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(54) Benævnelse: **FREMGANGSMÅDE OG ANLÆG TIL FREMSTILLING AF METHANOL**

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Description

The present invention relates to a process for preparing methanol by reaction of carbon dioxide and hydrogen and also a plant which can be used in this process, in which a product stream obtained in the methanol synthesis reaction is fed to a high-pressure separator and/or a low-pressure separator in which a gas stream is separated off from a methanol-containing product stream.

In the move away from electric energy generated from fossil fuels to renewably generated energy, power peaks which can no longer be integrated into conventional electric grids occur. Various technologies for storing or otherwise utilizing power surpluses in times of surplus availability of renewable energies are summarized under the term "Power-to-X". One variant of this technology is named "Power-to-gas". Here, the surplus electric power from renewable energy sources is firstly converted by means of electrolysis of water into hydrogen. The hydrogen is subsequently reacted, for example, with carbon dioxide to form methane or methanol. The methane produced can, for example, be fed into the natural gas grid. As an alternative, the electrolytically generated hydrogen can also be reacted with nitrogen to form ammonia (this variant is also referred to as "Power-to-ammonia"). In this way, the energy can be stored chemically in the form of ammonia.

In comparison to the sometimes quite large electrolysis plants in the megawatts range, these Power-to-X plants are relatively small [for example in the order of from a few 1000 metric tons/year to several 10 000 metric tons/year (t/a)]. Economical and environmentally friendly disposal of purge gas and offgas streams from such plants, which are very largely operated in a stand-alone manner, is not realistically given by means of conventional flare systems. The term purge gases refers to gases which are present in a gas stream and are inert in respect of the desired reaction in a reaction of feed gases to form a product gas. Since the gases reacting with one another are usually circulated in such reactions, the inert gases and/or undesirable by-products may have to be removed as purge gases from the synthesis circuit so that they do not accumulate in the circuit.

DE 20 2010 012 734 U1 discloses a process in which hydrogen is produced by electrolysis of water in an electrolysis unit using electric energy produced from a renewable energy source and this hydrogen is subsequently reacted catalytically with carbon dioxide in a reactor unit in order to produce methanol or methane. The methane or methanol obtained here is burnt as hydrocarbon-containing energy carrier stream in a combustion chamber and the thermal energy of the flue gas formed in the combustion is then utilized to generate electric energy in a gas turbine process or a steam turbine process.

The document WO 2014/173452 A1 describes a process and a reactor plant for the synthesis of methanol with recycle gas and purge gas recirculation, where the methanol is produced in an exothermic reaction of carbon dioxide and hydrogen and the hydrogen used here is obtained by electrolysis of water. The product gas mixture from the methanol synthesis is here separated at the product outlet into a fraction comprising methanol-containing product, a recycle gas fraction and a purge gas fraction, with part of the purge gas fraction being recirculated to an entry stage and again conveyed through the reactor. The purge gas contains carbon dioxide, hydrogen and carbon monoxide. In one variant of the process, there is a purge stream which is discharged via a conduit into the atmosphere. Catalytic offgas purification is not provided for here.

US 2007/0282021 A1 discloses a process for preparing ethanol by reaction of carbon dioxide with hydrogen, in which not only ethanol but also other organic compounds such as methanol and higher alcohols as by-products are obtained. This known process is comparatively nonspecific since the desired product ethanol is obtained in a proportion of only 52%, while 26% of methanol and further alcohols having up to six carbon atoms are additionally formed. The product mixture can firstly be treated by stripping and then distilled in order to obtain a purified ethanol having a purity of 87%.

DE 20 2010 012 734 U1 describes a process for the catalytic production of methanol or methane from an electrolytically produced hydrogen stream and carbon dioxide. This process serves to equalize generation peaks in the generation of electric energy from renewable energy sources. The methanol produced in this process is subsequently burnt with the introduction of a stream of oxygen in a combustion chamber, so that it is not important to produce methanol having a high degree of purity since the methanol is not marketed as synthesis product. The treatment of the methanol-containing product stream is not described in more detail in this document. Catalytic offgas purification is not provided for in this known process.

It is an object of the present invention to optimize a process for preparing methanol by reaction of carbon dioxide and hydrogen in respect of the efficiency, the energy consumption, the offgas streams and wastewater streams obtained and the product purity.

This object is achieved by a process for preparing methanol by reaction of carbon dioxide and hydrogen having the features of Claim 1.

The present invention primarily provides a process and a plant for preparing methanol. However, the process procedure described here and the plant conception are also suitable for the preparation of other alcohols, in particular lower alcohols such as ethanol.

According to the invention, the methanol-containing product stream obtained after the high-pressure separator and/or after the low-pressure separator are/is subsequently fed to at least one distillation step in which at least one component, in particular water, is separated off from the methanol-containing product stream.

In a preferred embodiment of the process, an at least one gas stream which has been separated off and contains volatile components is discharged in its entirety or only partly from the system as offgas and/or this gas stream or part of this gas stream which has been separated off is recirculated to the methanol synthesis reaction.

The process of the invention can, according to one of several possible alternative variants, be operated with such a plant configuration that an offgas stream is completely avoided or at least minimized. The offgas streams obtained as a result of the optimized configuration are so small in this variant of methanol production according to the invention that neither a flare nor offgas treatment are necessary in normal operation.

In one possible variant of the invention, catalytic offgas purification of an offgas stream and/or purge gas stream is preferably provided.

If such a catalytic offgas purification is provided, then this preferably comprises a catalytic after-combustion. This catalytic after-combustion is carried out with introduction of a supplementary combustion component.

If a catalytic after-combustion of the offgas stream is provided, the emission of, in particular, hydrocarbons into the environment can be produced. The offgas loaded with the pollutants is then passed through an apparatus in which at least one catalyst is present. The catalytic after-combustion operates according to the principle of heterogeneous catalysis. It is advantageous for this to be a process for offgas purification which can be carried out at a comparatively low reaction temperature. The hydrocarbons present in the offgas stream are generally oxidized to carbon dioxide and water. This oxidation can occur either directly or via intermediate stages.

As supplementary combustion component in the catalytic after-combustion, it is possible to use, for example, air or oxygen which is obtained in addition to H_2 in the electrolysis of water. Oxidation processes are assisted and/or accelerated by the addition of oxygen.

In the case of those variants in which no or only a minimal offgas stream is discharged from the system, volatile components separated off in the distillation or condensation can be recirculated back to the methanol synthesis reaction. An increase in the product yield and an improvement in the efficiency of the process overall are achieved in this way. In addition, these measures lead to avoidance of or a great reduction in environmental pollution.

The water separated off from the methanol- or methane-containing product stream in the distillation step can likewise be recirculated instead of being discharged as wastewater from the system; this is of particular interest in a preferred process variant in which the hydrogen used as starter material in the synthesis of methanol has previously been obtained from water by electrolysis. In this variant of the process of the invention, it is possible, for example, to use electric power previously obtained from, in particular, renewable energy sources for the electrolysis of water. The hydrogen produced here can then be reacted with carbon dioxide to form methanol (methanol synthesis). The product formed here is subsequently treated by suitable separation processes.

In principle, the process water can be sent directly to a sewage system in the processes according to the invention. However, disposal can be complicated in the case of decentralized plants. It is therefore advantageous for the process water to be able to be reused in the process according to the abovementioned process variant and not have to be disposed of. The utilization of the process water significantly reduces the freshwater requirement, for example by more than 30%.

In the variant with production of the hydrogen by electrolysis of water, treatment of the process water can be necessary, depending on the electrolysis technology used. This water treatment can, for example, comprise removal of methanol present in the water by means of a membrane process. Salts can be removed from the freshwater introduced from the outside by, for example, ion exchange and/or reverse osmosis.

The carbon dioxide used as starter material in the methanol synthesis reaction can, for example, at least partly be made available cryogenically. In this case, the heat from the return stream of a cooling medium used in the process can be utilized for vaporization and heating of the carbon dioxide. This coupling of the cooling of a cooling medium from a closed cooling circuit with the vaporization and heating of CO_2 is an advantageous variant since no separate removal of heat is necessary for CO_2 vaporization and separate complicated cooling of the cooling medium can be dispensed with. As cooling medium, it is possible to use, for example, a glycol/water mixture. This can, for example, be precooled in a preceding air or water cooling step.

In one possible preferred variant of the process, a mixing and compression section which is supplied from the outside with carbon monoxide or hydrogen or a synthesis gas containing carbon oxides and hydrogen is provided upstream of the methanol synthesis reaction. In the methanol synthesis, the operating life of the catalyst is increased by the addition of carbon monoxide since deactivation of the catalyst proceeds more quickly in the case of pure carbon dioxide. If hydrogen is available at a site, this can be fed into the system and load can thus be taken off the electrolysis of water, so that the electric power requirement is reduced.

Further optimization of the process can be effected by combining the above-described system with, for example, a conventional synthesis gas production operation, for example by steam reforming, combined reforming or catalytic POX (autothermal reforming). The optimum position for the addition of external gases depends, *inter alia*, on the pressure level at which the gas is available.

If components which are inert in respect of the product synthesis and are not obtained in a mixture with the product and not in the water in the subsequent separation processes, for example nitrogen, get into the system via the addition of gas from the outside, a small offgas stream can be necessary in order to avoid accumulation of the inert components in the system. In the case of pure components, on the other hand, no offgas stream or a minimal offgas stream is envisaged.

In a basic version of the process of the invention, cryogenic carbon dioxide and electric power by means of which the hydrogen necessary for the synthesis is produced electrolytically from water can, for example, be provided as starting components. However, many alternative variants of the invention are possible when, for example, CO_2 is already present in gaseous form in a water treatment plant, a power station or the like or when, for example, H_2 is available via a pipeline or at the site of a chemical factory. In these cases, the vaporization and heating of the CO_2 or the reuse of the process water in the system can be dispensed with.

