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(71) Demandeur/Applicant:
EVONIK FIBRES GMBH, AT

(72) Inventeurs/Inventors:
UNGERANK, MARKUS, AT;
BAUMGARTEN, GOETZ, DE;
PRISKE, MARKUS, DE;
ROEGL, HARALD, AT

(74) Agent: MARKS & CLERK

(54) Titre : PROCEDE DE SEPARATION DE GAZ
(54) Title: PROCESS FOR SEPARATION OF GASES

(57) **Abrégé/Abstract:**

The invention relates to a specific apparatus, more particularly a chain of gas separation membrane modules, for separation of gas mixtures into two fractions each of elevated purity.



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10168121.1 1. Juli 2010 (01.07.2010) EP(71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme von US): **EVONIK FIBRES GMBH** [AT/AT]; Werkstrasse 3, A-4860 Lenzing (AT).

(72) Erfinder; und

(75) Erfinder/Anmelder (nur für US): **UNGERANK, Markus** [AT/AT]; Münzbacherstraße 22, A-4320 Perg (AT). **BAUMGARTEN, Goetz** [DE/DE]; Reinhard-Freericks-Str. 20, 45721 Haltern am See (DE). **PRISKE, Markus** [DE/DE]; Brassertstraße 129, 45768 Marl (DE). **ROEGL, Harald** [AT/AT]; Mühlbachgasse 20, A-4702 Waltern an der Trattnach (AT).(74) Anwalt: **WOLF, Oliver**; Evonik Degussa GmbH, DG-IPM-PAT, Rodenbacher Chaussee 4, 63457 Hanau (DE).

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(54) Title: PROCESS FOR SEPARATION OF GASES

(54) Bezeichnung : VERFAHREN ZUR TRENNUNG VON GASEN

(57) Abstract: The invention relates to a specific apparatus, more particularly a chain of gas separation membrane modules, for separation of gas mixtures into two fractions each of elevated purity.

(57) Zusammenfassung: Die Erfindung betrifft eine spezielle Vorrichtung, insbesondere Verkettung von Gasseparationsmembranmodulen, zur Auftrennung von Gasgemischen in zwei Fraktionen von jeweils erhöhter Reinheit.



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Process for separation of gases

The invention relates to a specific apparatus, more particularly a chain of gas separation membrane
5 modules, for separation of gas mixtures into two fractions each of increased purity.

By means of a gas separation membrane, it is possible to separate gas mixtures on the basis of different
10 permeabilities (= flow rate per unit time, unit area, pressure differential and layer thickness) of the individual gases in a polymer. The polymers are generally processed to give hollow fibers or flat membranes. The membranes are notable for a very thin
15 separation layer at the surface of the membrane, such that the permeance (flow rate per unit time, unit area and pressure differential) of the membrane is at a maximum.

20 The separation outcome achievable with a membrane in a single pass depends not only on the selectivity of the membrane but also on the pressure ratio between high-pressure and low-pressure side of the membrane. The greater the pressure ratio, the better the maximum
25 separation outcome achievable.

In the range of low pressure ratios, the curves for the different selectivities run close to one another (see figure 1). The separation outcome in this range is
30 determined by the pressure ratio. This range is therefore referred to as "pressure-limited". In the range of high pressure ratios, the separation outcome can barely be influenced by the pressure ratio. This range is referred to as "selectivity-limited".

35

A series of membrane connection arrangements for the separation of gases is known from the literature. In Baker, IndEngChemRes, Natural Gas Processing with Membranes, 47 (2008), there is a comprehensive list of

various known connection arrangements. For instance, using the example of the separation of methane (retentate gas) and CO₂ (permeate gas) with a simple one-stage membrane separation step according to fig. 2, 5 high purities can be achieved in the product stream (98% CH₄). However, the quality of the permeate-side offgas stream cannot be influenced and is of low purity (44% CO₂). There is correspondingly large slippage, i.e. loss of methane.

10

In the case of a one-stage connection arrangement with recycling (fig. 3), the purities can be increased slightly. However, it is not possible thereby to solve the fundamental problem of the low retentate gas yield 15 and of the permeate gas quality.

For higher permeate purities and higher yields of the component retained, a series of multistage connection arrangements are known. In a connection arrangement 20 with a single permeate stage, with recompression and recycling of the first permeate (fig. 4), it is possible to improve permeate purity (86%) and methane yield.

25 If the better-permeating component occurs in increased concentrations (30%), a connection arrangement according to fig. 5 may be advantageous according to the literature. Two permeate gas-rich streams (82% CO₂, 93% CO₂) and one retentate gas-rich stream (82% CH₄) are 30 produced.

Bhide (MemSci, Hybrid processes for the removal of acid gases from natural gas, 1998) discloses a three-stage operation for the removal of acid gases from natural 35 gas (fig. 6). The gas stream to be treated is subjected to a coarse purification in an upstream membrane. The prepurified natural gas which remains on the pressure side is conducted through a further membrane. On the

retentate side, the target product stream forms, the natural gas depleted of the acid gases. The acid gas-enriched stream on the permeate side is compressed and supplied to a further membrane stage. The retentate of
5 this stage is compressed to the pressure level of the upstream stage and recirculated upstream thereof. This additional energy expenditure and financial investment is intended to increase the yield of methane. Disadvantages of this connection arrangement are the
10 expenditures for the compressors and the inadequate purities of the acid gas-enriched stream.

Chenar (MemSci Application of Cardo-type polyimide (PI) and polyphenylene oxide (PPO) hollow, 2008) describes
15 an operation with staged arrangement for permeate with recompression (fig. 7). Disadvantages of this connection arrangement are the severely limited purities of the retentate gas and the additional expenditure for the recompression.

