

COMBINED GAS PROCESSING

The present invention relates to energetically favourable processes for processing carbon dioxide-containing gas mixtures, in particular biogas.

In many industrial and agricultural processes, for example in municipal utilities, biomass is produced in the form of waste and by-products during the processing of foodstuffs and animal feed and in forestry. Agricultural and chemical industries, as well as public utilities, have a considerable interest in the development of processes for transforming such biomass into materials with a higher economic value. Thus, biomass of this type might potentially be transformed into bioethanol, biogas or chemicals, for example by using microorganisms and/or hydrolytic enzymes. However, most current known processes have not yet found large scale application because of their high production costs and energy requirements and the consequent inherent uncertain economic feasibility. Thus, it is an aim of many technological developments to provide for an increase in efficiency. Biogas, for example, is a mixture primarily of methane and carbon dioxide, normally containing in the range 45% to 70% methane and 30% to 55% carbon dioxide. Methane is the commercially valuable product here; it is used either in situ to produce electricity or it is stored in the natural gas grid. For the latter use, though, the crude biogas has to be purified and the by-product, carbon dioxide, has to be removed. Carbon dioxide depletion is a process which consumes a lot of energy, which compromises efficiency.

The publication DE 10 2005 051 952 describes a process for the production of methane and liquid carbon dioxide from refinery gas or biogas, wherein the original gas mixture is treated in an absorption column with a scrubbing solution. The carbon dioxide is absorbed and separated by the scrubbing solution, which contains amines for absorption.

The disadvantage is that in order to obtain a product gas with a high purity or a high methane content, relatively high pressures of up to 70 bar have to be used. This makes the process uneconomic.

WO 2008/034473 describes a similar process for the purification of biogas using scrubbing, wherein carbon dioxide is removed from the biogas by absorption into a scrubbing solution.

DE 10 2008 058 114 describes a process for the purification of crude biogas, wherein hydrogen sulphide, ammonia and carbon dioxide are separated by means of hydrogen peroxide and an alkali metal hydroxide in one or two steps.

US 2011/005392 concerns the separation of carbon dioxide from a gas by means of PSA (pressure swing adsorption).

DE 199 47 339 describes a process for the purification of biogas, wherein at least two PSA separation steps are used to separate methane and carbon dioxide.

In practice, processes which are based on gas permeation differentials are often used. An example of a process of that type is described in WO 02/26359 for the separation of nitrogen and oxygen, but it is also possible for carbon dioxide and methane to be separated using suitable membranes and pressures. Examples of membranes of that type are described, for example, in US 5 674 629 or WO 2008/077837. A disadvantage of the membrane-based process is the low separation efficiency with crude biogas. In one step, only up to 20% of the gas (i.e. with biogas, less than half of the carbon dioxide fraction) is separated, and therefore that process is usually carried out in a plurality of stages (in particular three) and at high starting pressures of more than 12 bar. In each of the first two steps, 20% of the gas and in the third step, 5% of the gas (carbon dioxide) is

separated, whereupon product gases with a high purity (~97% - 98% methane) are obtained. Finally, the separated carbon dioxide gas also has to be removed, is usually transformed into a transportable form by means of a liquefaction process. Liquefaction processes are described in EP 0 646 756 A1 or US 2004/0250682 A1, for example. High pressures and low temperatures are required for liquefaction, further worsening the energy balance of the process.

In DE 10 2010 006 649, the problem of the high cost of PSA or membrane-based purification, i.e. separation of carbon dioxide from methane in biogas, was recognized. Installation of an upstream dynamic purification stage was proposed, in which carbon dioxide and methane are separated in a centrifuge because of their different masses. However, centrifuges which can produce a meaningful high purity (80% according to DE 10 2010 006 649) are high-maintenance and have to be operated in several successive stages.

US 2004/099138 A1 describes a process for the purification of raw natural gas. In one step of the process, heavy hydrocarbons are bound with a CO<sub>2</sub> absorber. The CO<sub>2</sub> may have originated from a permeate separation of CO<sub>2</sub> and methane. In this absorber step, CO<sub>2</sub> is not absorbed, but CO<sub>2</sub> is used in order to physically extract hydrocarbons from the gas.