In embodiments of the process of the present invention, various further separation processes for the treatment and purification of the product stream can be provided in addition to the distillation. For example, a product stream obtained in the methanol synthesis reaction can firstly be fed to a low-pressure separator and a gas stream which has been separated off from the methanol-containing product stream in this low-pressure separator can subsequently be fed to the distillation step. Direct introduction of the gas phase from a low-pressure separator into a distillation apparatus has the advantages of minimizing the amount of offgas and increasing the total efficiency of the plant.

According to the invention, volatile components separated off in the distillation step are recirculated partly or in their entirety into a mixing and compression section located upstream of the methanol synthesis. This mixing and compression section can comprise one or more compressor stages connected in series. This is dependent on, *inter alia*, the reactor pressure. Many electrolyses of water operate at an elevated pressure of, for example, about 10 bara, so that CO_2 and H_2 can be mixed upstream of the compressor. In such a case, a recycled stream firstly has to be compressed in a first compressor stage before addition to CO_2 and H_2.

In other variants of the electrolysis of water, on the other hand, the hydrogen is obtained only at a small gauge pressure, for example in the region of a few 100 mbar. In this case, it is advantageous firstly to mix the recycled stream with H_2 and then compress it in a first compressor stage. CO_2 could then be added and the mixture then be compressed to the desired pressure.

In principle, it is possible to use a compressor having a plurality of stages or, as an alternative, two or more separate compressors.

In the methanol synthesis of the invention, water can be separated off at the bottom in the distillation step and the volatile components can be separated off at the top. The methanol obtained in this way can then, for example, be added to a spark-ignition fuel. If high-purity methanol is to be produced, it is advantageous to use two or more distillation columns.

In another preferred embodiment of the present invention, a product stream obtained in the methanol synthesis reaction is firstly fed to a high-pressure separator and a gas stream which has been separated off from a methanol-containing product stream in this high-pressure separator is partly recirculated as recycle gas to the methanol synthesis reaction and a further substream from the high-pressure separator is fed to the distillation step.

In a preferred further development of the abovementioned variant, it is possible, for example, for a gaseous product stream obtained in a methanol synthesis reaction firstly to be fed, after cooling, to a high-pressure separator in which a first gas stream is separated off from a liquid methanol-containing product stream and the methanol-containing product stream then to be fed, with a reduction in pressure, to a low-pressure separator in which a second gas stream is separated off from the methanol-containing product stream, with the first gas stream being at least partly recirculated as recycle gas to the methanol synthesis reaction, the second gas stream subsequently being fed to the distillation step and the remaining methanol-containing product stream likewise being fed to the distillation step.

The recirculation of the overhead product from the distillation step into a mixing and compression section advantageously results in a significant minimization of the amount of offgas and an increase in the overall efficiency of the plant.

Taking off a substream from the recycle gas to the distillation apparatus firstly enables a constant stream to be recirculated via a recycle compressor to the reactor. Secondly, the H_2 to CO_2 ratio can be set within particular limits by the division of the fluid stream. If this substream is omitted, it is advantageous to discharge part of the recycle stream (of the stream from the distillation apparatus to the mixing and compression section). At each of these two places, it is also possible to provide a small offtake stream (offgas stream).

A small offgas stream can occur when a catalyst having a poor selectivity is used, as a result of which there is increased formation of by-products, or when unfavourable operating parameters (for example high temperatures) are selected when deactivation of the catalyst has already progressed and by-products are thus formed to an increased extent.

If offgas streams to be purified, which are despite small amounts fed to the catalytic offgas purification, are obtained in the process of the invention, these can contain, for example, carbon monoxide and/or carbon dioxide and/or water and also residues of methanol, hydrogen and by-products such as methyl formate and dimethyl ether.

The synthesis of methanol by the process of the invention is preferably carried out at temperatures in the range from about 200°C to about 300°C.

The present invention further provides a plant for preparing methanol by reaction of carbon dioxide with hydrogen, comprising at least one reactor unit for the synthesis of methanol and comprising at least one first separation apparatus which is located downstream of the reactor unit and has the function of separating off volatile and/or liquid constituents from a methanol-containing product stream, wherein the plant further comprises at least one further separation apparatus which is located downstream of the first separation apparatus and has the function of separating off volatile constituents by distillation or of separating off water by condensation, with at least one return conduit connected to the separation apparatus being provided for at least partial recirculation of a gas stream separated off in the separation apparatus to a region upstream of the reactor unit and/or at least one offgas conduit connected to the separation apparatus being provided for partial or complete discharge of an offgas stream from the plant.

The plant of the invention preferably further comprises an electrolysis apparatus for producing hydrogen from water and also means for feeding the hydrogen produced in the electrolysis to the reactor unit for the preparation of methanol. The electric energy coming, for example, from power peaks can be used for the electrolytic production of hydrogen from water in the electrolysis apparatus. Since hydrogen cannot easily be stored, it is advantageous to convert the hydrogen into another energy carrier, for which purpose it is preferably reacted with carbon dioxide to form methanol according to the invention. The methanol can be stored in suitable tanks and can be utilized as energy carrier at a given point in time or else be used as reactive component for producing further basic chemicals.

If offgas streams which have to be discharged from the system arise in one of the abovementioned process variants, the plant of the invention preferably further comprises at least one apparatus for catalytic offgas purification of an offgas stream and/or purge gas stream to be discharged from the plant, which apparatus is indirectly or directly in active communication with the reactor unit via the offgas conduit.

This plant preferably further comprises at least one compressor which is arranged between the electrolysis apparatus and the reactor unit and by means of which the feed gas stream can be brought to the entry pressure necessary for the reactor unit.

Furthermore, the plant of the invention preferably comprises, as first separation apparatus, at least one high-pressure separator which is located downstream of the reactor unit and has the function of separating gaseous constituents from a methanol-containing product stream. In the high-pressure separator, liquid components such as methanol and water can be separated off from volatile components by means of prior cooling and high pressure. As cooling medium, it is possible to use, for example, the cooling medium which has been cooled in the CO_2 vaporizer. Cooling by means of water or air is likewise possible in principle.

Furthermore, the plant of the invention preferably comprises, as separator apparatus, at least one low-pressure separator which is located downstream of the reactor unit, preferably located downstream of a high-pressure separator, and has the function of separating off liquid and/or gaseous constituents from a methanol-containing product stream. In the low-pressure separator, the fluid mixture is depressurized so as to produce a gas phase which can then, for example, be fed either in its entirety or only partly to the distillation apparatus. In the latter variant, a substream from the low-pressure separator can be discharged as offgas from the system, optionally after catalytic purification. However, such discharge of offgas can, as an alternative, also occur after the distillation apparatus which according to the invention is preferably used as further separation apparatus.

In order to introduce the components which have been separated off in the distillation apparatus back into the methanol synthesis, the plant of the invention preferably comprises at least one return conduit for recirculation of a gas stream which has been separated off in the distillation apparatus into a region upstream of the reactor unit.

If discharge of a substream as offgas from the process is provided for, this can also occur, for example, after the separation operation in the high-pressure separator, so that in this case the plant preferably comprises at least one gas conduit from the high-pressure separator to the apparatus for catalytic offgas purification. As an alternative, discharge of a substream as offgas after the separation operation in the low-pressure separator can also be provided for, so that at least one gas conduit from the low-pressure separator to the apparatus for catalytic offgas purification is then preferably provided. Otherwise, the discharge of a substream as offgas or purge gas occurs after the distillation, so that at least one gas conduit which leads from the distillation apparatus to the catalytic offgas purification is then preferably provided. As a result of recirculation of the components separated off in the distillation and the routing according to the invention of the gas streams from the separators, possible offgas streams are minimized to such an extent that offgas purification is not absolutely necessary. However, it is advantageous to ensure a suitable position for blowing-off into the surroundings.

In a preferred embodiment of the present invention, a recycle gas is recirculated from the high-pressure separator into the methanol synthesis. In this variant, at least one return conduit for gases extending from the high-pressure separator to the entry region of the reactor unit is provided, with the plant then preferably further comprising a compressor arranged in the flow path between the high-pressure separator and an entry region of the reactor unit, preferably in the return conduit.

In the abovementioned area, it is also possible to provide for a substream of the recycle gas to be separated off from the high-pressure separator and conveyed into the distillation apparatus. In this preferred variant, a branch conduit branching off from the return conduit extending from the high-pressure separator is provided for feeding at least one substream of the volatile constituents separated off in the high-pressure separator into the upper region of the distillation apparatus. This branch conduit can then in turn open into a conduit which serves for feeding volatile constituents separated off in the low-pressure separator into an upper region of the distillation apparatus. A further possible variant of the invention provides for the hydrogen to be stored in a hydrogen store which is preferably arranged downstream of one or more compressors and upstream of the reactor unit for the methanol synthesis. In this way, a failure of the power supply could be bridged for a certain period of time and the capacity of the plant could thus be adapted in a regulated manner and the plant could continue to be operated at part load. It is also possible to provide a separate compressor for the hydrogen store in order to store the hydrogen at high pressure and then introduce it back into the compressor section when required.

Some preferred operating conditions for the methanol synthesis according to the process of the invention are indicated below. The reaction in the methanol synthesis reactor is preferably carried out at a temperature in the range from 200°C to 300°C, in particular from 210°C to 280°C, and at a pressure of preferably from 30 to 100 bara (bar absolute), in particular at from 40 to 100 bara. High temperatures can lead to increased deactivation of the catalyst and to increased formation of by-products.