20

EP0 799 634 discloses a connection arrangement according to fig. 8. However, disadvantages are an additional potential introduction of oil or water as a sealant and lubricant, additional high capital costs,
25 increased energy consumption resulting from additional compression, and increased likelihood of failure as a result of the moving parts.

Disadvantages of the abovementioned processes are the
30 additional recompression and the purities, which are still much too low, of retentate gas in the overall retentate stream, and the insufficient yields of the retentate gas in the retentate stream.

35 Fig. 9 shows a technology which is frequently proposed and has also been implemented particularly for the processing of biogas (Air Liquide and Harasek). What is disclosed is a connection arrangement with staged

arrangement for retentate with permeate recycling from the second stage.

Eindhoven University of Technology has developed a connection arrangement with an internal staged arrangement, which enables methane purities of more than 90% (see fig. 10). A disadvantage of this connection arrangement is the inadequate purity of the retentate gas.

10

EP 0 603 798 discloses a multistage connection arrangement for production of nitrogen. The disadvantage of this process is the insufficient purity of the permeating component and the use of at least two compressors.

15

EP0695574 discloses a connection arrangement with partial utilization of a permeate stream as a sweep stream for the production of a retentate of maximum purity. A disadvantage of this process is the insufficient quality of the overall permeate.

20

US5753011 discloses a process in which combination of membrane separation steps with staged arrangement for the permeate and pressure swing adsorption, PSA, achieves high purities for two product streams. A disadvantage of this process is the use of a costly and inconvenient PSA.

25

EP1634946 discloses a process for processing of biogas. Described therein is a thermal utilization of the methane from the methane-depleted stream. Disadvantages are the high costs and the loss of the gas.

30

EP0596268, finally, discloses various connection arrangements for production of three different gas compositions.

35

US 6,565,626 B1 and US 6,168,649 B1 each disclose
membrane separation processes with three membrane
separation stages, wherein a retentate stream and a
permeate stream from stages 2 and 3 respectively are
5 recycled to the crude gas stream.

A disadvantage of the processes known from the prior
art is that either a high purity of the permeate gas or
a high purity of the retentate gas can be achieved. For
10 the simultaneous achievement of high purities of
permeate gas and retentate gas, as necessary, for
example, in the processing and feeding of biogas into
the natural gas grid as a result of the high demands on
the methane purity and as a result of the limitation of
15 methane slippage, there are no processes which do not
need a recompression unit or a further purification of
the permeate or retentate stream (for example thermal
postcombustion of the permeate stream or pressure swing
adsorption for the retentate stream).

20

Proceeding from this prior art, it was an object of the
present invention to provide apparatuses and processes
for separation and purification of gas mixtures, which
have the disadvantages of the prior art processes and
25 apparatuses only to a reduced degree, if at all. More
particularly, processes and apparatuses which afford
both permeate gas and retentate gas are to be provided
in high purities. In a further specific object, this
process and this apparatus are to be advantageous in
30 terms of investment and operating costs and/or enable a
simpler process regime.

In a next specific object, a process/apparatus usable
with maximum universality is to be provided for any
35 desired gas mixtures. More particularly, it should be
possible to separate gas streams which are obtained in
the production of biogas and natural gas, or which

comprise carbon dioxide and methane in the presence of other gases such as water, hydrogen, hydrogen sulfide.

5 It was a further specific object of the present invention to provide a process or an apparatus which enables purification of methane-containing crude gas streams, with reduced methane emission compared to the prior art processes at the same throughput, and hence reduced environment pollution by this strong greenhouse
10 gas.

Further objects which are not stated explicitly are evident from the overall context of the claims, description, examples and figures which follow.

15

It has now been found that, surprisingly, the apparatus according to claim 1 or one of the claims dependent thereon can afford pure streams of permeate and retentate without requiring more than one compressor or
20 any need to purify the permeate or retentate stream further by other methods. The inventive apparatus thus enables simultaneous achievement of permeate and retentate streams in high purity. The capital costs for the plant are low; it does not need any additional
25 downstream purification processes. It was thus possible to achieve the stated objects with a pure membrane separation process.

The present claims therefore provide the apparatus and
30 process claimed in claims 1 to 12 and 13 to 18 respectively, and defined in detail in the description, examples and figures 11 to 13 which follow.

The present invention is described in detail
35 hereinafter. First, some important terms are defined.

The quotient of the permeances of the individual gases gives the **selectivity** of the membrane for separation

with regard to the two gases, and thus states how well the membrane can separate a gas mixture with regard to the two components. **Permeate** refers to the overall stream obtained on the low-pressure side of the membrane, membrane module or membrane separation step.

Permeate gas refers in each case to the component(s) enriched in each case in the **permeate stream** relative to the respective input stream at the membrane, at the membrane module or in the membrane separation step.

Retentate refers to the entire stream which is obtained on the high-pressure side of the membrane, membrane modules or membrane separation step and does not pass through the membrane.

Retentate gas refers to the component(s) enriched in each case in the **retentate stream** relative to the respective input stream at the membrane, at the membrane module or in the membrane separation step.

Crude gas or crude gas mixture or crude gas stream (17) refers to a gas mixture of at least two gases or a stream of this gas mixture which is to be separated by means of the process according to the invention or the inventive apparatus.

