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(54) Benævnelse: **FREMGANGSMÅDE TIL RENGØRING AF EN GASPERMEATIONSMEMBRAN**

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Description

The present invention relates to a method for cleaning or regenerating gas permeation membranes in separation units. Such separation units can be, for example, gas permeation membrane units in which gas mixtures are separated into a retentate flow and a permeate flow. Depending on the application, the retentate flow can constitute the product and the permeate the off-gas or vice versa.

A gas separation membrane essentially consists of a separation layer and a usually porous support layer, usually configured as hollow fibres. A plurality of such hollow fibres combined in a housing yield a membrane module.

The operation of a gas permeation membrane is based on the solution-diffusion principle, i.e. the different solution and diffusion properties of the individual gases of a gas mixture to be separated are used in a plastic (which can be a polymer) configured as a separation layer in order to achieve a separation of a gas mixture. The components of the gas mixture, depending on their properties, dissolve in the separation layer of a membrane in order to then, in accordance with a necessarily present partial pressure difference which acts as the driving force, diffuse or permeate on the side of the separation layer which has the lower partial pressure of the individual gas components. The side from which the membrane is impinged by the gas or gas mixture is called the retentate side, the gas flow accordingly retentate, and the other side is accordingly called the permeate side and the gas flow permeate.

Mentioned here as an example of a possible separation are nitrogen N_2 and oxygen O_2, which have a relative solubility O_2/N_2 of 5.5 in a polymer used specifically for the nitrogen/oxygen separation. That means that, under the same conditions such as pressure, temperature and area, the oxygen O_2 dissolves 5.5 times more than the nitrogen N_2 in the separation layer and separation material (polymer) used for the latter. For a separation of methane CH_4 and CO_2, the CO_2/CH_4 ratio today is already 50 or higher. This ratio of the different solubility of two gases in a plastic (polymer) is also called the selectivity of the two gases relative to one another. The flux triggered by the partial pressure difference (driving force) is also called the transmembrane flux (with the unit Nm^3/m^3.sec.bar) of a membrane and is the second essential performance characteristic of a membrane next to selectivity.

Besides chemical substances such as, e.g., organic solvents, which destroy the selective layer of a membrane definitively and

thus render the separation properties of the membrane ineffective, impurities in the form of particles can also mechanically block or plug the membrane rapidly or also slowly, depending on the degree of contamination, and gradually reduce the transmembrane flux to a standstill. The flow through the membrane fibres themselves or the path of the gas mixture through the porous support layer to the selective separation layer is restricted or prevented completely, whereby the performance of the membrane is essentially or entirely diminished.

In the event of the damaging or destruction of the membrane by chemical solvents or the damaging or destruction of the membrane by a mechanical blockage or plugging effect, a repair or regeneration of the membrane is practically impossible. In practice, the damaging of membranes by particles is prevented with filters, which let through a maximum particle size of 0.01 µm.

WO 2011/107898 A1 discloses membranes for separating oxygen from air; for the cleaning (or desorption), fresh air is guided through the gas inlet 12 or 22, wherein the membrane can be heated during desorption to a temperature in the range of 150-200°C.

According to US 2007/051238 A1, absorbers A and B are shown, which absorbers are filled with absorption agent particles and can be cleaned by directing a gas flow against the operating direction.

WO 2008/025077 A1 relates to a method for cleaning a permeable membrane, wherein the residual permeate in the system is placed under pressure by a gas, whereby the permeate backwashes the pores of the membrane.

EP 0 337 499 A2 relates to a method for regenerating used gas-permeable membranes, wherein the membrane comprises a gas-selective film and is brought into contact with an organic liquid medium in which the gas-selective film is insoluble or only poorly soluble.

WO 99/07459 A1 finally relates to a cleaning method for porous membranes which are used in oil refineries, wherein the membranes are backwashed first with a gas and then with an edible oil and subsequently treated with an alkaline material.

The most frequently occurring impairment of the effectiveness of a gas separation membrane to be cited is the blocking or plugging by long-chain, gaseous molecules, for the most part hydrocarbons, which hydrocarbons are carried into the membrane by the gas flow to be separated. This blocking by deposition of the long-chain hydrocarbons can already start in the porous support layer; however,

the essential, negative impact occurs by the blocking by these long-chain molecules on and in the selective separation layer.

Such a course of events is cited in the following as a practical example.

The unit consists of a nitrogen generator which produces with gas permeation membrane units a 95% N_2 inert gas mixture from the air.