The methanol synthesis can be controlled in a targeted manner and the formation of by-products minimized by means of the molar ratio of the two reactants hydrogen:carbon dioxide at the reactor inlet. The stoichiometric ratio for the synthesis of methanol from hydrogen and carbon dioxide is 3:1. However, a superstoichiometric ratio of H_2 to CO_2 at the reactor inlet in the range from 5 to 12 can preferably be selected in order to decrease the deactivation of the catalyst.

Any reactor type is in principle possible for the methanol synthesis reactor. For example, the reactor can be a water-cooled shell-and-tube reactor.

The catalysts known to a person skilled in the art for the reaction are in principle possible for the methanol synthesis according to the invention. There are no specific restrictions in respect of the catalyst for this reaction. Copper-based catalysts may be mentioned only by way of example.

The features specified in the dependent claims relate to preferred embodiments of the present invention. Further advantages can be derived from the following detailed description.

The present invention will be illustrated below with the aid of working examples with reference to the accompanying drawings. The drawings show:

Figure 1 a schematic flow diagram of a first illustrative plant for the preparation of methanol with incineration of part of the purge gases/offgases;

Figure 2 a schematic flow diagram of a second illustrative plant for the preparation of methanol with catalytic combustion of part of the purge gases/offgases;

Figure 3 a schematic flow diagram of a third illustrative plant for the preparation of methanol;

Figure 4 a schematic flow diagram of a fourth illustrative plant for the preparation of methanol with discharge of part of the purge gases/offgases;

Figure 5 a schematic flow diagram of a fifth illustrative plant for the preparation of methanol without discharge of an offgas stream;

Figure 6 a schematic flow diagram of a sixth illustrative plant for the preparation of methanol with introduction of further feed gases into the methanol synthesis;

Figure 7 a schematic flow diagram of a seventh illustrative plant for the preparation of methanol with a simplified plant configuration.

In the following, reference is made firstly to figure 1. In the working example, this is, in particular, a “small-scale” plant for methanol production having a capacity in the order of, for example, up to several 10 000 t/a. An external source of carbon dioxide is provided; this carbon dioxide can, for example, be present cryogenically and is fed to a vaporizer 10 from where the CO_2 goes via a conduit 11 into the compressor 12. The second starter material for the preparation of methanol is hydrogen, which is obtained electrolytically from water. Electric power 13 obtained from renewable energy sources is preferably used to operate the electrolysis apparatus 14. The starter material for the electrolysis is water which is conveyed via a conduit 15 firstly optionally into a work-up apparatus 16 in which, for example, a reverse osmosis and/or an ion exchange is provided. From there, the treated water goes via the conduit 17 as starter material into the electrolysis apparatus 14. At this point, a substream of freshwater for a possible steam and condensate system and/or a closed cooling medium circuit can, for example, be branched off. The wastewater from the treatment apparatus can in the simplest case be discharged from the system via the wastewater conduit 42.

The electrolysis of water forms not only hydrogen but also oxygen which can be discharged via a conduit 18 from the electrolysis apparatus 14 and either be used as supplementary combustion component in the catalytic after-combustion of the purged gases/offgases or else is passed to another use outside the system. The hydrogen produced in the electrolysis is fed via the conduit 20 to the compressor 12 to which the CO_2 is also fed via the conduit 11. From the compressor 12, the combined feed mixture of CO_2 and H_2 is then fed via the conduit 21 into the methanol synthesis reactor 22.

The methanol synthesis takes place in the methanol synthesis reactor 22 and the product stream leaving this reactor is fed via the conduit 23 to a high-pressure separator 24. From this, it is possible to provide a return conduit 25 to a compressor 19 in which a starter material-containing gas mixture which has been separated off from the product stream in the high-pressure separator 24 is compressed and, after compression, recirculated and fed back into the methanol synthesis reactor 22. In the present example, this methanol synthesis reactor 22 operates at an elevated temperature, for example in the order of from 200°C to 300°C, and at an elevated pressure which can be, for example, in the range from about 30 bar to 100 bar. In addition, a catalyst is generally used for the methanol synthesis. The methanol-containing product stream leaving the methanol synthesis reactor 22 is fed into a high-pressure separator 24, leaves the latter via the conduit 27 and is then optionally fed to a low-pressure separator 28 in which further separation of gases from the methanol-containing product stream occurs.

Further purification of this crude methanol takes place in a distillation apparatus 30 which is connected via a conduit to the low-pressure separator 38 and in which volatile components are separated off and are discharged from the top of the distillation apparatus 30 via a conduit 33 and in the simplest case can optionally be discharged as offgas from the system. Furthermore, a second conduit 31 extending from the low-pressure separator 28 is provided; volatile components separated off there can likewise be introduced via this conduit into the offgas stream. These volatile components can, particularly when small amounts are obtained, be burnt by means of a flare 39 and the offgas can be discharged from the system via the conduit 40.

Apart from the volatile components, water can be separated off from the methanol at the bottom of the distillation apparatus 30 and the waste water can in the case of this simple plant be discharged from the system via the conduit 41. The methanol is then discharged from the system in a high purity via the conduit 32 and can, for example, be stored in tanks.

Part of the volatile components separated off in the high-pressure separator 24 is conveyed as recycle gas via the return conduit 25 to a further compressor 19 and then from there fed into the conduit 21 for starter materials, so that these components can be recirculated to the methanol synthesis reactor 22.

A second working example of a plant according to the invention for preparing methanol is described below with reference to figure 2. The structure is similar to the working example described above with the aid of figure 1, since this is also a relatively small plant (small-scale) in a basic configuration, but, as a difference from the example of figure 1, an offgas purification is provided. All plant components which correspond to the structure according to the figure are not explained again here. In this respect, reference is made to what has been said above. The difference from the example of figure 1 is that an apparatus 36 for catalytic offgas purification is provided instead of the flare 39.

The gas stream leaving the top of the distillation apparatus 30 is conveyed via the gas conduit 33 (see figure 1) to a catalytic after-combustion 36. The proportion of volatile components separated off in the high-pressure separator 24 is taken as purge gas stream from the circuit and fed via conduit 35 to the apparatus 36 for catalytic after-combustion. This can be fed together with oxygen, which is obtained as by-product in the electrolysis apparatus 14, via the conduit 18, so that, depending on the composition of the purge gases, the oxygen introduced as supplementary combustion component can serve to promote the combustion. The catalytic after-combustion occurs in the apparatus 36, so that a purified offgas stream which leaves the plant via the discharge conduit 37 is produced.

A third working example of the present invention is explained below with reference to figure 3. This variant differs from the two above-described working examples firstly in that the formation of offgas has been minimized. The fluid stream of the volatile components separated off in the distillation apparatus 30 is here recirculated as recycle stream via the return conduit 34 into a region located upstream of a first compressor or a first compressor stage 12 and upstream of the methanol synthesis reactor 22. Unlike the above-described variants, a first compressor (compressor stage) 12 to which firstly the hydrogen from the electrolysis 14 and also this recycle stream is fed is provided here. The mixture leaving the first compressor 12 is then fed together with the carbon dioxide supplied from the vaporizer 10 via the conduit 11 to a further compressor or a further compressor stage 26, since multiple compression is necessary in order to bring the feed gases to the pressure envisaged for the methanol synthesis. From the outlet of this further compressor 26, the feed stream then goes into the methanol synthesis reactor 22 which is additionally supplied with the recycle gas recirculated from the high-pressure separator 24 via the return conduit 25 after it has been compressed in the compressor 19.

Furthermore, the water obtained at the bottom in the distillation is in this variant not discharged from the system but instead circulated via the return conduit as process water back into the water electrolysis 14. This water separated off in the distillation can optionally also firstly be treated, for example to remove methanol by means of a membrane process. Substances dissolved in the water or other impurities can optionally be separated off by suitable methods. If no treatment of the water separated off in the distillation is necessary, the reaction can be carried out without wastewater being formed in this variant of the process. If treatment of the water is necessary, the wastewater from the treatment 16 is discharged from the system via the wastewater conduit 42.

A further difference in the variant as shown in figure 3 is that cooling medium from a closed cooling circuit 46 is used to vaporize the cryogenic CO_2 in the vaporizer 10 and heat it before it is conveyed via the conduit 11 to the second compressor stage 26. A glycol/water mixture can be used as coolant. The heated cooling medium thus does not have to be cooled separately but instead the heat present in the cooling medium can be utilized for the vaporization of CO_2.

A fourth embodiment of the present invention is explained below with reference to figure 4. This plant concept for the methanol synthesis corresponds essentially to that described above with reference to figure 3, with the difference than in the variant as per figure 4 an offgas stream is provided and is discharged from the system. From the return conduit 34, which recirculates the recycle stream from the top of the distillation apparatus 30 into the region upstream of the first compressor (or the compressor stage) 12, a substream is branched off via an offgas conduit 37 and discharged from the system. However, the amount of offgas can be minimized since, both in the variant as per figure 4 and in that as per figure 3, the gas phase from the low-pressure separator 28 is passed directly via a further conduit 45 into the distillation apparatus (distillation column) 30. The total efficiency of the plant is increased thereby. The variant as per figure 4 also discloses the possibility of additionally providing a small offgas stream 47 which is branched off from the conduit 25 via which the recycled gas is recirculated to the methanol synthesis. Due to the offgas stream 47, the recycled gas stream does not become too large and the ratio of H_2 to CO_2 in the reactor can be set within certain limits. A further manipulated variable for setting the desired H_2 to CO_2 ratio is the introduction of the two starter materials CO_2 and H_2 upstream of the mixing and compression section.

