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(54) **Title**: A PROCESS FOR ENRICHING BIOGAS FROM SEWERAGE PLANTS OR AGRICULTURAL BASIC INDUSTRIES IN METHANE AND AN APPARATUS FOR CARRYING OUT THE SAME.

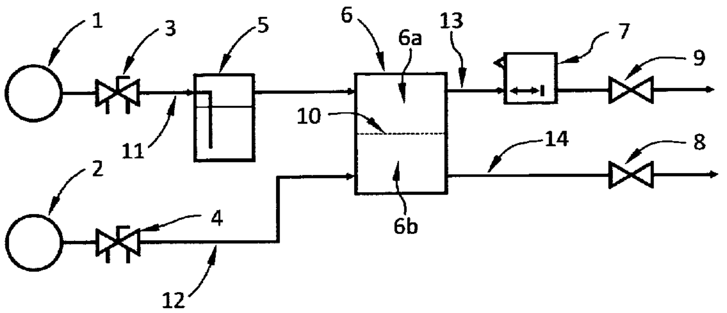

FIG. 1

(57) **Abstract**: A process for enriching the biogas from sewerage plants or agricultural basic industries in methane, which comprises introducing the biogas to one side of a liquid water membrane which is immobilized in/on a porous hydrophilic support, wherein a stream enriched in methane and depleted in carbon dioxide, sulfane and further undesirable components contained in the biogas is obtained as a retentate, and a stream depleted in methane and enriched in carbon dioxide and further undesirable components contained in the biogas components is obtained as a permeate. As liquid membrane water alone is used, and the losses of water from said membrane, which are caused by driving away said water in said permeate stream, are compensated by saturating said introduced biogas with steam at a temperature which is higher than the temperature at which said membrane separation takes place whereupon said steam is condensed when said biogas is cooled in said membrane. An apparatus for carrying said process which comprises a membrane separator (6), which is divided by a liquid water membrane immobilized in a porous hydrophilic support, into a retentate space (6a) and a permeate space (6b), said retentate space (6a) being connected with supply fittings (1, 3, 5, 11) for said gaseous mixture and discharge fittings (13, 7, 9) for said retentate stream whereas said permeate space is connected with discharge fittings (8, 14) for said permeate stream, wherein a saturator (5) for saturating said biogas with said steam is inserted into the supply tubing (11) for the introduced biogas.

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A process for enriching biogas from sewerage plants or agricultural basic industries in methane and an apparatus for carrying out the same.

Field of Invention

The present invention relates to a process for enriching the biogas from sewerage plants or agricultural basic industries in methane. The process comprises introducing the biogas to one side of a liquid water membrane which is immobilized in/on a porous support. A stream enriched in methane and depleted in carbon dioxide and further undesirable components contained in the biogas is obtained as a retentate and a stream depleted in methane and enriched in carbon dioxide and further components is obtained as a permeate. The invention also relates to an apparatus for carrying out said process. The apparatus comprises a membrane separator, which is divided by a water liquid membrane immobilized in/on a porous support, into a retentate space and a permeate space. The retentate space is connected with supply fittings for the biogas and discharge fittings for the retentate stream whereas the permeate space is connected with discharge fittings for the permeate stream. The proposed separation process makes possible to use biogas in a more effective manner.

Background Prior Art

Individual gas components have been separated by different separation techniques. These techniques include e.g. membrane processes, adsoprption, absorption and cryogenic distillation. Enriching the biogas from sewerage plants landfill or agricultural basic industries in methane has acquired great economic importance.

Biogas is a gaseous mixture which is formed by anaerobic digestion of the residues of plant and animal origin. During said process, biomass is decomposed by the action of bacteria in the absence of oxygen to form particularly methane, carbon dioxide and small amounts of further gases, such as ammonia or sulfane. The methane content of biogas ranges from 50 to 70 % by volume (W. Kossmann, U. Pönitz et. al.: Biogas Basics, Biogas Digest vol.1, project of Information and Advisory Service on Appropriate Technology (ISAT)).

It is just methane, which is also the main component of natural gas, that makes possible to use biogas as an ecological fuel.