Feed stream (5) refers to a gas stream which is supplied to the feed stream separation stage (1). This stream, for the performance of the process, may correspond to the crude gas stream (17) or to the crude gas stream compressed by a compressor. After recycling of the second permeate stream (9) or of the third retentate stream (10), the feed stream (5) is composed of the gases of the crude gas stream (17), of the second permeate stream (9) and of the third retentate stream (10). The feed stream (5) can be produced either by mixing streams (9) and (10) both with the uncompressed crude gas stream (17), or mixing both with the compressed crude gas stream or mixing one with the uncompressed crude gas stream and one with the

compressed crude gas stream, or by mixing streams (9) and/or (10) with the crude gas stream (17) in the compressor. Combinations of the variants described above are also encompassed by the present invention.

5

Feed stream separation stage (1) refers to a membrane separation stage for separation of the feed stream (5) into a first permeate stream (6) and a first retentate stream (7).

10

Retentate separation stage (2) refers to a membrane separation stage, which may be of identical or different construction to the feed stream separation stage (1), for separation of the first retentate stream (7) into a second permeate stream (9) and a second retentate stream (8).

15

Permeate separation stage (3) refers to a membrane separation stage, which may be of identical or different construction to the feed stream separation stage (1) and retentate separation stage (2), for separation of the first permeate stream (6) into a third permeate stream (11) and a third retentate stream (10).

20

25

The descriptions which follow of preferred and specific embodiments of the process according to the invention and the preferred and particularly suitable executions and the drawings and descriptions of the drawings illustrate the invention in detail merely by way of example, which means that it is not restricted to these execution and use examples or to the respective combinations of features within individual execution examples.

30

35

Individual features which are specified and/or described in connection with specific execution examples are not restricted to these execution examples

or the combination with the other features of these execution examples; instead, they can be combined, within the range of technical possibilities, with any other variants, even if they are not discussed
5 specifically in the present documents.

Identical reference symbols in the individual figures and diagrams of the drawings refer to identical or similar or identically or similarly acting components. The diagrams in the drawing also make clear those
10 features which are not provided with reference numerals, irrespective of whether such features are described hereinafter or not. On the other hand, features which are included in the present description but are not visible or represented in the drawing are
15 also immediately understandable to a person skilled in the art.

The inventive apparatus (see, for example, figures 11 to 13) comprises a chain of three membrane separation
20 stages. Each stage consists of one or more physical gas separation modules, which are connected in parallel and/or in series within one stage. The driving force produced for the gas separation in the modules is a partial pressure differential between the retentate
25 side and the permeate side in the respective membrane separation stages. The partial pressure differential can be generated either by means of a compressor (4) arranged on the feed side of the feed stream separation stage (1) and/or by means of at least one, preferably
30 one or two, vacuum pump(s) (not shown in figs. 11 to 13), preferably in the second permeate stream (9) on the permeate side of the retentate separation stage (2) and/or in the third permeate stream (11) on the permeate side permeate separation stage (3). It may
35 optionally be advantageous, in one or more of the membrane separation stages, to generate or to enhance the partial pressure difference by means of a permeate-side purge gas stream.

In a preferred configuration of the present invention, a compressor (4) brings the crude gas mixture or the gas mixture of the crude gas stream (17) and the second permeate stream (9) and/or the third retentate stream (10) to the desired pressure in the range from 5 to 100 bar, but preferably to a pressure of 9 to 75 bar. The resulting feed stream (5) is introduced into the feed stream separation stage (1). In the feed stream separation stage (1), a pre separation of the crude gas mixture into more easily permeating components (permeate gas), which pass mainly into the permeate of the first stage, and components which permeate less quickly (retentate gas), which are predominantly retained by the membrane and are enriched in the retentate, is obtained.

The process according to the invention or the inventive apparatus is notable in that it is configured such that the concentration of at least one permeate gas of the feed stream separation stage (1), after recycling of the second permeate stream (9) and of the third retentate stream (10), is increased in the feed stream (5), preferably by at least 2%, more preferably by at least 3% and most preferably by 3 to 40%, in each case compared to the concentration in the crude gas stream (17). The increase may depend on the composition of the crude gas stream (17) and is particularly marked in the case of low concentrations of a permeate gas (10 to 20%). In general, the increase in concentration of one of the permeate gases is between 2 and 15%, more preferably between 3 and 8%, when the content of the permeate gas in the crude gas stream (17) is between 30 and 70%. This is because the inventors have found that the yield of retentate gas in the overall process increases and hence the loss of retentate gas decreases when the concentration of the permeate gas in the feed stream separation stage (1) is increased. At the same

cut in the separation stage (=ratio of permeate stream to feed stream in the stage in question), much less permeate gas passes into the permeate of the feed stream separation stage (1) when the concentration of at least one component A which permeates relatively easily in the feed stream separation stage (1) or of a permeate gas (A) is increased in feed stream (5). Analogously, a lowering was found when the concentration of component A or of a permeate gas A in the feed stream (5) to be purified is reduced. For instance, the cut in the separation stage for a concentration of 50% of a component A or of a permeate gas A in the feed stream (5) to be purified is between 10 and 60%, preferably between 15 and 55% and more preferably between 20 and 50%. In a particularly preferred embodiment of the present invention, the process according to the invention or the inventive apparatus is therefore configured such that the content of permeate gas(es) of the feed stream separation stage (1) in feed stream (5) is greater than or equal to 40% by volume, preferably more than 50% by volume and very particularly more than 55% by volume, based on the volume of the feed stream (5), after recycling of the second permeate stream (9) and of the third retentate stream (10).