DE 10 2008 058114 A1 concerns a unit for the purification of crude biogas. In a first step, hydrogen sulphide, ammonia and carbon dioxide are cleaned from the useful gas in an absorption column as a pre-scrubber. In a second step, the purified methane can be supplied to an adsorber in order to obtain higher levels of purity, but there were no details as to which materials bind with this adsorbent.

US 2011/219949 A1 describes a process for separating carbon dioxide from combustion gases, wherein on the one hand a

"capture step" is employed, as well as a membrane separation. These two process steps were used in parallel, i.e. not in series, as is the case with a two-step process. A first portion of the exhaust gas is supplied to the "capture step" and a second portion is supplied to the membrane.

FR 2 951 959 A1 describes a process for removing toxic substances initially and then a further step for removing other contaminants of the gas, wherein the system pressure is kept almost constant.

Thus, it is an aim of the present invention to provide a process for separating carbon dioxide from gas mixtures which is much more efficient and thus more advantageous.

In a first aspect, the invention concerns a process for removing carbon dioxide from a carbon dioxide-containing gas mixture, comprising a multistage gas purification, characterized in that the gas mixture is brought into contact with a carbon dioxide-absorbing liquid in at least one first stage to provide a prepurified gas mixture, and the prepurified gas mixture is brought into contact with a carbon dioxide adsorber or a molecular sieve in at least one second stage, in order to separate carbon dioxide from the gas mixture. In brief, the invention concerns a process wherein carbon dioxide is absorbed from a gas mixture in a gas scrubber and then, in a refining purification, more carbon dioxide is removed from the gas mixture, wherein in total, the remaining gas is of high purity. In the context of the invention, due to this combination of process steps, particularly unexpected increases in efficiency are obtained (such as, for example, a lower pressure required as well as synergistic effects between the two process steps), which are accompanied by an increase in the yield - something which is desperately needed in upgrading biogas. The absorption process of the first step and adsorption or

permeation (molecular sieve, primarily a membrane process) for the second step are serially coupled and combined, and thus give rise to heretofore unknown efficiency. In this regard, the absorption acts as a coarse upgrade and the second step as a fine-tuning for the final purification to a final concentration of the carbon dioxide-depleted product gas, in particular methane, which is thus enriched. Both processes are independently known per se, but in combination in this implementation and with this efficiency, they have never been used together prior to the present invention.

The invention also concerns an apparatus with a gas scrubber (or a gas-liquid contactor) with an inlet for a gas mixture, inlets and outlets for a scrubbing solution, an outlet for a prepurified gas mixture, and with a carbon dioxide adsorption unit (for example PSA) or a molecular sieve unit (for example membrane unit) for separating carbon dioxide from the prepurified gas mixture. This apparatus is suitable for or designed for carrying out the process of the invention. Further aspects are defined in the claims. The embodiments described here concern both the process and the apparatus, for which means for implementing the individual features of the process can be provided. The apparatus and its parts can be used in the process of the invention. All of the embodiments can be combined with each other - even in the second stage for which examples of alternatives are provided herein (adsorption or molecular sieve technology), so that both variations can be deployed in parallel or in series.

In the first stage of the invention, large quantities of carbon dioxide are chemically absorbed; preferably, the capacity is provided for absorbing at least 15% of the gas mixture. For a fraction of carbon dioxide in the gas mixture (for example in biogas) of 45%, then, one third of the carbon dioxide contained in the gas mixture can be absorbed. Preferably, at least 18%, particularly preferably at least

20%, at least 25% or at least 30% of the gas mixture can be absorbed. With respect to the carbon dioxide fraction, at least 25%, preferably at least 30%, at least 35%, at least 40%, at least 45%, at least 50%, at least 55%, at least 60%, at least 65%, at least 70% or at least 75% or at least 80% of the carbon dioxide of the gas mixture is absorbed in this first state. Preferably, this first stage for carbon dioxide removal is free from hydrogen peroxide or other oxidants. All of the percentages are given with respect to the gas mixture as volume percentages. If the gas mixture is a methane-containing gas, such as biogas, in this first stage, the methane fraction can be raised to between 75% and 92%, preferably between 80% and 90%, in particular to approximately 85%.

