/hour relative to the product obtained from step b). The temperature rises to 950 °C and the pressure is 35 bar in reactor 5.

Of the product obtained from step b), the CO₂ is separated in separator 8 (step c)) by means of absorption with a liquid organic amino compound. The quantity of separated CO₂ corresponds to 10%v of the product formed in step b).

Of the product obtained from step c), 97%v (on a dry basis) consists of H₂ and CO in a molar H₂/CO ratio of 3.9:1.

EXAMPLE 2

Synthesis gas is prepared according to the embodiment shown schematically in Figure 2; the preparation is carried out in a similar manner as described in Example 1, except that in addition to natural gas carbon dioxide (combined space velocity 1350 1(S.T.P.)/1 catalyst/hour) is introduced into reactor 1 after having been separated in separator 8. The product obtained from step c) contains 98%v (on a dry basis) H₂ and CO in a molar H₂/CO ratio of 2.4:1.

Claims

1. A process for the preparation of synthesis gas from a hydrocarbon-containing feed which comprises the following steps:

(a) at least part of the hydrocarbon-containing feed is partially converted at elevated temperature and pressure with steam into a product containing H₂ and CO;

b) product from step a) and any remaining part of the feed is subjected to catalytic partial oxidation with an oxygen-comprising gas; and

c) CO₂ is removed from the product obtained from step b).

2. Process according to claim 1 wherein step a) is carried out at a temperature from 400-1500 °C, a pressure from 3-50 bar, a space velocity from 600-12001(S.T.P.) hydrocarbon-containing feed/1 catalyst/hour and from 3500-4500 1(S.T.P.) steam/1 catalyst/hour.

3. Process according to claim 1 or 2 wherein step a) is carried out in the presence of a catalyst, preferably containing nickel.

4. Process according to any one of the preceding claims wherein 50-99%v of the hydrocarbons present in the feed for step a) are converted into H₂ and CO.

5. Process according to any one of the preceding claims wherein in step b) a nickel-containing catalyst is employed.

6. Process according to any one of the preceding claims wherein in step b) an oxygen-comprising gas is employed containing 90-100%v O₂, and preferably substantially pure oxygen.

7. Process according to any one of the preceding claims wherein step b) is carried out at a temperature from 600-1100 °C, a pressure from 10-50 bar and a space velocity relating to the product of step b) from 5000-10000 1(S.T.P.)/1 catalyst/hour.

8. Process according to any one of the preceding claims wherein step b) is carried out in the presence of additional steam.

9. Process according to any one of the preceding claims wherein part of the hydrocarbon-containing feed is employed in step a) and the remainder is led directly to step b).

10. Process according to any one of the preceding claims wherein CO₂ is removed in step c) by means of absorption.

11. Process according to any one of the preceding claims wherein at least part, and preferably substantially all of the CO₂ removed in step c) is led to step a) and/or b).

12. Process according to any one of the preceding claims, wherein a hydrocarbon-containing feed is partially converted in an additional step d) at elevated temperature and pressure with steam into a product containing H₂ and CO, the product thus obtained is subjected to catalytic partial oxidation in an additional step e) with an oxygen-comprising gas, and CO₂ is removed from the product obtained from step e) in an additional step f) and led to at least one of steps a) and b).

13. Process for the preparation of synthesis gas from a hydrocarbon-containing feed substantially as described hereinbefore with reference to the Examples.