At present, biogas is only used in the so-called cogeneration units (Combined heat and power plant) for the combined production of electricity and heat, in the Czech republic. However, in other countries, such as Sweden or Germany, methods of processing biogas so as to obtain a product similar to natural gas, which could be used for instance as a fuel for transportation vehicles, have been put into operation. (M. Persson, O. Jonssen, A. Wellinger, Biogas Upgrading to Vehicle Fuel Standards and Grid Injection. IEA Bioenergy task 37, Impressium, 2006)

The above mentioned method of biogas processing requires however a multi-step procedure which comprises drying biogas and removing aggressive gases therefrom, as well as carbon dioxide separation. The following procedures are e.g. used during said purification (compare the citation M. Persson et al., above and moreover, also M. Persson: Evaluation of Upgrading Techniques for Biogas. School of Environmental Enginering, Lund University, Sweden, 2003):

- drying – cryogenic units, adsorption on silicagel or lyophilization;
- sulfane removal – scrubbing with NaOH solution, adsorption on active carbon with further oxidation,
- ammonia removal - absorption in sulphuric acid;
- carbon dioxide separation - water absorption, lyophilization, PSA, membrane separation with the use of polymeric membranes.

It is just the membrane separation that seems to be a promising method of upgrading biogas. The term membrane separation is used to designate a process in which a mixture is separated on the basis of different permeability of individual components across a selective membrane by means of which two spaces are separated from one another. The transport of the components across the membrane is influenced by their physical and chemical properties, and the interactions of the components between each other and the membrane, itself. With the use of porous membranes the components are most frequently separated on the basis of their particle size. With the use of non-porous membranes the transport properties are particularly dependent on the solubility of the components within the membrane or optional possibility of chemical interactions between the individual components and the membrane, and the diffusion coefficients of the components in the membrane.

In now-a-days practice the separation of gaseous mixtures is mostly carried out with the help of non-porous membranes made of polymeric materials (R. Barker: Recent Developements in Membrane Vapour Separation System. Membrane Technology 114 (1999) 9-12). Their main disadvantage is that they become contaminated by toxic materials, which are often present in the biogas from sewerage plants or agricultural biogas (see Table 1).

Table 1

Concentration of some hydrocarbon derivatives and organo-sulphur compounds in biogas (F. Straka,: Bioplyn. Praha, GAS (2006) 706.

Component	**c[ppm]**
methanol	2- 210
ethanol	16- 1450
1- propanol	4.1- 630
1- butanol	2.3- 73
acetone	0.27- 4.1
butyl acetate	60
acetic acid	0.06- 3.4
butanoic acid	0.02- 6.8
methanethiol	0.1- 30
dimethyl sulphide	1.6- 4
dimethyl disulphide	0.02- 40
carbon disulphide	0.5- 22
ethanethiol	0- 20

Due to such contamination the separation membranes lose their original selectivity and the permeation flow is also reduced. Contaminated membranes have to be replaced and moreover, they must be handled as toxic waste, which is very expensive.

Another possible approach is gas separation with the help of so called liquid membranes (J.E. Bara, S. Lessmann, C. J. Gabriel, E. S. Hatakeyama, R. D. Noble, D. L. Gin, Synthesis and Performance of Polymerizable Room-Temperature Ionic Liquids as Gas Separation Membranes, *Ind. Eng. Chem. Res.* 46 (2007) 5397). At present, the liquid membrane technology is being tested for the separation of carbon dioxide from methane. The most recent trend in this respect are so-called anchored ionic membranes (J. E. Bara, S. E. Hatakeyama, D. L. Gin, R. D. Noble; Improving CO_2 Permeability in Polymerized Room-temperature Ionic Liquid Gas Separation Membranes through the Formation of a Solid Composite with a Room-temperature Ionic Liquid, *Polym. Adv. Technol.*; 19 (2008) 1415.

Immobilized ionic membranes comprise ionic liquids which, owing to their high selectivity and molecular diffusion, as well as negligible vapour tension, represent ideal materials for the preparation of liquid membranes. (J. E. Bara , Ch. J. Gabriel , E. S. Hatakeyamaa, T. K. Carlisle: Improving CO_2 Selectivity in Polymerized Room-temperature Ionic Liquid Gas Separation Membranes through Incorporation of Polar Substituents, *Journal of Membrane Science* 321 (2008) 3–7). In general, the main diadvantage of the liquid membranes consists in that their stability depends on capillary forces which are not always capable of resisting to the long-termed (or even operational) duty. Moreover, ionic liquids more or less absorb moisture, which leads to relatively quick breakdown of the membrane structure and stability.