The first stage herein is also known as gas scrubbing and the liquid for the first stage is also known as the scrubbing solution (liquid). Here, the stream of gas is brought into contact with a stream of liquid in order to absorb carbon dioxide from the gas stream into the liquid. Methane should not be or only slightly be absorbed from the gas mixture by the liquid, for example by less than 5%, preferably less than 1%. The liquid is preferably an aqueous liquid, in particular water. The liquid may contain at least 50% or at least 80% water as a solvent.

Separation by scrubbing means that the carbon dioxide is bound in the liquid in the liquid form, without having to carry out a complicated (cryogenic) liquefaction. The bound carbon dioxide can thus be transported to any location for upgrading. As an example, the carbon dioxide as described in WO 2006/006164 can be used in order to produce a fuel by reaction with hydrogen after desorption from the absorbent (for example  $K_2CO_3$ , but also other known substances such as amines or bases).

As an example, the liquid may be water, which absorbs carbon dioxide, preferably under high pressure (for example 8 - 30 bar). Higher absorptions can be obtained using carbon dioxide-absorbing substances which bind carbon dioxide chemically. Preferably, the liquid contains a carbon dioxide-absorbing substance of this type. Carbon dioxide-absorbing substances have been known for a long time; examples are carbonate, hydrogen carbonate or bicarbonate-forming agents such as, for example, lime, dolomite,  $\text{CaO}$ ,  $\text{Ca(OH)}_2$ ,  $\text{Me}_2\text{CO}_3$ , wherein Me is a single-valency metal ion (forms 2  $\text{MeHCO}_3$  with water and  $\text{CO}_2$ ), bases or amines, in particular alkyl- or alcoholamines, such as those described in DE 10 2009 056 661 A1. Preferably, Me is K or Na. Examples of suitable amines are MEA (monoethanolamine), DEA (diethanolamine), TEA (triethanolamine), diethyldiamine and 1,4-diethylenediamine (piperazine). A carbonate (preferably  $\text{K}_2\text{CO}_3$ ) together with an amine as an inoculant, preferably piperazine, may be used. The inoculant is used in small doses and catalytically increases the absorption of  $\text{CO}_2$  by means of the carbonate. Preferably, an amine, in particular a diamine such as piperazine, is used as the (primary)  $\text{CO}_2$ -absorbing agent. This type of application is possible without carbonate-forming agents. The amine is preferably used in quantities of 30-60% (% by weight) of the liquid. Preferably, however, a carbonate is used to regulate the pH. Examples of possible pH values are a pH of 7-12, preferably a pH of 8-11. As will be explained in more detail below, the liquid can readily be regenerated, whereupon the  $\text{CO}_2$  is released once again. To this end, a desorber may be installed in the apparatus. Thus, for example, the heat from a thermal power station can be used efficiently. When using suitable absorption means, in particular amines, it is not necessary to operate at high pressures. Preferably, absorption is carried out at about atmospheric or ambient pressure, for example at only slight overpressures, preferably at an overpressure (pressure above atmospheric or ambient pressure) of up to 800 mbar, particularly preferably

up to 500 mbar, in particular up to 200 mbar. Particularly preferably, no caustic bases (for example KOH) and then acids (for example  $\text{H}_2\text{SO}_4$ ) are used, as these are complicated (high pressures) and result in toxic products.

Preferably, in the first stage the liquid is counter-current to the gas mixture. Thus, the process is continuous, wherein the gas mixture is continuously introduced into the gas scrubber, prepurified gas is discharged and liquid is continuously introduced and discharged. The liquid which is discharged contains large proportions of chemically absorbed carbon dioxide, for example as the hydrogen carbonate.

In order to increase the absorption of carbon dioxide by the liquid, for example by the substance, the surface area between the gaseous and the liquid phase is increased as much as possible. To this end, for example, the liquid in the first stage can be atomized, or the gas mixture can be fed through a tank with the liquid so as to form gas bubbles, or the gas mixture can be brought into contact with the liquid via a gas-permeable and liquid-tight membrane.