This increase in concentration of the permeate gases in the feed stream (5), as already explained, increases the efficiency of the feed stream separation stage (1), which in turn has the result that less retentate gas B passes into the first permeate stream (6). This in turn increases the efficiency of the permeate separation stage (3) and ensures that less unwanted retentate gas passes into the third permeate stream (10) here too. Especially in the case of separation of methane-containing crude gases, this leads to the advantage that the unwanted emissions of methane, which is harmful to the climate, were reduced significantly.

In general, it can be stated that, in the feed stream separation stage (1), preferably 20 to 100%, more preferably 40 to 70%, of component A or of a permeate gas A are transferred from the feed stream (5) to the permeate.

The retentate of the feed stream separation stage (1), optionally with pressure reduction by an optionally present pressure-reducing valve (12), or with a pressure increase, is supplied by means of the first retentate stream (7) to the retentate separation stage (2) in which the fine purification is effected. On the retentate side of the retentate separation stage (2), i.e. in the second retentate stream (8), there is preferably a pressure-reducing valve (13), by means of which the pressure in the system can be maintained and kept constant. The content of the less easily permeating components or of a retentate gas B is increased further in the retentate separation stage (2), such that the content of component B or of a retentate gas B in the second retentate stream (8) is more than 90%, preferably more than 95% and more preferably more than 97%. In a particularly preferred variant, the process according to the invention or the inventive apparatus is thus notable in that at least 95%, preferably at least 97%, more preferably at least 99% and most preferably at least 99.5% of the retentate component of the feed stream separation stage (1) which has been introduced into the apparatus with the crude gas stream (17) is discharged via the second retentate stream (8).

The cut in the separation stage of retentate separation stage (2), at a concentration of component A or of a permeate gas A of 50% in the first retentate stream (7), is between 10 and 60%, preferably between 20 and 50%.

The permeate of the retentate separation stage (2) is recycled by means of the second permeate stream (9), supplied to the feed stream (5) and reprocessed. This
5 can, as already explained above in the definition of the term "feed stream", be effected in different ways according to whether a compressor (4) or even a multistage compressor (4) is used. In the case of a one-stage compressor (4), the second permeate stream
10 (9) is preferably supplied to the suction side of the compressor (4) (see fig. 11). If a multistage compressor is used, it is preferable that the second permeate stream (9) is introduced into the compressor between two compression stages (see figs. 12 and 13).

15

The permeate of the feed stream separation stage (1) which has been greatly enriched with component A or a permeate gas A is supplied by means of the first permeate stream (6) to the permeate separation stage
20 (3). If necessary, it is possible by means of a pressure-reducing valve (14) in the retentate stream of the permeate separation stage (3), i.e. the third retentate stream (10), to prevent the pressure of the permeate of the feed stream separation stage (1) from declining to ambient pressure (see fig. 11). In this
25 way, the driving force for the permeate separation stage (3) can be maintained. The permeate separation stage (3) produces a permeate with a content of component B or of a retentate gas B of greater than 95%, preferably greater than 97% and more preferably
30 greater than 99%, which is discharged from the apparatus via the third permeate stream (11). In a particularly preferred embodiment, the inventive apparatus is configured such that not more than 5%,
35 preferably not more than 3%, more preferably not more than 1% and most preferably not more than 0.5% of the retentate component of the feed stream separation stage (1) introduced into the apparatus with the crude gas

stream (17) is discharged via the third permeate stream (11).

The cut in the separation stage of the permeate
5 separation stage (3) is between 50 and 95%, preferably between 70 and 93%.

The third retentate stream (10) is recycled, supplied to the feed stream (5) and reprocessed. This can, as
10 already explained above, be effected in different ways and may depend, for example, on whether a compressor (4) or even a multistage compressor (4) is used. In the case of a one-stage compressor (4), the third retentate stream (10) is preferably supplied to the suction side
15 of the compressor (4) (see fig. 11). If a multistage compressor is used, it is preferable that the third retentate stream (10) is introduced into the compressor between two compression stages (see figs. 12 and 13).

20 The process according to the invention or the inventive apparatus is notable particularly in that it is configured such that the gas volume recycled in the second permeate stream (9) and in the third retentate stream (10) totals less than 60% by volume, preferably
25 10 to 50% by volume, most preferably 20 to 40% by volume, of the volume of the crude gas stream (17). The control of the amount of the retentate gas streams to be recycled can be controlled, for example, through selection of the respective membrane modules in the
30 membrane separation stages (1) to (3) or by the pressures in the system or by the flows. The process according to the invention or the apparatus is thus notable in that, in spite of very low return streams, the increase in the concentration of the permeate
35 component in the feed stream (5), which has been explained in detail above, is ensured. This distinctly increases the efficiency of the overall process.

The first permeate stream (6) is preferably conducted such that the feed pressure of the permeate separation stage (3), preferably by means of a pressure-reducing valve (14) on the retentate side of the permeate separation stage (3), is between 1 and 30 bar, preferably between 2 and 20 bar and more preferably 3 and 10 bar.

As already explained, it is particularly advantageous when a multistage compressor (4) is used. This is because it is possible in this case to dispense with a complete decompression of the retentate of the permeate separation stage (3), since the retentate of the permeate separation stage (3) can be fed in between two compressor stages of the compressor (4) (see figs. 12 and 13).