A fifth working example of the present invention is explained below with reference to figure 5. This plant concept for the methanol synthesis represents a variant in which no stream of offgas, or a minimal stream of offgas, is discharged from the system. It differs from the above-described variant as per figure 3 in that a substream is branched off via conduit 44, which opens into the further conduit 45, from the recycle gas which is recirculated from the high-pressure separator 24 via the return conduit 25 and the compressor 19 to the methanol synthesis 22. An alternative to this would be direct introduction into the distillation apparatus 30. In this way, this substream can be mixed into the gas stream which goes directly from the low-pressure separator 28 to the distillation apparatus 30. Taking off a substream from the recycle gas enables a constant stream to be recirculated via the recycle compressor 19 to the methanol reactor 22. The division of the stream creates flexibility in respect of the amount recirculated.

The return conduit 34 provided in the variants as per figures 3 to 7 conveys the gas stream from the distillation apparatus 30 back to a point upstream of the compressor 12 by means of which the feed gas is compressed. The gas stream from the low-pressure separator 28 is fed into the distillation apparatus 30. A substream of the gas stream from the high-pressure separator 24 can, as is shown in the working examples as per figures 5 to 7, likewise be fed via the conduits 44 and 45 to the distillation apparatus 30. As an alternative, the gas stream from the high-pressure separator 24 can, however, be recirculated either in its entirety as in the variants shown in figures 3 and 4 or partly as in the variants shown in figures 5 to 7, optionally with compression by means of the further compressor 19, to the inlet of the methanol synthesis reactor 22. The efficiency of the methanol plant of the invention is significantly improved by these measures.

The integrated configuration of the methanol plant in the working examples shown in figures 3 to 5 has the advantage that the amount of offgas obtained in the process can be significantly reduced. In addition, the amount of the feed gases carbon dioxide and hydrogen can be reduced considerably, for example by a few percentage points, at the same amount of methanol produced. The quantity of electric power required in the electrolysis for obtaining the hydrogen is also reduced in this way.

The vaporizer 10 for vaporizing the cryogenic carbon dioxide, as shown in the working examples as per figures 2 to 6, produces cold which can, for example, be used for cooling the stream of hydrogen from the electrolysis. The stream of hydrogen can in this way be cooled down to temperatures in the region of, for example, less than 5°C. As a result, it is possible to recover a high proportion of water which can then be conveyed back into the electrolysis apparatus 14 for the water electrolysis. A glycol/water mixture, for example, serves as cooling medium here.

Furthermore, the process water obtained as coproduct in the process can advantageously be recirculated to the electrolysis apparatus 14, for example via the return conduit 43 depicted in figure 3.

Further advantages of the process are given by the apparatus 36 for catalytic offgas purification as described above with the aid of figure 2.

A sixth working example of the present invention will be explained below with reference to figure 6. This plant concept for the methanol synthesis provides for discharge of a small offgas stream 37 from the return conduit 34 via which the recycle stream is recirculated to the region upstream of the compressor 12. Such a small offgas stream 37 can, for example, be obtained when a catalyst having poor selectivity is used or unfavourable operating parameters are selected when deactivation of the catalyst has progressed and by-products are thus formed to an increased extent.

This embodiment as per figure 6 also differs from the above-described variants in that further feed gases are introduced from outside the system into the mixing and compression section which comprises the two compressors 12 and 26 or compressor stages. A further conduit 48 which leads from outside to the mixing and compression section and via which CO, H_2 or a synthesis gas comprising CO, CO_2 and H_2 can be introduced is provided. These further gases are mixed in the mixing and compression section with the hydrogen from the electrolysis 14 and/or the carbon dioxide from the vaporizer and the mixture is then fed to the methanol synthesis reactor 22.

A seventh working example of the present invention is explained below with reference to figure 7. This variant relates to a somewhat simplified plant concept for the synthesis of methanol. Here, carbon dioxide is fed from outside the system in the gaseous state via the conduit 11 into a region which is arranged downstream of the first compressor or the first compressor stage 12. The hydrogen is not produced in the system by electrolysis but is instead also supplied from outside via the conduit 20, which comes into consideration when, for example, hydrogen is available at a site. Any other combinations for provision of the feed gases are also possible, for example the use of H_2 from the electrolysis in combination with gaseous CO_2 or, for example, the use of H_2 from outside in combination with cryogenic CO_2. In figure 7, too, an offgas stream 37 can be provided in a manner analogous to that described above in the case of figure 6.

The two feed gases go into the region between the first compressor or the first compressor stage 12 and the second compressor or the second compressor stage 26. Here, the way in which compression is carried out is also dependent on the pressure level of the gases present. Introduction downstream of the first compressor stage represents one of several alternative possibilities. The gases can, in a manner analogous to figure 7, be introduced into the mixing and compression section at any point, depending on the pressure level at which the gas is present. The recycle stream recirculated from the distillation apparatus 30 via the return conduit 34 is, on the other hand, fed into a region upstream of the first compressor 12 and is there firstly compressed and then, at the outlet end of the first compressor 12, mixed with the fresh feed gases hydrogen and carbon dioxide introduced from the outside and this mixture is fed into the second compressor 26. The recycle gas is, as described above in the case of the variant of figure 1, conveyed from the high-pressure separator 24 via the return conduit 25 through the compressor 19, compressed there and then mixed in the region downstream of the second compressor 26 with the fluid stream produced there and fed into the methanol synthesis reactor 22.

The process water is not recycled in this variant since no production of hydrogen by electrolysis is provided in the system but instead, as in the variant in accordance with figure 1, the water separated off in the distillation apparatus 30 can be discharged from the system via a conduit 31 from the bottom of the column. In an alternative variant of the invention, it is also possible to provide an additional H_2 store in the plant, with, for example, the H_2 being stored under superatmospheric pressure in a vessel. For example, in a plant concept as has been described above with reference to figure 3, the H_2 store can be arranged in the region of the first compressor 12, with, for short-term equalization of relatively small fluctuations, a conduit which leads to the inlet side of the H_2 store being branched off downstream of the first compressor 12 and upstream of the second compressor 26 and a conduit being able to lead back from the outlet side of the H_2 store into the region upstream of the first compressor 12. Thus, for example, when there is low power availability, the capacity of the actual methanol plant can be adapted in a regulated manner. This is especially advantageous for the distillation column 30. Pure hydrogen is not stored by means of the branch downstream of the first compressor stage 12. However, the H_2 content is, for example, above 98%. Further components such as CO_2, CO, methanol, dimethyl ether and methyl formate get in via the recycle stream. In return, however, there is the advantage that no additional compressor is necessary.

When, for example, proton exchange membrane electrolysers (PEM electrolysers) are used, the H_2 is obtained at relatively high pressures (for example up to 35 bar) and can then be stored directly without a compressor stage.

When relatively large storage capacities for hydrogen are necessary, an alternative variant can be chosen. For example, a branched conduit for hydrogen which branches off downstream of the water electrolysis 14 and upstream of the first compressor 12 and leads firstly to a further compressor in order to bring the hydrogen to a higher pressure and store it at a higher pressure can be provided in the plant flow diagram depicted in figure 3. The hydrogen store from the outlet of which a conduit leads into the region between the first compressor 12 and the second compressor 26 is then arranged downstream of this further compressor (see plant flow diagram in figure 3). In this way, pure H_2 can be stored at higher pressures by means of the additional compressor. Here too, the introduction can also be effected, as an alternative, upstream of the first compressor 12.

List of reference numerals

10	Vaporizer
11	Conduit for CO_2
12	Compressor
13	Inlet conduit for stream
14	Electrolysis apparatus
15	Feed conduit for water
16	Water treatment
17	Feed conduit for water
18	Conduit for oxygen
19	Compressor
20	Conduit for hydrogen
21	Conduit for starter materials
22	Methanol synthesis reactor
23	Conduit for product
24	High-pressure separator
25	Return conduit (recycle gas conduit)
26	Compressor
27	Conduit
28	Low-pressure separator
29	Conduit
30	Distillation apparatus
31	Second conduit
32	Outlet conduit for methanol
33	Conduit
34	Return conduit
35	Conduit to after-combustion
36	Apparatus for catalytic offgas purification
37	Outlet conduit
38	Crude methanol tank
39	Flare
40	Offgas conduit
41	Wastewater conduit
42	Wastewater conduit
43	Return conduit for process water
44	Conduit for substream
45	Conduit
46	Coolant circuit

47	Offgas stream
48	Further conduit to mixing and compression section

Patentkrav

1. Fremgangsmåde til fremstilling af methanol ved hjælp af omsætning af carbondioxid med hydrogen, hvor en ved methanolsyntesereaktionen opnået produktstrøm tilføres til en højtryksudskiller og/eller en lavtryksudskiller (28), hvori en gasstrøm udskilles fra en methanolholdig produktstrøm, idet den methanolholdige produktstrøm efterfølgende tilføres til i det mindste et destillationstrin (30), hvori i det mindste en bestanddel, navnlig vand, udskilles fra den methanolholdige produktstrøm, kendetegnet ved, at i destillationstrinnet (30) udskilte letflygtige bestanddele delvist eller fuldstændigt føres tilbage til en foran methanolsyntesen koblet blande- og kompressionssektion.

2. Fremgangsmåde ifølge krav 1, kendetegnet ved, at en gasstrøm indeholdende i det mindste en udskilt letflygtig bestanddel udledes fuldstændigt eller kun delvist af systemet som udstødningsgas, og/eller denne gasstrøm eller en del af denne udskilte gasstrøm føres tilbage igen til methanolsyntesereaktionen (22).