The operating pressure of the unit is 7 – 12 bar g; an oil-lubricated screw compressor was used in the generator as the compressor. In the past, through improper maintenance of the unit, an oil vapour content, which was higher than the value of 0.01 mg of oil per absolute Nm^3 of air allowed by the membrane manufacturer, managed to permanently enter into the membranes together with the compressed air. By means of this introduction of the long-chain higher hydrocarbons (oil vapour), the support layer, but above all the selective layer, of the membrane was progressively blocked over time and thus the free area on or the free space in the separation layer for the gas permeation was reduced, with the consequence that the performance of the unit (in Nm^3/h of retentate) declined proportionally to the continuously decreasing membrane area caused by the blocking. The performance of the unit could thus only be maintained by a corresponding increase in pressure and/or temperature within the framework of the possible or allowable unit parameters. Once these parameters were exhausted, the performance of the unit declined steadily until the unit could no longer be operated.

As a further example analogous to the above example, the field of biogas treatment is cited, in which membrane engineering is becoming increasingly important as a technology for the treatment of biogas (namely the separation of CO_2 from the raw biogas flow). By biogas treatment, methods are understood with which biogas is cleaned so that it can subsequently be supplied for energetic or material uses.

Biogas is a combustible gas which can be produced by fermentation of biomass of any kind. Suitable base products for fermentation are first and foremost biogenic materials, for example fermentable waste materials containing biomass such as sewage sludge, organic waste or food waste, industrial fertilizers (slurry, manure), previously unused crops as well as crop parts (for example catch crops, crop remains and the like) as well as specifically grown

energy crops as renewable raw materials. Biogas is formed by the microbial decomposition of the organic materials under for the most part anoxic conditions, wherein microorganisms convert the carbohydrates, proteins and fats to methane and carbon dioxide.

Biogas also contains, besides short-chain thiols and thioethers, sometimes predominantly, terpenes (camphor, limonene, etc.), alkanes/alkenes, and aliphatic alcohols/ketones or generally higher hydrocarbons as its main impurities. These impurities are partly fermentation products and partly also directly ascribable to the substrate such as, for example, the merely poorly bio-degradable terpenes. The above-mentioned impurities must be separated off before a further use of the biogas. Such a separation currently occurs primarily by means of the filters, in particular activated carbon filters, arranged upstream from the separation unit.

It is not always necessarily the case, however, that the separating off of these impurities is complete, which can occur, e.g. by means of an imprecise analysis of the gas constituents of the feed gas and thus a false interpretation or selection of the activated carbons, or a service life of the activated carbon filters that is too long, so that an overloading and thus a breakthrough of the impurity occurs, or also simply by errors in the operation of the unit.

The insufficiently separated impurities of the biogas then lead over a longer operation of gas permeation membrane units to a blocking of the gas permeation membrane. These impurities are for the most part organic compounds with a boiling point between approximately 50°C and 150°C. Blocked membranes are currently regenerated by blowing in hot air, nitrogen or CO_2 under positive pressure, wherein, as a result of the increased temperature, the volatile impurities are carried off from the surface. A considerable portion of the impurities is, however, pressed further and still deeper into the selective layer of the gas permeation membrane by the application of pressure and the retention of the permeation direction of the flushing gas with the permeation direction of the process gas. It is not possible to clean a gas permeation membrane completely this way. With this flushing process, a flushing gas inlet, a flushing gas outlet as well as, as parts of the flushing gas also always permeate, a permeate outlet are necessary.

The object of the present invention is to overcome the previous disadvantages and to provide a method for the cleaning or

regeneration of a gas permeation membrane. The method can preferably be performed while the unit is in operation and the removal/ installation of the gas permeation membrane units is no longer necessary.

This object is solved according to the invention in that, in a method for cleaning a gas permeation membrane in a gas permeation membrane unit of impurities from higher hydrocarbons, in particular from alkanes/alkenes, aliphatic alcohols/ketones and short-chain thiols and thioethers and terpenes, such as camphor and limonene, as well as oil vapour,

- the impurities are carried away against the operating direction of the gas permeation membrane and
- a suitable gas or gas mixture, for example nitrogen or air, preferably hot air, is introduced in the permeate side of a gas permeation membrane unit to be cleaned,
- wherein the gas or gas mixture laden with impurities after passing through the gas permeation membrane is discharged via the feed-gas inlet and/or the retentate outlet of the gas permeation membrane unit, and
- wherein the method is carried out at a temperature between 50°C and 150°C, even more preferably between 90°C and 150°C,
- the temperature of the gas or gas mixture, preferably the hot air, introduced into the gas permeation membrane unit or the temperature of the gas permeation membrane unit itself is increased gradually in the course of the cleaning, starting from 50°C, preferably 90°C, and
- the gas or gas mixture, preferably the hot air, introduced into the gas permeation membrane unit, or the gas permeation membrane unit itself, is then heated to the next temperature stage when a change in the flow and/or partial pressure of the impurities boiling at or up to the particular temperature stage is no longer detectable.