The first stage can be used to carry out efficient binding of carbon dioxide in the liquid form - without having to use a complicated liquefaction procedure using high pressures or low temperatures to liquefy the  $\text{CO}_2$ . Preferably, the first stage is also used in order to bind carbon dioxide in the liquid phase separated in the second stage. To this end, carbon dioxide separated in the second stage, in particular carbon dioxide gas, can be supplied to the first stage. Carbon dioxide liquefaction can thus be dispensed with, or the apparatus of the invention preferably has no carbon dioxide liquefaction system, although naturally, in certain embodiments, this can easily be provided. Preferably, the apparatus of the invention has a gas line which feeds separated carbon dioxide from the carbon dioxide adsorption unit or the molecular sieve unit to the gas scrubber.

Insofar as carbon dioxide liquefaction is carried out away from of the first stage, this can be carried out cryogenically. In this, carbon dioxide is separated from the product gas by cooling (cryogenic separation), if necessary under pressure as well. In this, carbon dioxide is preferably also liquefied, a procedure which makes separation from the product gas easier. A process of this type is, for example, disclosed in EP 0 646 756 A1 or US 2004/0250682 A1 and can be deployed in the invention. Cryogenic separation is based on the different boiling points of methane and carbon dioxide. Normally, the biogas mixture is compressed to an overpressure of more than 10 bar, preferably at least 12 bar, at least 14 bar, at least 16 bar, at least 17 bar, at least 18 bar, at least 19 bar, at least 20 bar or more and cooled to a temperature of less than or equal to the boiling point of CO<sub>2</sub> at this pressure, for example to -40°C. By means of a gas stripper, the small amounts of methane dissolved in the liquid carbon dioxide can be separated as necessary, so that very pure liquid CO<sub>2</sub> is obtained.

The second stage is preferably a membrane separation. In the apparatus of the invention, the carbon dioxide adsorption unit is preferably a pressure swing adsorption unit or the molecular sieve unit is a membrane unit for membrane separation. Membranes, like other possible molecular sieves, can be used to allow good selection of carbon dioxide over methane from the gas mixture. The membrane is provided between two exhaust streams, a carbon dioxide-depleted stream and a carbon dioxide-enriched stream. The zones of the two streams in the unit may, for example, be delimited by providing hollow fibres through which (or round which) the prepurified gas mixture is fed. The exhaust gas stream from the interior of the hollow fibres and the exhaust gas stream around the hollow fibres form the two separated product gases.

A process for membrane separation is described, for example, in US 2009/156875 and can be deployed in the invention. Suitable membranes for the separation of CO<sub>2</sub> and methane are described in patent US 5 674 629, for example polyimide membranes. In brief, membrane separation exploits the different membrane permeation properties of various gas components, including methane and CO<sub>2</sub>, in order to separate them from each other. In polyimide membranes, the permeation difference for methane and CO<sub>2</sub> is relatively high; CO<sub>2</sub> passes through the membrane much faster. With existing membranes, the following series of permeation behaviours is observed, from fast to slow: H<sub>2</sub>O, H<sub>2</sub>, He, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>. It is generally possible to obtain product concentrations of 99% methane or carbon dioxide with only membrane separation stages. With an increasing concentration in the pure gas, however, the energy consumption increases for gas compression and a multistage process profile is required.

Because of the coarse purification of the invention in the first stage, it is not necessary to carry out this second stage in a multistage manner as well. This means, for example, a single or two-stage molecular sieve separation (in particular membrane separation) or adsorption separation (for example PSA) is sufficient. In preferable embodiments of the present invention, then, a separation in the second stage (for example a membrane separation) is single or dual-stage as a maximum.

Alternatively (or in addition) to membrane separation, adsorption, for example by PSA, may be carried out. In PSA, carbon dioxide (or alternatively methane) is adsorbed discontinuously, wherein a carbon dioxide-depleted product gas is produced and subsequently, carbon dioxide (or methane) is desorbed again, wherein a carbon dioxide-rich gas - separately from the carbon dioxide-depleted product gas - is obtained. Two adsorbers are usually employed, wherein adsorption/desorption is alternated between the two

adsorbers. Adsorbers are known, for example from US 2011/005392. The adsorbers may also be supplemented by or replaced with chemical absorbers, which are also suitable for discontinuous absorption or desorption. Preferably, switching between absorption and desorption is accomplished by applying a different pressure. As an example, a high pressure (overpressure) can be used for absorption and a low pressure can be used for desorption (underpressure, vacuum), for example by adjustment at the product gas outlet. Alternatively or in addition - depending on the adsorber material - adsorption and desorption can be regulated by using different temperatures.