3. Fremgangsmåde ifølge krav 1 eller 2, kendetegnet ved, at i det mindste en delstrøm af den af den methanolholdige produktstrøm udskilte gasstrøm tilføres til en katalytisk rensning af udstødningsgassen (36).

4. Fremgangsmåde ifølge krav 3, kendetegnet ved, at den katalytisk rensning af udstødningsgassen (36) omfatter en katalytisk efterforbrænding under tilførsel af et tilsætningsbrændstof.

5. Fremgangsmåde ifølge krav 4, kendetegnet ved, at der ved den katalytiske efterforbrænding tilføres oxygen, navnlig ved hjælp af elektrolyse udvundet oxygen, som tilsætningsbrændstof.

6. Fremgangsmåde ifølge et af kravene 1 til 5, kendetegnet ved, at den ved syntesen af methanol som edukt anvendte hydrogen forinden udvindes af vand ved hjælp af elektrolyse (14).

7. Fremgangsmåde ifølge krav 6, kendetegnet ved, at det i destillationstrinnet (30) eller ved hjælp af kondensation eller på anden måde af en methanolholdig produktstrøm udskilte vand i det mindste delvist føres tilbage til den elektrolytiske udvinding af hydrogen (14) fra vand.

8. Fremgangsmåde ifølge et af kravene 1 til 7, kendetegnet ved, at der ved methanolsyntesereaktionen (22) gås ud fra flydende (kryogent) carbondioxid.

9. Fremgangsmåde ifølge et af kravene 1 til 8, kendetegnet ved, at der er tilvejebragt en fordampning og opvarmning af det til methanolsyntesen anvendte carbondioxid, idet der hertil anvendes varmen fra tilbageløbet af et kølemiddel.

10. Fremgangsmåde ifølge et af kravene 1 til 9, kendetegnet ved, at en ved methanolsyntesereaktionen (22) opnået produktstrøm i første omgang tilføres til en lavtryksudskiller (28), og en i denne lavtryksudskiller fra den methanolholdige produktstrøm udskilt gasstrøm efterfølgende tilføres til destillationstrinnet (30).

11. Fremgangsmåde ifølge et af kravene 1 til 10, kendetegnet ved, at blande- og kompressionssektionen omfatter en eller flere efter hinanden koblede kompressorer eller kompressionstrin.

12. Fremgangsmåde ifølge et af kravene 1 til 11, kendetegnet ved, at en delstrøm af den i destillationstrinnet (30) udskilte letflygtige bestanddel udledes af systemet som udstødningsgas.

13. Fremgangsmåde ifølge et af kravene 1 til 12, kendetegnet ved, at en ved methanolsyntesereaktionen (22) opnået produktstrøm i første omgang tilføres til en højtryksudskiller (24), og en i denne højtryksudskiller fra en methanolholdig

produktstrøm udskilt gasstrøm delvist føres tilbage til methanolsyntesereaktionen (22) som genbrugsgas, og en yderligere delstrøm fra højtryksudskilleren (24) tilføres til destillationstrinnet (30).

14. Fremgangsmåde ifølge et af kravene 1 til 13, kendetegnet ved, at en ved methanolsyntesereaktionen (22) opnået produktstrøm i første omgang tilføres til en højtryksudskiller (24), hvori en første gasstrøm udskilles fra en methanolholdig produktstrøm, og den methanolholdige produktstrøm derefter tilføres til en lavtryksudskiller (28), hvori en anden gasstrøm udskilles fra den methanolholdige produktstrøm, idet den første gasstrøm i det mindste delvist føres tilbage til methanolsyntesereaktionen (22) som genbrugsgas, den anden gasstrøm efterfølgende tilføres til destillationstrinnet (30), og den resterende methanolholdige produktstrøm ligeledes tilføres til destillationstrinnet.

15. Fremgangsmåde ifølge et af kravene 6 til 14, kendetegnet ved, at der er tilvejebragt en vandrensning af det til elektrolysen (14) som edukt anvendte vand ved hjælp af ionudbytning og/eller omvendt osmose.

16. Fremgangsmåde ifølge et af kravene 1 til 15, kendetegnet ved, at der er tilvejebragt en før methanolsyntesereaktionen (22) koblet blande- og kompressionssektion, hvortil der udefra tilføres carbonmonoxid eller hydrogen eller en carbonoxid og hydrogenholdig syntesegas.

17. Fremgangsmåde ifølge et af kravene 5 til 16, kendetegnet ved, at en i destillationstrinnet (30) udskilt gasstrøm føres tilbage til en blande- og kompressionssektion, og der ikke udledes nogen eller kun en minimal strøm af udstødningsgas af systemet, og i destillationstrinnet (30) udskilt vand som procesvand føres tilbage til den elektrolytiske hydrogenudvinding (14).

18. Fremgangsmåde ifølge et af kravene 1 til 17, kendetegnet ved, at en i destillationstrinnet (30) udskilt gasstrøm føres tilbage til en før methanolsyntesen koblet blande- og/eller kompressionssektion og i første omgang komprimeres i en første kompressor eller et første kompressionstrin, i det mindste en af eduktgasserne, fortrinsvis begge eduktgasserne carbondioxid og hydrogen, efter denne første komprimering forenes med den komprimerede tilbageførte strøm, eller først forenes med hydrogen og så komprimeres, og den således opståede forenede blanding herefter tilføres til i det mindste en yderligere kompressor eller et yderligere kompressionstrin og efter denne yderligere kompression tilføres til methanolsyntesereaktionen (22).

19. Fremgangsmåde ifølge et af kravene 1 til 18, kendetegnet ved, at der er tilvejebragt en før methanolsyntesereaktionen (22) koblet blande- og kompressionssektion, som udefra tilføres carbonmonoxid eller hydrogen eller en carbonoxid- og hydrogenholdig syntesegas, og som endvidere tilføres i systemet ved hjælp af elektrolyse (14) frembragt hydrogen, og/eller som endvidere tilføres af kryogent foreliggende carbondioxid efter fordampning af frembragt gasformet carbondioxid, og/eller som endvidere tilføres en strøm af i destillationstrinnet (30) udskilte og tilbageførte letflygtige bestanddele.

20. Anlæg til fremstilling af methanol ved hjælp af omsætning af carbondioxid med hydrogen omfattende i det mindste en reaktorenhed (22) til methanolsyntese samt omfattende i det mindste en efter reaktorenheden (22) koblet første skilleanordning (24, 28) til udskillelse af letflygtige og/eller flydende bestanddele fra en methanolholdig produktstrøm, kendetegnet ved, at anlægget endvidere har i det mindste en efter den første skilleanordning (24, 28) koblet yderligere skilleanordning (30) til udskillelse af letflygtige bestanddele og vand ved hjælp af destillation, idet der er tilvejebragt i det mindste en med skilleanordningen forbundet returledning (34) til en i det mindste delvis tilbageførsel af en i skilleanordning (30) udskilt gasstrøm i et område opstrøms

for reaktorenheden (22), og der er tilvejebragt i det mindste en med skilleanordningen forbundet ledning til udstødningsgas til delvis eller fuldstændig udledning af en strøm af udstødningsgas fra anlægget.

21. Anlæg ifølge krav 20, kendetegnet ved, at dette endvidere omfatter i det mindste en anordning (36) til den katalytiske rensning af en udstødningsgas og eller purgegasstrøm, der skal udledes fra anlægget, som står direkte eller indirekte i aktiv forbindelse med reaktorenheden (22) via ledningen til udstødningsgassen.

22. Anlæg ifølge krav 20 eller 21, kendetegnet ved, at dette endvidere omfatter en elektrolyseanordning (14) til fremstilling af hydrogen fra vand samt midler til tilførsel af det ved elektrolysen fremstillede hydrogen til reaktorenheden (22) til syntesen af methanol.

23. Anlæg ifølge krav 22, kendetegnet ved, at dette endvidere omfatter i det mindste en mellem elektrolyseanordningen (14) og reaktorenheden (22) placeret kompressor (12).

24. Anlæg ifølge et af kravene 20 til 23, kendetegnet ved, at dette som første skilleanordning omfatter i det mindste en efter reaktorenheden (22) koblet højtryksudskiller (24) til udskillelse af gasformede bestanddele fra en methanolholdig produktstrøm.

25. Anlæg ifølge et af kravene 20 til 24, kendetegnet ved, at dette som første skilleanordning omfatter i det mindste en efter reaktorenheden (22) koblet, fortrinsvis endvidere efter en højtryksudskiller (24) koblet lavtryksudskiller (28) til udskillelse af flydende og/eller gasformede bestanddele fra en methanolholdig produktstrøm.

26. Anlæg ifølge et af kravene 20 til 25, kendetegnet ved, at den yderligere skilleanordning omfatter en destillationsanordning (30), og der er tilvejebragt i det

mindste en returledning (34) til tilbageførsel af en i destillationsanordningen (30) udskilt gasstrøm i et område opstrøms for reaktorenheden (22).

27. Anlæg ifølge et af kravene 20 til 26, kendetegnet ved, at dette endvidere har i det mindste en anordning (16) til oprensning af vand ved hjælp af udskillelse af i vandet opløste substanser samt midler til tilførsel af det oprensede vand til elektrolyseanordningen (14).

28. Anlæg ifølge et af kravene 20 til 27, kendetegnet ved, at dette omfatter i det mindste en anordning til tilvejebringelse af carbondioxid, i det mindste en efter denne anordning koblet fordamper (10) og i givet fald i det mindste en efter fordamperen (10) koblet kompressor (12, 26) samt midler til tilførsel af carbondioxid fra fordamperen og/eller fra kompressoren til reaktorenheden (22).