The impurities are carried away against the operating direction of the gas permeation membrane. It is thus prevented that impurities that have not yet been carried away are pressed into the selective layer of the gas permeation membrane; on the contrary, it is ensured by means of the removal against the operating direction that the selective layer of the membrane is reliably freed of impurities. According to the invention, as a result, only two of the outlets/inlets provided in the membrane unit are still required for cleaning or regeneration in gas permeation membrane units, namely a

flushing gas inlet (which occurs via the provided permeate outlet) and a permeating flushing gas outlet (which occurs via the feed- or product-gas outlet).

Alternatively, in a gas permeation membrane unit to be cleaned, said unit is pre-heated, after which negative pressure is applied on the retentate side and/or feed-gas side and impurities contained in the gas permeation membrane are removed therefrom and are discharged via the retentate outlet and/or the feed-gas inlet.

In cases where hot air is introduced, this means that compressed air is heated beforehand; in the case of a cleaning by means of negative pressure, the gas permeation membrane unit must itself be heated. This can, for example, occur by removal of the gas permeation membrane unit and placing the same in an oven; alternatively, the gas permeation membrane unit can also be at least partially equipped with a suitable heat exchanger, for example an electrical heating jacket, via which heat exchanger the heating occurs. In the latter case, it is not necessary to remove the gas permeation membrane unit for cleaning; should the unit comprise a plurality of gas permeation membrane units, the cleaning can be carried out during operation by means of a suitable line arrangement and activation of the gas permeation membrane unit to be cleaned.

It is provided in the method according to the invention that the temperature of the introduced into the gas permeation membrane unit or the temperature of the gas permeation membrane unit itself is increased gradually in the course of the cleaning, starting from 50°C, preferably 90°C, wherein a temperature stage is preferably between 10°C and 20°C.

According to a preferred embodiment of the method in accordance with the invention, the gas or gas mixture, preferably the hot air, is introduced with a positive pressure of 1.0-2.0 bar, preferably approximately 1.5 bar (corresponding to an absolute pressure of 2.0-3.0 bar, preferably approximately 2.5 bar).

The cleaning method is preferably ended when, after two consecutive temperature stages, a change in flow and/or partial pressure of the impurities boiling at or up to the particular temperature stage is no longer detectable.

The present invention will now be explained in greater detail with the aid of the following examples, to which, however, the invention is not to be restricted.

In a gas permeation membrane unit with polyimide fibres, an

initial output of 4.5 Nm^3/h of nitrogen, and a residual oxygen content of 1%, a recovery of 30% (recovery = product Nm^3/h : by the amount of air required for the recovery in Nm^3/h), an inlet pressure of 7 bar g and an inlet temperature 25°C, a cleaning or regeneration was carried out in accordance with the method according to the invention after a drop in output of 52% in relation to the initial output, so that the output was then only 2.34 Nm^3/h of nitrogen and a residual oxygen content of 1%, a recovery of 30%, an inlet pressure of 7 bar g and an inlet temperature of 25°C. Hot air with a temperature of 60°C and a positive pressure of 1.5 bar (2.5 bar absolute) was then introduced in the membrane unit on the permeate side, which hot air laden with impurities after passing through the gas permeation membrane was discharged via the feed-gas inlet of the gas permeation membrane unit. The flow of the hot air through the membrane together with the impurities boiling at the particular temperature stage was measured by means of a flowmeter after external cooling. The inflowing hot air was heated to the next stage of 90°C for 240 minutes after a change in flow failed to materialize; the pressure remained unaltered. The temperature of the hot air remained unaltered for 240 minutes until a change in flow and/or in partial pressure failed to materialize; the hot air was subsequently heated to the next stage of 100°C; the pressure remained unaltered. This process was carried out up until a temperature increase of 140°C. After there was no incidence of a change in flow and/or in partial pressure despite temperature increases, the hot air was heated after a further 240 minutes to the next stage of 150°C; after there was no incidence of a change in flow and/or in partial pressure at this stage either, the cleaning method was ended. Overall, by means of the method according to the invention, the gas permeation membrane unit used was freed of 120g of impurities while 100% of the initial output was attained.