Normally, the second stage is carried out at overpressures (pressures of more than 1 bar) of the prepurified gas mixture which is introduced. Since the second stage must only be single- or dual-stage, lower pressures can be employed than in the usual membrane separation process. Preferably, the second stage is operated at gas pressures for the prepurified gas mixture of up to 10 bar, preferably up to 8 bar, in particular from up to 7 bar, particularly preferably between 1.5 bar and 6.5 bar, highly preferably 2 to 6 bar. Preferably, the membrane separation is operated at 4 to 7 bar, particularly at approximately 6 bar. A PSA separation is preferably operated at pressures between 1.5 bar and 4.5 bar, in particular at approximately 3 bar. By way of comparison, the first stage is preferably operated at gas pressures between 0.8 bar and 1.4 bar, but the first stage may also be operated at higher pressures. These details regarding pressure should be understood to mean absolute pressures and are preferably obtained by compression of the gas mixture. The compression ratios correspond to the given pressures; thus, for example, in order to obtain a pressure of 3 bar, a compression of 1:3 is provided. In the apparatus of the invention, for this purpose, a gas compressor to compress the prepurified gas

mixture can be provided before the inlet into the carbon dioxide adsorption unit or into the membrane unit.

The two-stage process of the invention for carbon dioxide separation results in a high purity for the product gas in which, for example, only 0.1% to 5%, or only up to 3% of the carbon dioxide remains. The combination of the invention of a coarse chemical purification (1<sup>st</sup> stage, absorption) and a primarily physical refining purification (2<sup>nd</sup> stage, adsorption or sieve separation) means that this is achieved with an unexpectedly low consumption of energy. Preferably, the gas mixture contains methane, which is purified to a purity of at least 96%, preferably at least 98% by the stages of the process of the invention.

Preferably, the gas mixture is a methane-containing gas, preferably of biogenic origin ("biogas") which, for example, can be obtained by fermentation of biomass under anaerobic conditions. The biogas can be fed from the biomass fermenter via a line and optionally one or more prepurification units to the gas scrubber.

Biogas is produced by the natural process of the microbial decomposition of organic materials under anoxic conditions. In this, microorganisms transform the carbohydrates, proteins and fats contained in it into the main products methane and carbon dioxide. Processes for fermentation to form biogas are described, inter alia, in WO 03/06387 A2, EP 0 646 756 A1, WO 2009/137948 A2 and DE 3 243 103 A1, and can be used in accordance with the invention for fermentation of the biomass.

Prior to preparing biogas, the water-saturated gas mixture consists of the main components methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>). There are also usually traces of nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>), hydrogen sulphide (H<sub>2</sub>S), carbonyl sulphide (COS), hydrogen (H<sub>2</sub>) and ammonia (NH<sub>3</sub>). In order to upgrade

biogas, the methane fraction is the most important because burning it releases energy.

Further gas purification steps as pre- or post-purification - before or after the first or second stages of the invention - are possible. As an example, in certain embodiments, prior to entering the first stage the gas mixture is prepurified in order to remove sulphur or sulphur compounds, in particular hydrogen sulphide ( $H_2S$ ) and/or ammonia and/or silanes and/or heavy metals (which can be introduced by fermentation of contaminated organic waste in the gas). This step is distinct from the ("first") absorption step cited above for  $CO_2$  absorption with the special scrubbing solution. The prepurification step is intended to remove contamination and toxins so that the subsequent steps are not compromised. The use of the scrubbing solution of the invention in such a prepurification step would be of little assistance, since the continuous process of absorption and regeneration would not be possible, since otherwise the pollutants would become concentrated. The valuable scrubbing solution would have to be discarded.

Examples of additional purification steps of this type are ammonia scrubbing (for example with water to remove ammonia by forming soluble ammonium) or activated carbon filtration to remove sulphur compounds, in particular  $H_2S$ , and heavy metals. In this case, the ammonia in the gas mixture can be reduced to a few ppm (for example 7 ppm) or less.

The enriched carbon dioxide in the (scrubbing) solution of the first step of the invention may (optionally) be transported and then desorbed again, for example - depending on the liquid or the absorbing substance therein - chemically or, preferably, by increasing the temperature (for example for hydrogen carbonates). Preferably, the carbon dioxide obtained is used for upgrading in glasshouses

greenhouses or hothouses, where it is taken up by plants. This is a true CO<sub>2</sub> sink which does not harm the environment.