29. Anlæg ifølge et af kravene 24 til 28, kendetegnet ved, at dette omfatter i det mindste en gasledning fra højtryksudskilleren (24) til anordningen til den katalytiske rensning af udstødningsgas (36) og/eller i det mindste en gasledning fra lavtryksudskilleren (28) til anordningen til den katalytiske rensning af udstødningsgassen (36) og/eller i det mindste en gasledning (33) fra destillationsanordningen (30) til den katalytiske rensning af udstødningsgassen (36).

30. Anlæg ifølge et af kravene 24 til 29, kendetegnet ved, at dette har i det mindste en fra højtryksudskilleren (24) udgående returledning (25) til gasser til indgangsområdet på reaktorenheden (22), og/eller omfatter en i strømningsretningen mellem højtryksudskilleren (24) og et indgangsområde på reaktorenheden (22), fortrinsvis i returledningen (25), placeret kompressor (26).

31. Anlæg ifølge krav 30, kendetegnet ved, at der er tilvejebragt en fra højtryksudskilleren (24) udgående returledning (25) forgrenet ledningsgren til tilførsel af i det

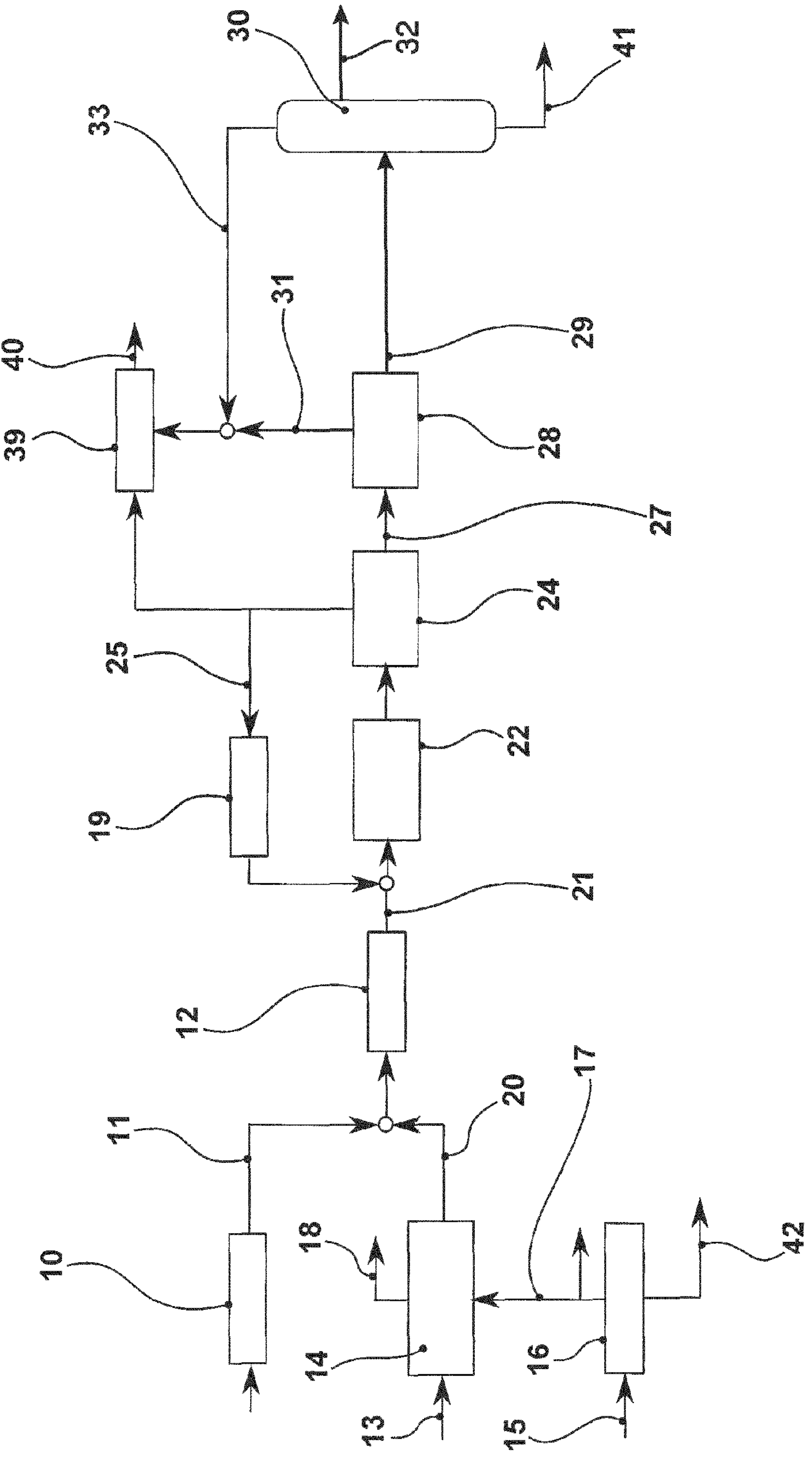
mindste en delstrøm i de i højtryksudskilleren (24) udskilte letflygtige bestanddele i hovedområdet på destillationsanordningen (30).

32. Anlæg ifølge krav 31, kendetegnet ved, at ledningsgrenen munder ud i en ledning, som tjener til tilførsel af i lavtryksudskilleren (28) udskilt letflygtige bestanddele til hovedområdet på destillationsanordningen (30).

33. Anlæg ifølge et af kravene 20 til 32, kendetegnet ved, at dette omfatter en blande- og kompressionssektion omfattende en eller flere kompressorer eller kompressionstrin, hvori en af disse fra en fordamper tilført carbondioxidgasstrøm blandes og komprimeres med en eller flere i anlægget ved hjælp af vandelektrolyse frembragt hydrogengasstrøm og/eller en uden for anlægget tilført eduktgasstrøm omfattende carbondioxid og/eller carbonmonoxid og/eller hydrogen og/eller en syntesegas, idet blandings- og kompressionssektionen i reaktorenheden (22) til methanolsyntesen er koblet foran denne og står i aktiv forbindelse med denne.

34. Anlæg ifølge et af kravene 20 til 33, kendetegnet ved, at dette omfatter et lager til hydrogen, fortrinsvis et tryklager, som er placeret nedstrøms for vandelektrolysen (14), idet der i givet fald er tilvejebragt en yderligere kompressor for at tilføre under forøget tryk stående hydrogen til lageret.

Fig. 1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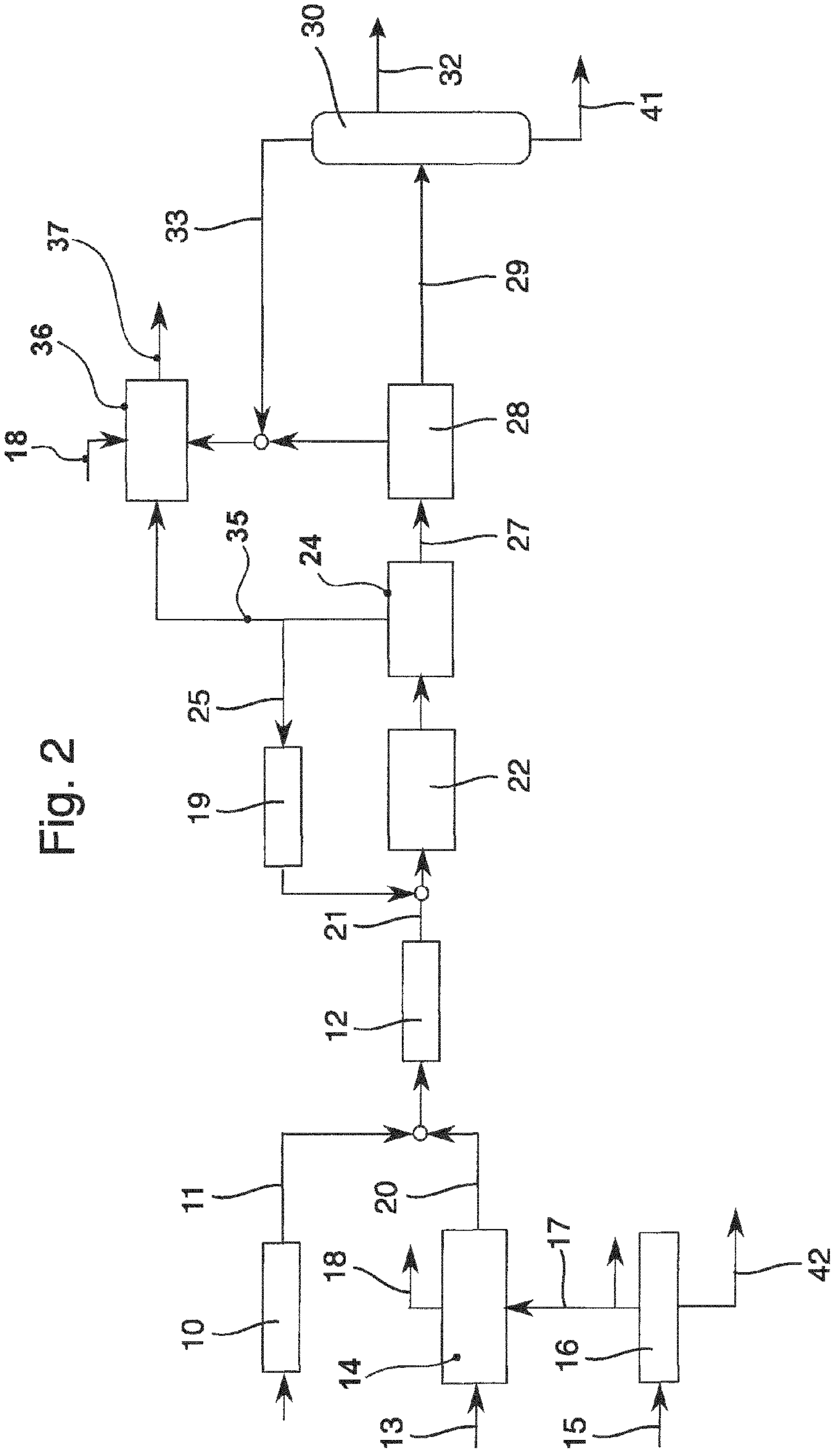
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Fig. 2