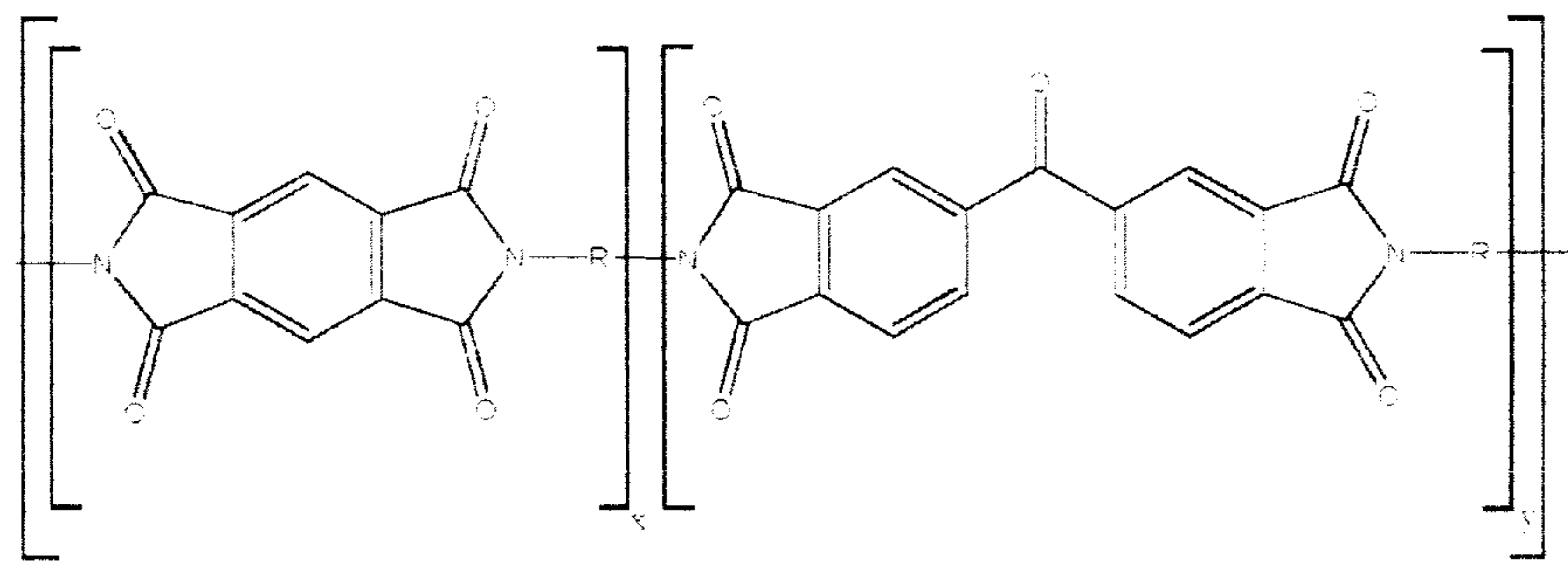
Since the retentate separation stage (2), in the case of decompression to feed pressure, would generally be operated in the selectivity-limited range, it may be advisable to decompress the second permeate stream (9) merely to a higher pressure level of a multistage pressure-increasing unit, i.e. of a multistage compressor (4), since this reduces the operating costs for the compression unit without distinctly worsening the separation outcome. In a particularly preferred embodiment of the present invention, therefore, a multistage compressor (4) is used and the gas streams (9) and (10) are supplied to this compressor in each case between two compression stages. Such a connection arrangement is shown in fig. 12.

As already mentioned, the inventive apparatus may comprise one or more pressure-reducing valves (12), (13) or (14). In a preferred embodiment, preferably by means of a pressure-reducing valve (14), it is ensured that the pressure drop over the feed stream separation stage (1) is restricted to 1 and 30 bar, preferably

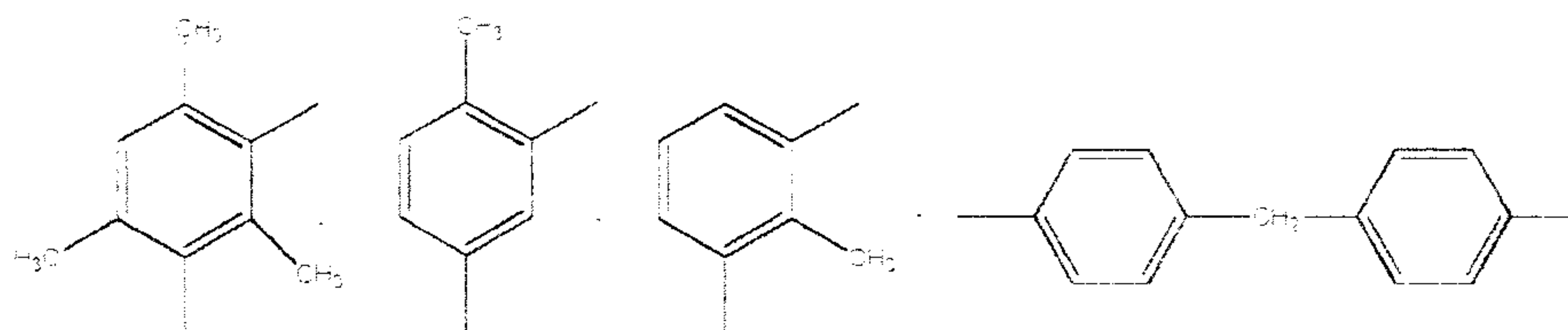
between 2 and 20 bar and more preferably between 3 and 10 bar. Simultaneously or alternatively, preferably by means of a pressure-reducing valve (13), it is ensured that the pressure drop over the feed stream separation stage (1) and the retentate separation stage (2), is restricted to 1 and 100 bar, preferably between 5 and 80 bar and more preferably between 10 and 70 bar.