In general, continuous circulation of the absorber liquid can be established. After the first step, the liquid which contains chemically bound CO<sub>2</sub> can be supplied continuously to a desorption step (in a desorber), wherein the liquid is regenerated for use again as a CO<sub>2</sub> absorber in the first step. This desorption may be accomplished using increased temperatures (for example 65-60°C) and/or low pressures (for example less than 0.5 bar absolute, preferably less than 0.3 bar absolute, particularly preferably approximately 0.2 bar absolute). It is also possible to evaporate the water and the amine during regeneration.

The methane obtained after the first or after the second stage or a portion of the original gas mixture can be used to operate a thermal power station. In the thermal power station, electrical energy and heat are produced, preferably using a gas turbine. Heat produced by combustion, in particular the waste heat from the power station, is preferably used for desorption of carbon dioxide from the liquid or the adsorbent substances. In this manner, the liquid is regenerated and can be used again in the process of the invention. Preferably, regeneration of the liquid/CO<sub>2</sub> desorption is carried out at a temperature between 60-95°C, preferably from 65°C to 85°C, which is preferably accomplished by thermal coupling with the thermal power station. The major proportion of the purified methane is stored in the natural gas grid. In this manner, the process of the invention can exploit many synergistic effects, thus resulting in high efficiency, wherein in addition, economically valuable products can be discharged.

The present invention will now be described in more detail with the aid of the accompanying drawings and examples; the

specific embodiments of the invention are non-limiting in nature.

In the figures,

Figure 1 diagrammatically shows an apparatus for gas purification and concentration of the product gas with an external source of heat;

Figure 2 diagrammatically shows an apparatus for gas purification and concentration of the product gas with CO<sub>2</sub> liquefaction of the CO<sub>2</sub> from the gas scrubber and the membrane process;

Figure 3 diagrammatically shows an apparatus for gas purification and concentration of the product gas with upgrading of the CO<sub>2</sub> from the gas scrubber in a glasshouse;

Figure 4 represents the components of a gas turbine;

Figure 5 diagrammatically shows an apparatus for gas purification and concentration of the product gas with liquefaction of the CO<sub>2</sub> for the production of a CO<sub>2</sub> gas with a very low residual methane content integrated with a gas turbine for the production of heat and for the production of electrical power;

Figure 6 is a simplified representation of a BTTP (bio or block-type thermal power station);

Figure 7 diagrammatically shows an apparatus for gas purification and concentration of the product gas with liquefaction of the CO<sub>2</sub> for the production of a CO<sub>2</sub> gas with a very low residual methane content integrated with a BTTP for the production of heat and for the production of electrical power;

Figure 8 diagrammatically shows an apparatus for gas purification and concentration of methane with a scrubbing process;

Figure 9 diagrammatically shows an apparatus for gas purification and concentration of the product gas with a liquefaction of the CO<sub>2</sub>.

In the Figures, identical or corresponding zones, components, sets of components or process steps are indicated by the same reference numeral. The directions of flow in the lines are indicated with arrows.

#### Examples

Figure 1 shows the process of the invention, wherein crude biogas is introduced via the pipeline 1. The crude biogas is compressed with the pre-compressor 2 and fed to the ammonia scrubber 3, then fed to the activated carbon filter 4. The gas scrubber of the invention is shown in box 100. External heat is added via the heat exchanger 5, the CO<sub>2</sub> (carbon dioxide) separated from the scrubbing process is discharged via the line 6. The biogas, concentrated in methane, is cooled via the heat exchanger 7 so that water contained in the gas is eliminated by dropping below the dew point. Next, high compression 8 is carried out so that the biogas can be fed to the membrane 9 as a feed. The permeate is concentrated biomethane which, together with the residual methane 10, provides the biomethane 14. The CO<sub>2</sub> separated in the membrane process 13 is fed for CO<sub>2</sub> liquefaction, 101, from which the liquid CO<sub>2</sub> is stored in the tank 11.