The hitherto conducted investigations have shown that it is the solubility of a separated component in a liquid membrane that is critical for the selectivity of a liquid membrane (P. Izák, L.Bartovská, K. Friess, M. Šípek, P. Uchytil; Comparison of Various Models Flat for Transport of Binary Mixtures through Dense Polymer Membrane, *Polymer*, 44 (2003) 2679-2687).

A suitable liquid for the separation has to comply with the requirement that the separated gases be at least by one order of magnitude more soluble in the selected liquid than methane which is the predominant component of biogas. Hence, the selection of a liquid for the impregnation of a porous membrane is a key factor.

For proper membrane function, an appropriate selection of the so-called support, in which the selected liquid is anchored, is very important, in particular in view of the rigidity and the stability of the system. Moreover, high affinity between the liquid and the porous support is a must.

The hitherto known liquid membranes for the separation of biogas aimed at obtaining a stream enriched in methane and depleted in carbon dioxide and detrimental components, such as sulphur-containing components, have suffered from certain complexity and expensiveness of the used liquid systems, e.g. consisting of compounds which at the same time may contain hydroxy and amino groups, such as aminic derivatives of glycols, etc. If water systems are used, the liquid membrane need not be sufficiently stable. Stability may be impaired by a varying amount of the liquid embedded in the membrane support. In water systems such undesirable variations can be caused by the fact that under the operational conditions water from the membrane is evaporated the separated gas whereby the membrane is in fact getting dried. The membrane stability is however very important from the point of view of the continuous operation of a separation unit.

Subject Matter of Invention

The above mentioned disadvantages are solved by a process and an apparatus according to the invention, which are described below.

The subject matter of the present invention is a process for enriching the biogas from sewerage plants, landfill or agricultural basic industries in methane, which comprises introducing the biogas to one side of a liquid water membrane which is immobilized in/on a porous hydrophilic support. A stream enriched in methane and depleted in carbon dioxide, hydrogen sulfide and further undesirable components contained in the biogas is obtained as a retentate, and a stream depleted in methane and enriched in carbon dioxide and further undesirable components contained in the biogas components is obtained as a permeate. The improvement of said process lies in that as liquid membrane water alone is used, and the losses of water from said membrane, which are caused by driving away said water in said permeate stream, are compensated by saturating said introduced biogas with steam at a temperature which is higher than the temperature at which said membrane separation takes place whereupon said steam is condensed when said biogas is cooled in said membrane (below dew point of the introduced biogas).

In general, as the porous hydrophilic supports any materials having high affinity to water in the pores of which vapor with which the introduced biogas has been saturated can spontaneously condense as soon as it is cooled to the temperature below its dew point. Such materials can include polymer porous membranes e.g. made of hydrophilized polytetrafluoroethylene, polyamide or other hydrophilic polymers or ceramic membranes e.g. on the basis of alumina.

In a preferred embodiment of said process the permeation takes place into sweeping gas. In another embodiment reduced pressure can be maintained on the permeate side of a permeation cell.

The subject matter of the present invention also includes an apparatus for carrying out said process. Said apparatus comprises a membrane separator, which is divided by a liquid water membrane immobilized in/on a porous hydrophilic support, into a retentate space and a permeate space. Said retentate space is connected with supply fittings for said gaseous mixture and discharge fittings for said retentate stream whereas said permeate space is connected with discharge fittings for said permeate stream. The improvement of said apparatus lies in that a saturator for saturating said biogas with vapor is inserted into the supply tubing for the introduced biogas.

For the correct function of both the process and the apparatus according to the invention it is critical that the solubility of the separated gases in the separation liquid may be substantially different. This prerequisite is duly met in the case of water as a separation membrane for the system methane/carbon dioxide. Moreover, the fact that no further components need to be added to said water substantially adds to cost reduction. For the correct function of the system it should be also ensured that water content is maintained in the the pores of the support. To this end, in a preliminary step the biogas introduced to the membrane is saturated with the separation liquid., i.e. water. The saturation takes place at a temperature, which is higher than the temperature in the membrane separator in which the liquid water membrane immobilized in/on the pores of the support is located. The temperature difference between the introduced biogas and the water membrane is such that spontaneous condensation of water in/on the pores may take place. The amont of water in the membrane can be controlled by adjusting the temperature, at which biogass is saturated by water.