Fig. 3

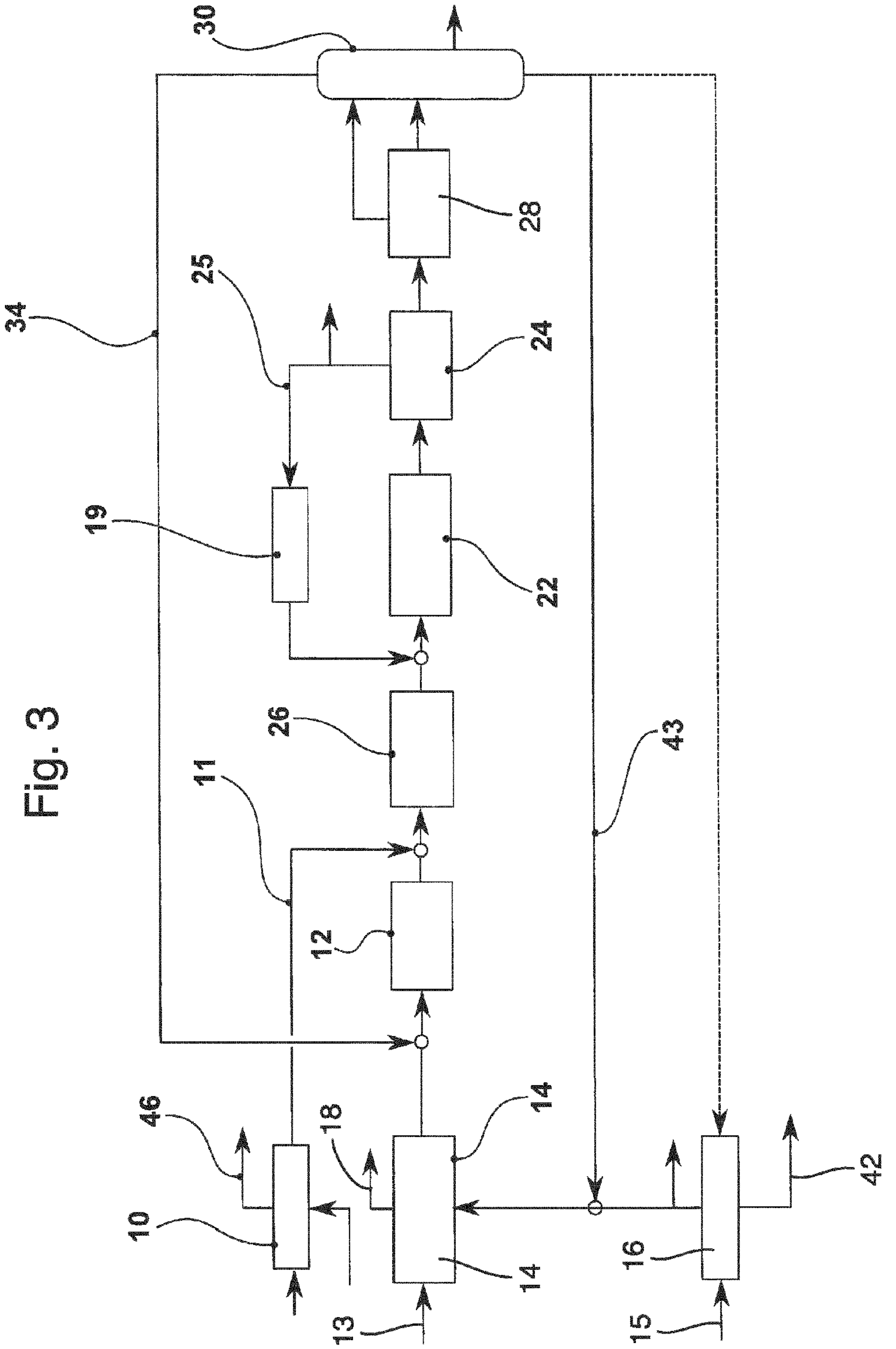

Fig. 4

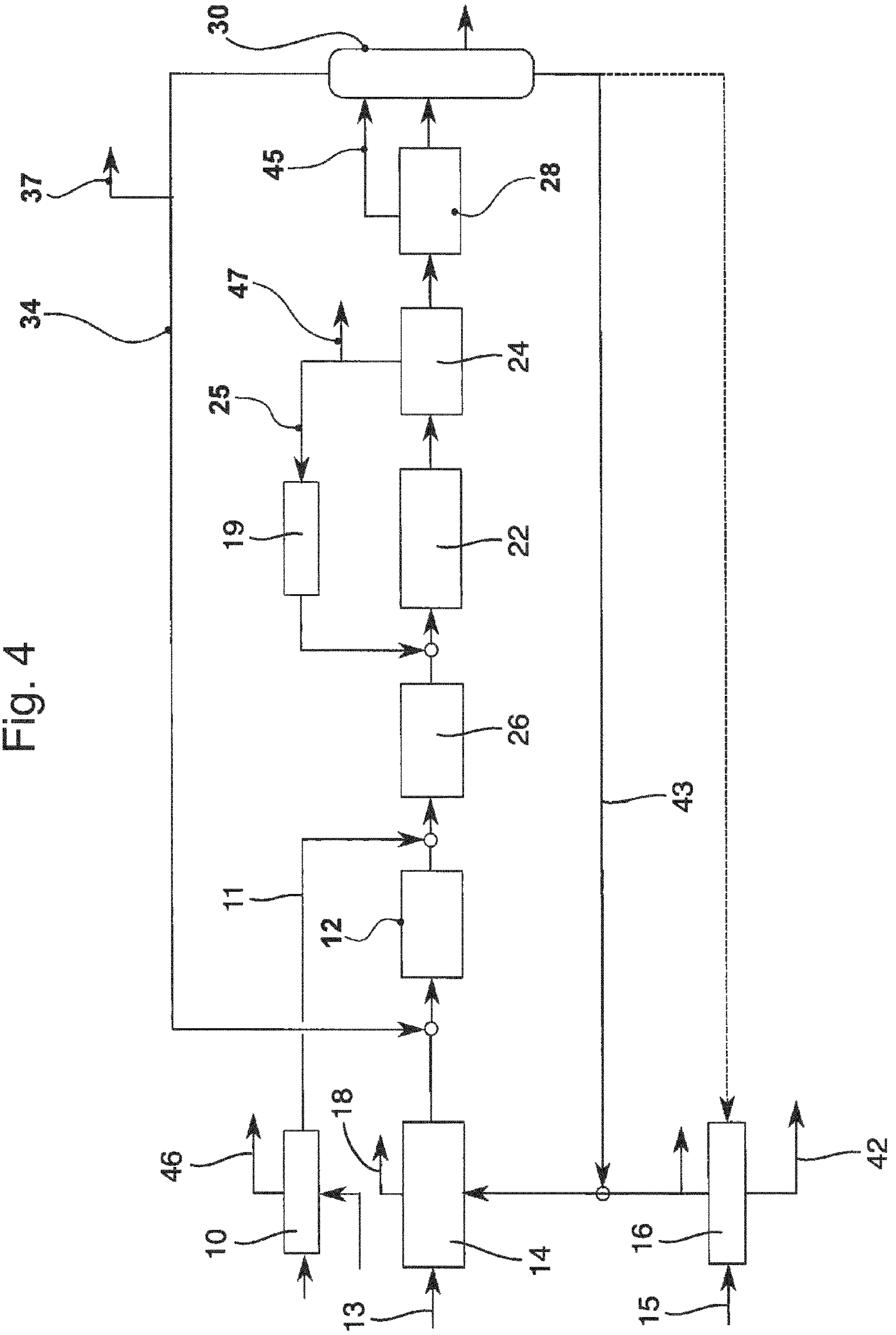

Fig. 5

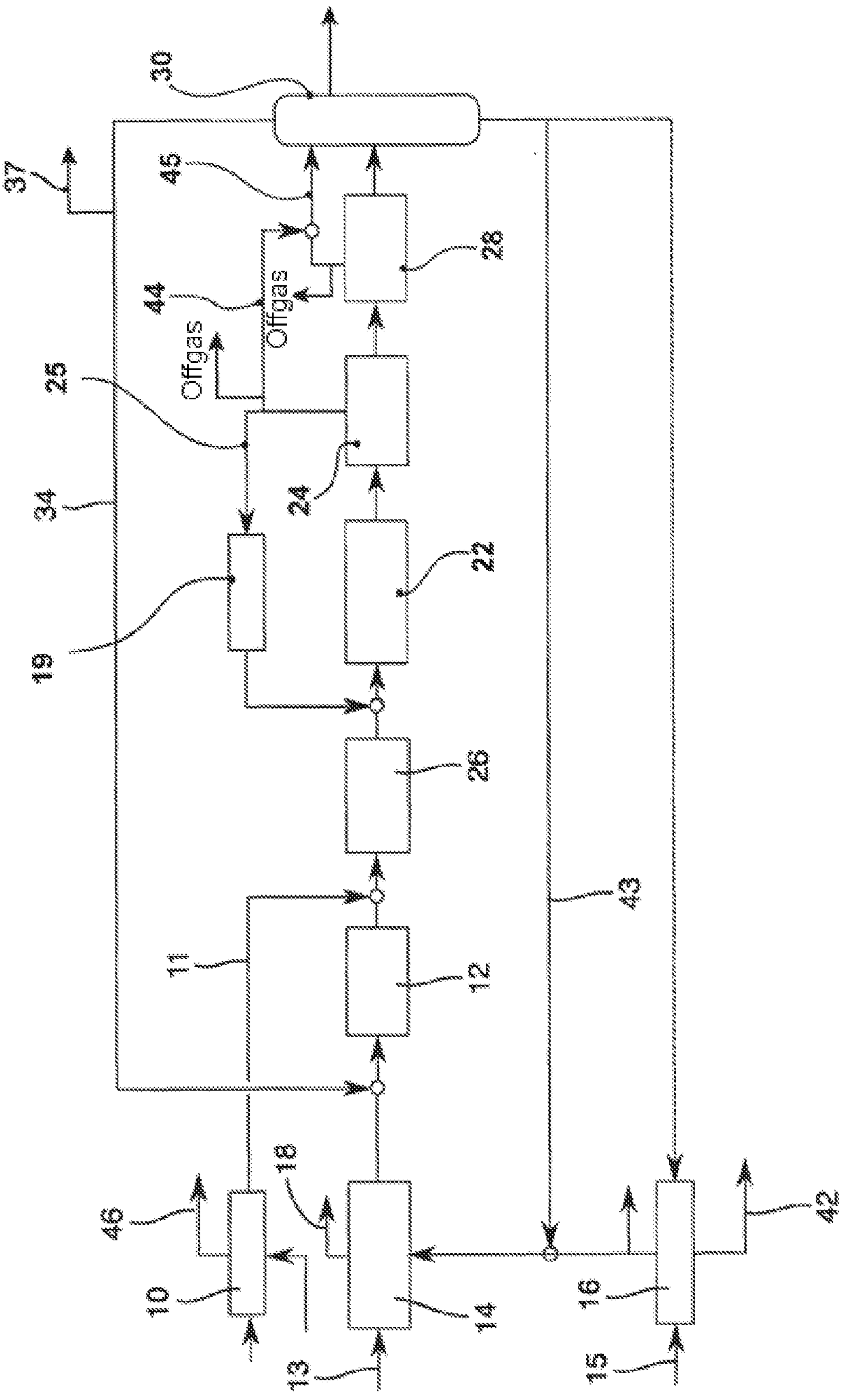