Figure 2 shows the process of the invention for the production of biomethane as described in Figure 1. The CO<sub>2</sub> separated from the gas scrubber is fed via the throttle valve to the CO<sub>2</sub> liquefaction system and the liquid CO<sub>2</sub> is stored in tank 11.

Figure 3 shows the process of the invention for the production of biomethane as described in Figure 1. The CO<sub>2</sub> separated out in the gas scrubber is supplied to a glasshouse or greenhouse or hothouse via the throttle valve and then processed to sugar, starches and oxygen in the plants.

Figure 4 shows a gas turbine consisting of an air inlet and muffle 19, a compressor 20, which is connected to the turbine 23 via a shaft, which former is connected to a generator 24. The compressed combustion air is heated via the regenerator 21 and fed to the combustion chamber 22. The hot exhaust gas is decompressed via the turbine and the exhaust gas is fed to the regenerator.

Figure 5 shows the inventive integration of the gas turbine into the process wherein, via the valve 17, an appropriate fraction of crude biogas is fed to the gas turbine combustion chamber 22. The exhaust heat of the exhaust gas from the regenerator 22 is then sent via the heat exchanger 18 to the hot water circuit which provides the heat necessary for the desorber in the gas scrubbing via the heat exchanger 5. The remaining exhaust heat in the exhaust gas is converted into electricity. Electrical power for personal requirements for storage in the local electrical grid is produced via the generator 24.

Figure 6 shows the simplified layout of a BTTP with the supply of crude biogas 25 to the BTTP (bio-thermal power station) 28 and the exhaust gas 31. In the exhaust gas line is an exhaust heat exchanger 30. The low temperature heat from the oil and cooling water circuit is utilized in the heat exchanger 27.

Figure 7 shows the inventive integration of a BTTP 28 for the production of electrical energy and heat. The exhaust heat 30 from the exhaust gas is used for the scrubbing

process 100. The crude biogas 25 is fed to the BTTP via the valve 17. The cooled exhaust gas 31 is released to the environment.

Figure 8 shows the inventive integration of a scrubbing process with the supply of crude biogas 44 and discharge of the crude biogas 45 from the absorber. The absorber 36 is charged with the scrubbing agent which absorbs  $\text{CO}_2$  from the crude biogas as it flows through. The pump turbines 37, 42, 43, consisting of the pump 42, turbine 42 and motor 43, compresses the scrubbing agent to a desorption pressure. The scrubbing agent is fed to a regenerator 40 and then via a heat exchanger 42 to the desorber 39 where regeneration of the scrubbing agent is carried out. The separated  $\text{CO}_2$  6 is cooled via the heat exchanger 41.

Figure 9 shows the integration of the invention of a liquefaction process where the vaporous  $\text{CO}_2$  is brought to a pressure of 18 bar via a compressor 32, the compressed  $\text{CO}_2$  gas is cooled via the heat exchanger 34 to a temperature of  $-25^\circ\text{C}$ . The liquid  $\text{CO}_2$  is stored in the tank 11, the gaseous  $\text{CH}_4$  is discharged via the line 35.

This unit can be used to show that firstly, economical biomethane (methane content  $> 96\%$ ) can be obtained in an energetically favourable manner. Scrubbing the gas with the liquid usually results in prepurification to methane contents of 85% and the membrane stage results in a purification to the desired 96% - all in just one step!

An essential factor is the electrical energy consumption in the various steps of the process. Electrical energy is the most expensive but most versatile form of energy. Thus, if possible, the electrical energy should be minimized and synergistic effects exploited in order to change from operational steps which consume a lot of energy to other

forms of energy which are preferably already present in the process.

The essential factor as regards the electrical energy consumption is the operation of compressors or gas compressors. These have to be constructed to withstand the pressures necessary for membrane permeation (counter-pressure).

In a prior art unit with the usual 3-stage membrane purification, for example, an electrical energy of approximately 0.33 kW per m<sup>3</sup>/h of crude biogas is required (m<sup>3</sup> under normal conditions, also known as "normal cubic metre", formerly "Nm<sup>3</sup>"). This means that, per cubic metre of crude biogas under normal conditions, 330 Wh of electrical power is required in order to transform crude biogas into biomethane, and in which in addition, many gas membranes have to be used (~ 60 membrane modules).

In contrast, the process of the invention can be used to carry out energetically favourable intense purification using a membrane, since biogas which has already been prepurified is used.