In a gas permeation membrane unit with polyimide fibres, an initial output of 3.8 Nm^3/h of nitrogen, and a residual oxygen content of 1%, a recovery of 28% (recovery = product Nm^3/h : by the amount of air required for the recovery in Nm^3/h), an inlet pressure of 7 bar g and an inlet temperature of 25°C, a cleaning or regeneration was carried out in accordance with the alternative embodiment of the method according to the invention. To this end, a negative pressure of 0.85 bar was applied in the unit laden with impurities on the retentate side by means of a negative pressure pump via a cooling

unit while the unit was heated to a temperature of 60°C by means of an oven. The gas laden with impurities removed in this manner via the retentate outlet of the gas permeation membrane unit was measured with respect to the flow and/or the partial pressure of the impurities boiling at or up to the particular temperature stage by means of a flowmeter after the vacuum pump. The temperature of the unit was increased to the next stage of 90°C after 240 minutes due to the failure of a change in the flow and/or the partial pressure to materialize; the applied negative pressure remained unaltered. The temperature of the unit remained unaltered for 240 minutes until there was no change in flow and/or partial pressure; it was subsequently increased to the next stage of 140°C; the applied negative pressure again remained unaltered. After there was no longer any incidence of a change in flow and/or partial pressure despite temperature increases, the temperature of the unit was increased after 240 minutes to the next stage of 150°C; after there was no incidence of a change in flow and/or partial pressure at this stage either, the cleaning method was ended. Overall, by means of the alternative embodiment of the method according to the invention, the gas permeation membrane unit used was freed of 80g of impurities while 80% of the initial output was attained.

P A T E N T K R A V

1. Fremgangsmåde til rengøring af en gaspermeationsmembran i en gaspermeationsmembranenhed for urenheder af højere carbonhydrider, især af alkaner / alkener, alifatiske alkoholer / ketoner og kortkædede thioler og thioethere og terpener, såsom kamfer og limonen, og oliedamp, **kendetegnet ved, at**

- urenhederne fjernes imod driftsretningen af gaspermeationsmembranen og

- en dertil egnet gas eller gasblanding, for eksempel nitrogen eller luft, fortrinsvis varmluft, indføres på permeatsiden af en gaspermeationsmembranenhed som skal rengøres,

- gassen eller gasblandingen ladet med urenheder efter dens passage igennem gaspermeationsmembranen udledes via fødegasindløbet og / eller retentatudløbet af gaspermeationsmembranenheden,

- fremgangsmåden udføres ved en temperatur mellem 50°C og 150°C, mere fortrinsvis mellem 90°C og 150°C,

- temperaturen af gassen eller gasblandingen, fortrinsvis varmluften, indført i gaspermeationsmembranenheden eller temperaturen på selve gaspermeationsmembranenheden øges gradvist i løbet af rengøringen, startende fra 50°C, fortrinsvis fra 90°C, og

- gassen eller gasblandingen, fortrinsvis varmluften, indført i gaspermeationsmembranenheden eller selve gaspermeationsmembranenheden opvarmes til det næste temperaturniveau, når der ikke er nogen ændring i gennemstrømningen og / eller partialtrykket af urenhederne, som koger ved eller op til det respektive temperaturniveau.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** gassen eller gasblandingen indføres ved et overtryk på 1,0 - 2,0 bar, fortrinsvis omkring 1,5 bar.

3. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** en gaspermeationsmembranenhed, som skal rengøres, opvarmes på forhånd, hvorefter der påføres undertryk på retentatsiden og / eller fødegassiden, og hvor urenhederne indeholdt i gaspermeationsmembranen fjernes derfra og udledes via retentatudløbet og / eller fødegasindløbet.

4. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 3, **kendetegnet ved, at** et temperaturniveau omfatter mellem 10°C og 20°C.

5. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 4, **kendetegnet ved, at** fremgangsmåden til rengøring afsluttes når der efter to på hinanden følgende temperaturniveauer ikke kan måles nogen ændring i gennemstrømningen og / eller partialtrykket af urenhederne, som koger ved eller op til det respektive temperaturniveau.