The advantages of the proposed separation method can be summarized as follows:

1. A very low cost of the separation medium.
2. The continuous regeneration of the membrane liquid in the course of the separation process.
3. The prevention of accumulation of residual toxic substances contained in the biogas. As a consequence the pretreatment with a sorbent and further handling problems with the used sorbent, which shall be disposed off as a toxic waste, both of which are demanding from the economic point of view, may be avoided.

Brief Description of Drawings

The attached figure contains a schematic diagram of an example of an apparatus according to the invention.

The process according to the invention is illustrated by the following working examples which are carried out in the apparatus depicted in the attached figure. The examples are only illustrative, and they do not limit the claimed scope in any respect.

Working Examples

Example 1

Enrichment of model biogas

The real biogas from sewerage plants (represented by a ternary mixture (70% vol. methane, 30% vol. carbon dioxide a 2800 ppm sulfane) is introduced from a pressure container 1 of biogas over a flow controller 3 of the biogas into a saturator 5, in which the biogas is saturated with steam, and then into a membrane separator 6. The temperature in the saturator 5 of the biogas with steam is higher than the temperature in the membrane separator 6, in which a water impregnated porous support of hydrophilized polytetrafluoroethylene is mounted. Partial gas flows through this condensing water membrane at the pressure over the membrane 350 kPa are as follows: $J_{CO2} = 22.3$ l/(m^{2}h), $J_{CH4} = 1.26$ l/(m^{2}h) a $J_{H2S} = 0.08$ l/(m^{2}h).

Table 2

Separation of model biogas with the help of a condensing water membrane

Pressure over the membrane 350kPa	Feed	Permeate	Permeation flow ($l/m^2/h$)	Gas flow over the membrane (ml/min)
Methane	70 vol. %	5.4 vol. %	22.3	24
Carbon dioxide	29.7 vol. %	94.2 vol. %	1.26	10
Sulfane	2800 ppm	3429 ppm	0.08	10

The temperature difference is such that spontaneous water condensation in the pores of the porous membrane may take place. The driving force of the separation process is the different concentration of individual gas components and the overall pressure over and under the membrane. The permeation takes place into the carrier gas, which is nitrogen, introduced below the membrane from a pressure container 2 of the carrier gas over the carrier gas flow controller 4. Optimal total pressure over the membrane is controlled by a reverse pressure controller 7.

Example 2

Enrichment of real biogas

For the separation a real biogas from a sewerage plant is used. The composition of the biogas is shown in Table 3. The biogas is introduced from a pressure container 1 of biogas over a flow controller 3 of the biogas at a flow rate 10 ml/min into a saturator 5, in which the biogas is saturated with vapour which is formed from the introduced tap water, and then into a membrane separator 6. The temperature in the saturator 5 of the biogas with steam is higher (27 °C) than the temperature in the membrane separator 6 (14 °C). In the membrane separator 6 a membrane 10 of hydrophilic teflon (having pores 0.1 µm, thickness 30 µm and porosity 80 %), impregnated with tap water, is mounted. The effective area of the membrane having the radius of 13 cm is 132,7 cm^2. The permeation is carried out into the carrier gas, which is nitrogen. The conducted experiments show (see Table 3) that methane can be efficiently concentrated with the use of a porous membrane of hydrophilic teflon in which water condensation takes place.

Table 3

Enrichment of real biogas in methane with the use of a condensing water membrane

Sample designation	amount	feed	retentate	permeate
Aromatic hydrocarbons				
toluene	mg/m³	38.6	6.26	15.2
ethylbenzene	mg/m³	10.9	<0,07	2
xylenes	mg/m³	37.6	1.66	6.6
Total aromatic hydrocarbons	mg/m³	87.1	7.92	23.8
Chlorinated and aliphatic hydrocarbons				
cis-dichloroethene	mg/m³	1.57	<0,10	<0,10
trichloroethene	mg/m³	2.54	0.960	1.74
tetrachloroethene	mg/m³	4.15	1.04	1.29
Total chlorinated and aliphatic hydrocarbons	mg/m³	8.26	2	3.8
BASIC GAS ANALYSIS				
carbon dioxide	% v/v	30	21.3	86
methane	% v/v	69	76	14
sulfane	mg/m³	7,95	<0,91	<0,61
SILOXANEs				
L3 - oktamethyltrisiloxane	mg/m³	4.13	<0,1	<0,1
D4 - oktamethylcyclotetrasiloxane	mg/m³	14.4	<0,1	<0,1
L4 - decamethyltetrasiloxane	mg/m³	2.2	<0,1	<0,1
D5 - decamethylcyclopentasiloxane	mg/m³	109.6	9.1	13
Total siloxanes	mg/m³	130.3	9.1	13