Thermal scrubbing results in concentration of the methane content from 50% to 85% methane. For this coarse scrubbing process, thermal scrubbing is very well suited and also energetically favourable, since electrical energy is only required in minimal amounts and the thermal energy for regeneration of the scrubbing solution is available from equipment which is normally present in a biogas unit and can be diverted from it - for example in a thermal power station, such as a BTTP. In the subsequent intense purification in a physical separation process, membrane permeation is carried out.

In comparison, the crude biogas in the combination process of the invention only requires 0.22 kW/m<sup>3</sup>/h of electrical energy (m<sup>3</sup> under normal conditions), i.e. a saving of 30% of expensive electrical energy (pure energy). In addition, in the single membrane permeation step, fewer membrane modules are necessary (~ one third fewer). Electrical energy as pure energy is expensive and has been used in the invention with the utmost efficiency. This means that for the first time, the biogas process is profitable.

Although this has only been illustrated for membrane separation, the same is true for other physical adsorbent materials or a PSA unit which has similar requirements and energy balances.

CLAIMS

1. A process for removing carbon dioxide from a carbon dioxide-containing gas mixture, comprising a multistage gas purification, characterized in that the gas mixture is brought into contact with a carbon dioxide-absorbing liquid in at least one first stage, thereby providing a prepurified gas mixture, and the prepurified gas mixture is brought into contact with a carbon dioxide adsorber or a molecular sieve in at least one second stage, thereby providing carbon dioxide remaining in the prepurified gas mixture.
2. The process as claimed in claim 1, characterized in that the second stage comprises a membrane separation.
3. The process as claimed in claim 2, characterized in that the membrane separation is carried out with at most one or two stages.
4. The process as claimed in any one of claims 1 to 3, characterized in that the second stage is carried out at gas pressures for the prepurified gas mixture of up to 10 bar, preferably up to 8 bar, particularly preferably up to 7 bar, more particularly preferably between 1.5 bar and 6.5 bar.
5. The process as claimed in one of claims 1 to 4, characterized in that the first stage is carried out at gas pressures of between 0.8 bar and 1.4 bar.
6. The process as claimed in one of claims 1 to 5, characterized in that in the first stage, the liquid flows as a counter-current to the gas mixture.
7. The process as claimed in one of claims 1 to 6, characterized in that the liquid in the first stage is

atomized, or in that the gas mixture is fed through a tank with the liquid with the formation of gas bubbles, or in that the gas mixture is brought into contact with the liquid via a gas-permeable and liquid-impermeable membrane.

8. The process as claimed in one of claims 1 to 7, characterized in that carbon dioxide, in particular carbon dioxide gas separated in the second stage is fed to the first stage.
9. The process as claimed in one of claims 1 to 8, characterized in that prior to its introduction into the first stage, the gas mixture is prepurified in order to remove sulphur or sulphur compounds, and/or ammonia, and/or heavy metals.
10. The process as claimed in one of claims 1 to 9, characterized in that the carbon dioxide-absorbing liquid contains a carbon dioxide-absorbing substance, preferably selected from a water-soluble carbonate, hydrogen carbonate or bicarbonate-forming agent, or a base or an amine.
11. An apparatus suitable for carrying out a process in accordance with claims 1 to 10, having a gas scrubber with an inlet for a gas mixture, inlet and outlet for a scrubbing solution, an outlet for a prepurified gas mixture, and with a carbon dioxide adsorption unit or a molecular sieve unit for separating carbon dioxide from the prepurified gas mixture.
12. The apparatus as claimed in claim 11, characterized in that the carbon dioxide adsorption unit is a pressure swing adsorption unit, or the molecular sieve unit is a membrane unit.

13. The apparatus as claimed in claim 11 or claim 12, having a gas compressor for compressing the prepurified gas mixture before introduction into the carbon dioxide adsorption unit or into the membrane unit.
14. The apparatus as claimed in one of claims 11 to 13, having a gas line which feeds carbon dioxide separated from the carbon dioxide adsorption unit or the molecular sieve unit to the gas scrubber.
15. The apparatus as claimed in one of claims 11 to 14, having a biomass fermenter from which biogas is fed to the gas scrubber via a line and optionally via one or more prepurification units.