The inventive apparatus or the process according to the invention can in principle be implemented with all membranes which are capable of separating binary gas mixtures or multigas mixtures. The membrane materials used are preferably but not exclusively polymers. Useful polymers in the separation-active layer are more preferably polyimides, polyamides, polysulfones, cellulose acetates and derivatives, polyphenylene oxides, polysiloxanes, polymers with intrinsic microporosity, mixed matrix membranes, facilitated transport membranes, polyethylene oxides, polypropylene oxides, carbon membranes or zeolites, or mixtures thereof.

Particularly preferred membranes comprise, as materials for the separation-active layer or as a material for the complete membrane, a polyimide of the general formula



R is selected from the group consisting of



x, y : mol fraction where $0 < x < 0.5$ and $1 > y > 0.5$.

5

Such membranes are obtainable from Evonik Fibres GmbH under the Polyimide P84 and Polyimide P84 HT names. A process for producing these preferred membranes is disclosed in WO 2011/009919 A1. All membranes disclosed
 10 in this publication can be used with preference in the process according to the invention. To avoid straightforward repetition, reference is hereby made completely to the content of this patent application. It has been found that these membranes can achieve the
 15 best separation outcomes.

The membranes are preferably used in the form of hollow fiber membranes and/or flat membranes. The membranes are assembled into modules, which are then used in the
 20 separation task. The modules used may be all gas separation modules known in the prior art, for example but not exclusively hollow fiber gas separation modules, spiral-wound gas separation modules, cushion gas separation modules or tube bundle gas separation
 25 modules.

According to the invention, the gas separation membrane modules have a mixed gas selectivity of components A and B (= ratio of stream A to stream B through the
 30 membrane) of at least 30, preferably at least 35, more preferably at least 40, even more preferably of at least 45 and especially preferably of at least 45 to 80. Membranes of higher selectivity have the advantage that the separation becomes more effective and less
 35 permeate has to be recycled from retentate separation

stage (2), or less retentate from permeate separation stage (3). Thus, especially in the case of use of a one-stage compressor (4), it is necessary to compress less gas twice, which entails economic advantages in the operation of the plant. In the case of very selective membrane modules having a selectivity of 45, only approx. 35% of the gas introduced into the feed stream separation stage (1) as crude gas need be compressed twice; with a membrane module having a selectivity of only 10, it may be the case that the double compression is up to 300%. The figures of 35% and 300% are based on experiments in which a gas mixture with equimolar amounts of components A and B (= feed) was applied, with 98.5% component B present in the retentate gas of stage (2) and 99% of component B in the permeate stream of stage (3).

It is evident that the inventive operation can be conducted in a much more economically viable manner with more selective membranes, and the necessary size of the compressor and the energy required can be reduced.

The process according to the invention / the inventive apparatus has the particular advantages that it is a pure membrane process and does not need any additional purification of the permeate and/or retentate streams (11) or (8) for many applications. For example, in the case of purification of biogas or natural gas (= removal of carbon dioxide from methane), there is no longer any need for a pressure swing adsorption or amine scrubbing for fine purification of the retentate, and so it can be fed into the natural gas grid.

In addition, with the process according to the invention / the inventive apparatus, it is possible at the same time to produce a pure retentate stream (8) and a pure permeate stream (11) in the biogas and

natural gas purification. It can therefore be released into the atmosphere without any great losses of methane and without any great impairment of the environment, without any need for further treatment of the gas by a catalytic postcombustion or utilization in a combined heat and power plant. There is therefore no need for investment in further plant parts, which leads to a more economically viable purification process for biogas and natural gas.

10

A further advantage is considered to be that the process according to the invention / the inventive apparatus needs a much lower level of apparatus complexity and energy expenditure than the known prior art processes.

15

Especially through the combination of the inventive features of mixed gas selectivity, control of the amount of the retentate streams recycled and increase in the permeate component in the feed stream (5), an apparatus or a process much superior to the prior art processes can be provided.

20

The inventive apparatus or the process according to the invention can especially be used for separation of gas mixtures comprising at least two gases, the gas mixture separated most preferably being a mixture of predominantly but not exclusively carbon dioxide and methane or predominantly but not exclusively hydrogen and methane or predominantly but not exclusively carbon monoxide and hydrogen or crude biogas or crude natural gas.

30

The examples which follow are intended to illustrate and describe the present invention in detail, but do not restrict it in any way.

35

In the examples which follow, it was shown that, according to inventive connection arrangement of the modules and application of particular pressures, it was possible to simultaneously produce methane with a
5 purity of more than 96% and carbon dioxide with a purity of more than 97% from a mixture of carbon dioxide and methane in a ratio of 50 to 50.

Comparative example 1: Separation of a mixture of
10 methane and carbon dioxide with a mixing ratio of 50 to 50 with a moderately selective polyimide membrane

The fig. 11 shown connection arrangement was used. Each stage consisted of a hollow fiber membrane module
15 consisting of hollow polyimide fibers from UBE (NM B01 A type). 1.78 m³/h of a crude gas mixture of 50% methane and 50% carbon dioxide, which corresponds approximately to a gas mixture of biogas, is introduced into a mixing chamber (not shown in fig. 11) and then
20 compressed to 25 bar together with recycled gas composed of gas streams (9) and (10). The gas which has been compressed and cooled to 20°C is applied to the feed stream separation stage (1). The retentate of the feed stream separation stage (1) is subsequently passed
25 via the first retentate stream (7) to the retentate separation stage (2). A reducing valve (13) on the retentate side of the retentate separation stage (2) is set to 18.2 bara and thus determines the driving force through the membrane of membrane separation stages (1) and (2). The retentate of the retentate separation
30 stage (2) has a content of 98.5% methane and 1.5% carbon dioxide. 0.895 m³/h of this mixture leaves retentate separation stage (2). The permeate of retentate separation stage (2) has a volume flow rate
35 of 0.743 m³/h with a methane content of 34.5% and a carbon dioxide content of 65.5%, and is recycled via the second permeate stream (9) into the mixing chamber and compressed again by the compressor (4).