The temperature difference (13 °C) is such that spontaneous water condensation in the pores of the porous membrane may take place. The driving force of the separation process is the different concentration of individual gas components and the overall pressure over and under the membrane. The permeation takes place into the carrier gas, which is nitrogen, introduced below the membrane from a pressure container 2 of the carrier gas over the carrier gas flow controller 4. Optimal total pressure over the membrane is controlled by a reverse pressure controller 7.

List of Reference Numerals

1 – pressure container for gaseous mixture

2 – pressure container for carrier gas

3 – gaseous mixture flow controller

4 – carrier gas flow controller

5 – saturator of gaseous mixture with vapour of selected liquid

6 – membrane separator

6a - retentate space

6b - permeate space

7 – reverse pressure controller

8 – permeate discharge valve

9 – valve for retentate effluent

10 - hydrophilic porous support

11 - 14 – piping

11 - feeding pipe for gaseous mixture

12 - feeding pipe for carrier gas

13 - discharging pipe for retentate

14 - discharging pipe for permeate

Claims

1. A process for enriching the biogas from sewerage plants or agricultural basic industries in methane, which comprises introducing the biogas to one side of an liquid water membrane which is immobilized in/on a porous hydrophilic support, wherein a stream enriched in methane and depleted in carbon dioxide, sulfane and further undesirable components contained in the biogas is obtained as a retentate, and a stream depleted in methane and enriched in carbon dioxide and further undesirable components contained in the biogas components is obtained as a permeate **characterized in that** as liquid membrane water alone is used, and the losses of water from said membrane, which are caused by driving away said water in said permeate stream, are compensated by saturating said introduced biogas with steam at a temperature which is higher than the temperature at which said membrane separation takes place whereupon said steam is condensed when said biogas is cooled in said membrane.

2. A process according to claim 1 **characterized in that** said permeation is carried out into the sweeping gas.

3. An apparatus for carrying out the process according to claim 1 or 2 **characterized in that** it comprises a membrane separator (6), which is divided by a liquid water membrane immobilized in a porous hydrophilic support, into a retentate space (6a) and a permeate space (6b), said retentate space (6a) being connected with supply fittings (1, 3, 5, 11) for said gaseous mixture and discharge fittings (13, 7, 9) for said retentate stream whereas said permeate space is connected with discharge fittings (8, 14) for said permeate stream, **characterized in that** a saturator (5) for saturating said biogas with said steam is inserted into the supply tubing (11) for the introduced biogas.

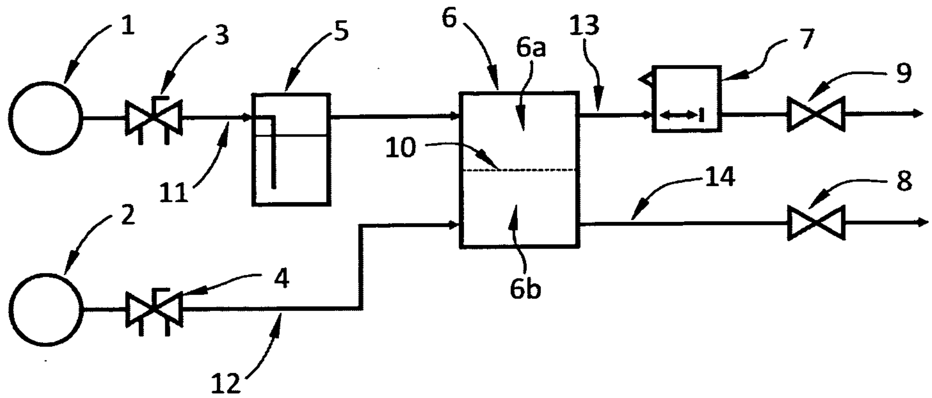

FIG. 1