14. Synthesis gas prepared according to a process as claimed in any one of the preceding claims.

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FIG.1

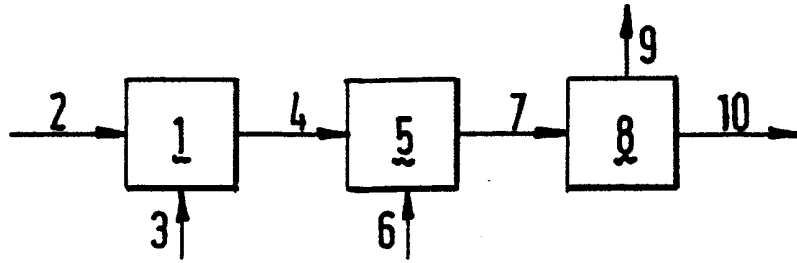


FIG.2

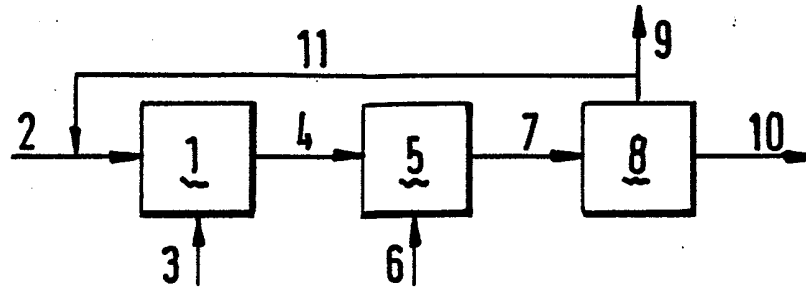


FIG.3

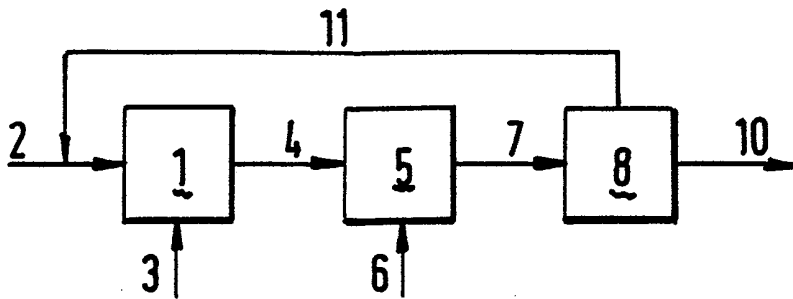


FIG.4

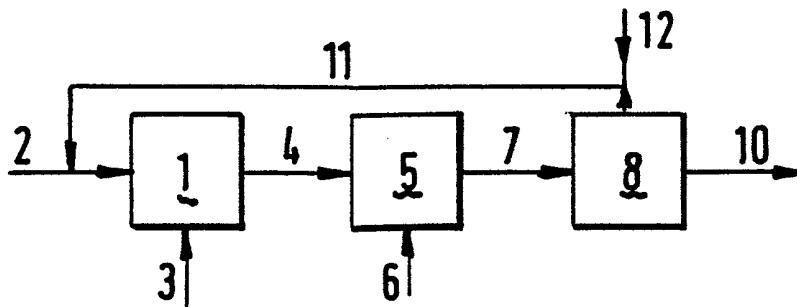
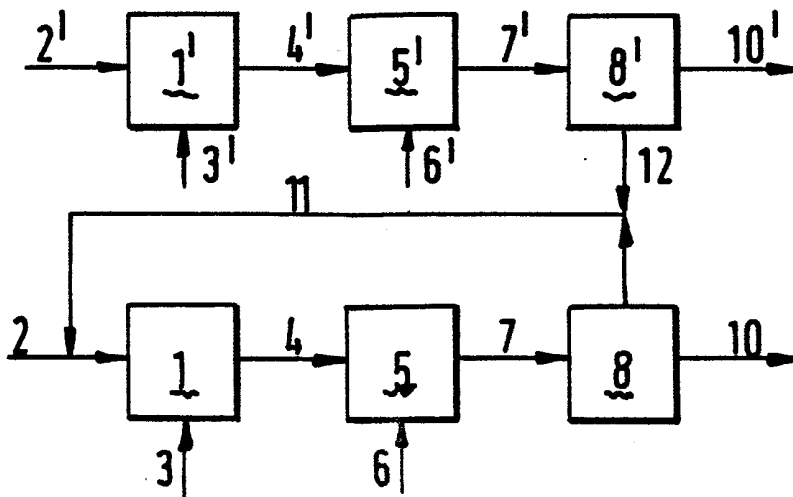


FIG.5



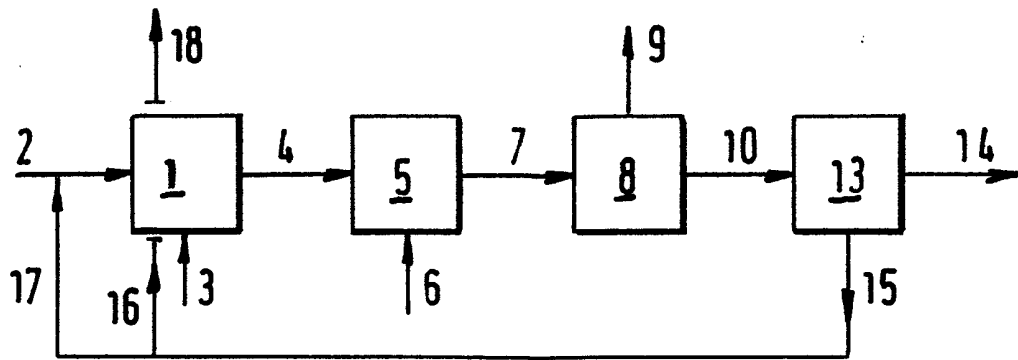


FIG. 6

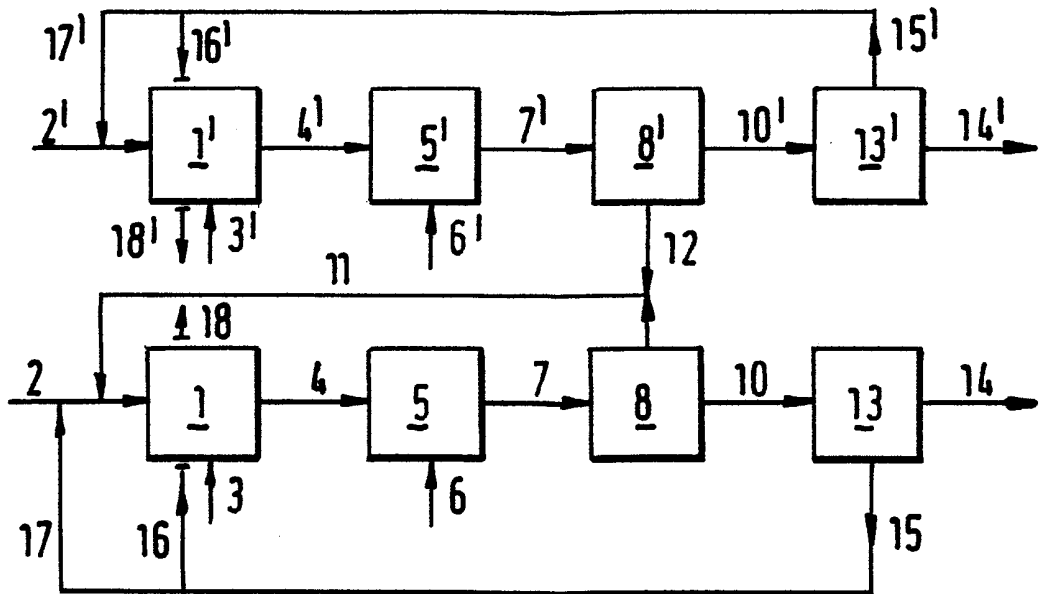


FIG. 7