The permeate of the feed stream separation stage (1) has a volume flow rate of $1.67 \text{ m}^3/\text{h}$ with a carbon dioxide content of 91.0% and a methane content of 9.0%, and is passed via the first permeate stream (6) as feed
5 into the permeate separation stage (3). The pressure drop over the membrane of stage (1) does not extend to ambient pressure, but is limited to 4.2 bara by a reducing valve (14) on the retentate side of the permeate separation stage (3). This gives a third
10 permeate stream (11) from permeate separation stage (3) of $0.885 \text{ m}^3/\text{h}$ with a composition of 99.0% carbon dioxide and only 1.0% methane. The third retentate stream (10) from the permeate separation stage (3) is $0.801 \text{ m}^3/\text{h}$ with a composition of 17.9% methane and 82.1% carbon
15 dioxide and is recycled into the mixing chamber and compressed again. The sum of recycled gas streams (9) and (10) is therefore $1.544 \text{ m}^3/\text{h}$ or 86.7% based on the amount of gas to be separated supplied. Pure product streams are obtained with a relatively high double
20 compression rate. The membranes used exhibit a moderate mixed gas selectivity for carbon dioxide over methane of 20.

Example 1: Separation of a mixture of methane and
25 carbon dioxide with a mixing ratio of 50 to 50 with a highly selective polyimide membrane

The fig. 11 shown connection arrangement was used. Each stage consisted of a hollow fiber membrane module
30 consisting of highly selective hollow polyimide fibers with a separation area of about 5 m^2 per module. These hollow polyimide fibers were produced according to example 19 of Austrian patent application A1164/2009, except working with a precipitation bath temperature of
35 40°C rather than 10°C . $1 \text{ m}^3/\text{h}$ of a crude gas mixture of 50% methane and 50% carbon dioxide, which corresponds approximately to a gas mixture of biogas, is introduced into a mixing chamber and then compressed to 25 bar

together with recycled gas composed of gas streams (9) and (10). The gas which has been compressed and cooled to 20°C is applied to the feed stream separation stage (1). The retentate of this stage is passed via the first retentate stream (7) to the retentate separation stage (2). A reducing valve (13) on the retentate side of the retentate separation stage (2) is set to 18.4 bara and thus determines the driving force through the membrane of membrane separation stages (1) and (2). The retentate of the retentate separation stage (2) has a content of 98.5% methane and 1.5% carbon dioxide. 0.503 m³/h of this mixture leaves retentate separation stage (2). The permeate of retentate separation stage (2) has a volume flow rate of 0.262 m³/h with a methane content of 24.6% and a carbon dioxide content of 75.4%, and is recycled via the second permeate stream (9) into the mixing chamber and compressed again by the compressor (4).

The permeate of the feed stream separation stage (1) has a volume flow rate of 0.547 m³/h with a carbon dioxide content of 92.4% and a methane content of 7.6%, and is passed via the first permeate stream (6) as feed into the permeate separation stage (3). The pressure drop over the membrane of stage (1) does not extend to ambient pressure, but is limited to 5.0 bara by a reducing valve (14) on the retentate side of the permeate separation stage (3). This gives a third permeate stream (11) from permeate separation stage (3) of 0.497 m³/h with a composition of 99.0% carbon dioxide and only 1.0% methane. The third retentate stream (10) from the permeate separation stage (3) is 0.050 m³/h. The sum of recycled gas streams (9) and (10) is therefore 0.312 m³/h or 31.2% based on the amount of gas to be separated supplied. Pure product streams are obtained with a moderate double compression rate. The membranes used exhibit a high mixed gas selectivity for carbon dioxide over methane of 45. The high selectivity of 45 compared to 20 in the comparative example

therefore enables a more economically favorable process by a lower recompression of 31.2% rather than 86.7%.

Example 2: Separation of a mixture of methane and carbon dioxide with a mixing ratio of 50 to 50 with a highly selective polyimide membrane with a methane content in the permeate stream of less than 0.5%

In order to satisfy various legislators, it is necessary to minimize the methane loss into the atmosphere. The fig. 11 shown connection arrangement was used to lower the concentration of methane in the third permeate stream (11) to below 0.5% by volume. Each stage consisted of a hollow fiber membrane module consisting of highly selective polyimide with a separation area of about 5 m² per module. These hollow polyimide fibers were produced according to example 19 of Austrian patent application A1164/2009, except working with a precipitation bath temperature of 40°C rather than 10°C. 1 m³/h of a crude gas mixture of 50% methane and 50% carbon dioxide, which corresponds approximately to a gas mixture of biogas, is introduced into a mixing chamber and then compressed to 25 bar together with recycled gas composed of gas streams (9) and (10). The gas which has been compressed and cooled to 20°C is applied to the feed stream separation stage (1). The retentate of this stage is passed via the first retentate stream (7) to the retentate separation stage (2). A reducing valve (13) on the retentate side of the retentate separation stage (2) is set to 18.1 bara and thus determines the driving force through the membrane of membrane separation stages (1) and (2). The retentate of the retentate separation stage (2) has a content of 98.5% methane and 1.5% carbon dioxide. 0.505 m³/h of this mixtures leaves retentate separation stage (2). The permeate of retentate separation stage (2) has a volume flow rate of 0.244 m³/h with a methane content of 26.1% and a carbon dioxide content of 73.9%,

and is recycled via the second permeate stream (9) into the mixing chamber and compressed again by the compressor (4).