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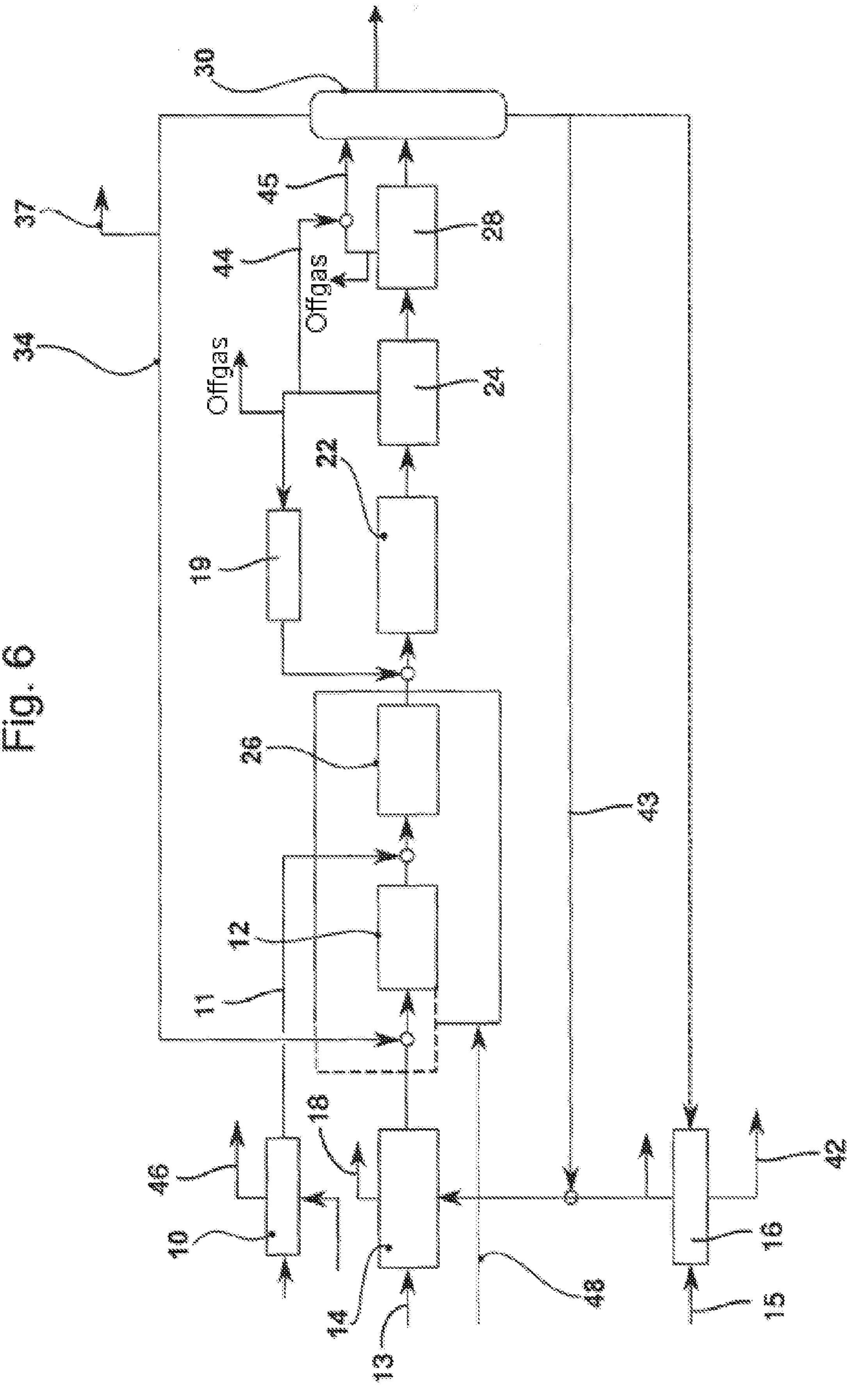
Fig. 6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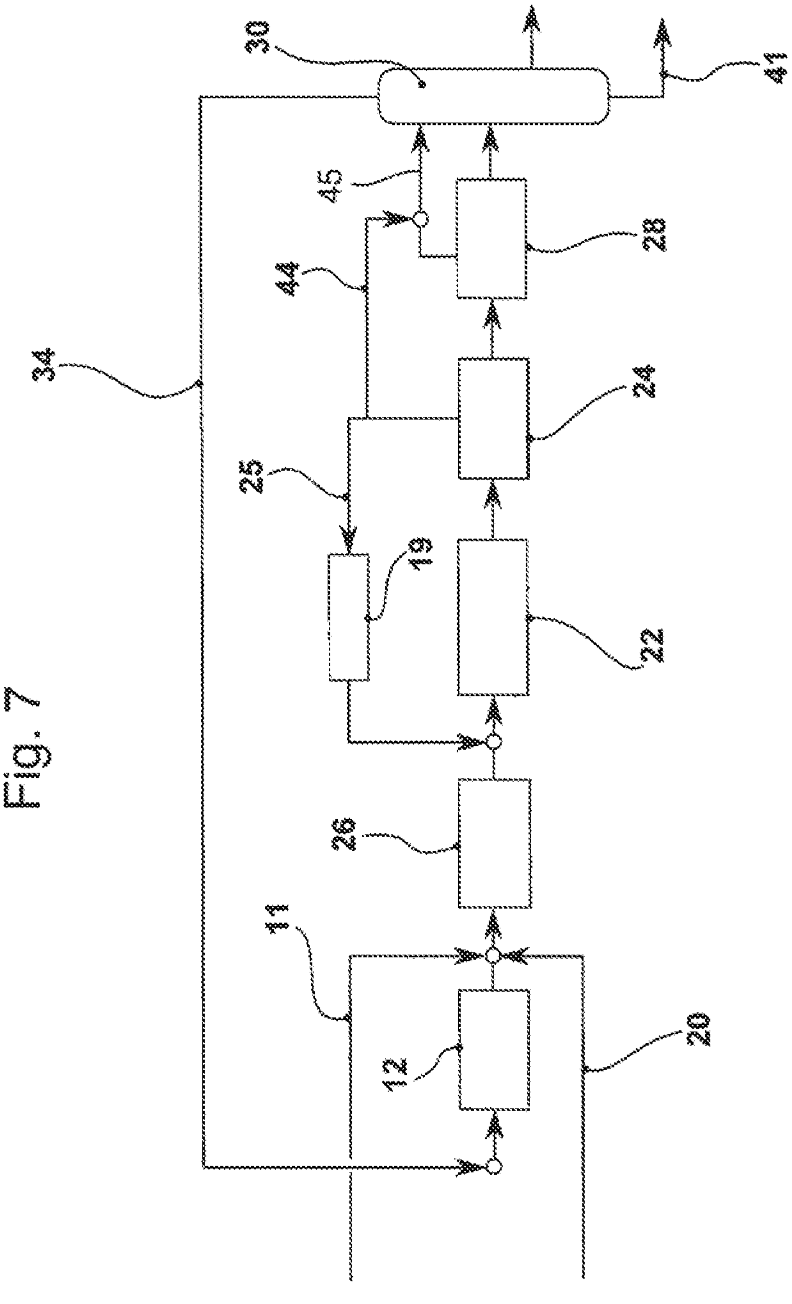

Fig. 7