The permeate of the feed stream separation stage (1) has a volume flow rate of 0.607 m³/h with a carbon dioxide content of 93.1% and a methane content of 6.9%, and is passed via the first permeate stream (6) as feed into the permeate separation stage (3). The pressure drop over the membrane of stage (1) does not extend to ambient pressure, but is limited to 4.4 bara by a reducing valve (14) on the retentate side of the permeate separation stage (3). This gives a third permeate stream (11) from permeate separation stage (3) of 0.495 m³/h with a composition of 99.5% carbon dioxide and only 0.5% methane. The third retentate stream (10) from the permeate separation stage (3) is 0.112 m³/h and has a composition of 35% methane and 65% carbon dioxide and is recycled into the mixing chamber and compressed again. The sum of recycled streams (9) and (10) is therefore 0.356 m³/h or 35.6% based on the amount of gas to be separated supplied. Pure product streams are obtained with a moderate double compression rate. The membranes used exhibit a high mixed gas selectivity for carbon dioxide over methane of 45.

25

Example 3: Separation of a mixture of methane and carbon dioxide with a mixing ratio of 50 to 50 with a highly selective polyimide membrane with a methane content in the permeate stream of less than 0.5% with the aid of a vacuum pump for the permeate of stage 2

30

In order to satisfy various legislators, it is necessary to minimize the methane loss into the atmosphere. The fig. 11 shown connection arrangement, supplemented with a vacuum pump not shown in fig. 11, was used to lower the concentration of methane in the third permeate stream (11) to below 0.5% by volume. Each stage consisted of a hollow fiber membrane module

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consisting of highly selective hollow polyimide fibers with a separation area of about 5 m² per module. These hollow polyimide fibers were produced according to example 19 of Austrian patent application A1164/2009, except working with a precipitation bath temperature of 40°C rather than 10°C. 1 m³/h of a crude gas mixture of 50% methane and 50% carbon dioxide, which corresponds approximately to a gas mixture of biogas, is introduced into a mixing chamber and then compressed to 25 bar together with recycled gas composed of gas streams (9) and (10). The gas which has been compressed and cooled to 20°C is applied to the feed stream separation stage (1). The retentate of this stage is passed via the first retentate stream (7) to the retentate separation stage (2). A reducing valve (13) on the retentate side of the retentate separation stage (2) is set to 14.5 bara and thus determines the driving force through the membrane of membrane separation stages (1) and (2). The retentate of the retentate separation stage (2) has a content of 98.5% methane and 1.5% carbon dioxide. 0.505 m³/h of this mixture leaves retentate separation stage (2). The permeate of retentate separation stage (2) has a pressure of 0.2 bara, established by a vacuum pump, and has a volume flow rate of 0.371 m³/h with a methane content of 13.3% and a carbon dioxide content of 86.7%. The gas stream is recycled from the pressure side of the vacuum pump via the second permeate stream (9) into the mixing chamber and compressed again by the compressor (4).

The permeate of the feed stream separation stage (1) has a volume flow rate of 0.542 m³/h with a carbon dioxide content of 94.8% and a methane content of 5.2%, and is passed via the first permeate stream (6) as feed into the permeate separation stage (3). The pressure drop over the membrane of stage (1) does not extend to ambient pressure, but is limited to 4.4 bara by a reducing valve (14) on the retentate side of the permeate separation stage (3). This gives a third

permeate stream (11) from permeate separation stage (3) of 0.495 m³/h with a composition of 99.5% carbon dioxide and only 0.5% methane. The third retentate stream (10) from the permeate separation stage (3) is 0.047 m³/h and
5 has a composition of 54.9% methane and 45.1% carbon dioxide and is recycled into the mixing chamber and compressed again. The sum of recycled streams (9) and (10) is therefore 0.417 m³/h or 41.7% based on the amount of gas to be separated supplied. Pure product
10 streams are obtained with a moderate double compression rate. The membranes used exhibit a high mixed gas selectivity for carbon dioxide over methane of 45. In contrast to the above example 2, less pressure is required (14.5 bar rather than 18.1 bar = 80.1% of the
15 pressure), and only 6.1% more double compression, which leads to a saving in compression work.

Example 4: Separation of a mixture of methane and carbon dioxide with a mixing ratio of 50 to 50 with a
20 highly selective polyimide membrane with a methane content in the permeate stream of less than 0.5% with the aid of a vacuum pump for the permeate of stage 2 and improved retentate purity

In order to satisfy various legislators, it is
25 necessary to minimize the methane loss into the atmosphere.

The fig. 11 shown connection arrangement, supplemented with a vacuum pump not shown in fig. 11, was used to increase the concentration of methane in the second
30 retentate stream (8). The vacuum improves the pressure ratio in the retentate separation stage (2) by reducing the pressure in the second permeate stream (9), such that the driving force is increased and higher purities can be achieved in the second retentate stream (8).

35 Each stage consisted of a with a separation area of about 5 m² per module. These hollow polyimide fibers were produced according to example 19 of Austrian patent application A1164/2009, except working with a

precipitation bath temperature of 40°C rather than 10°C. 1 m³/h of a crude gas mixture of 50% methane and 50% carbon dioxide, which corresponds approximately to a gas mixture of biogas, is introduced into a mixing chamber and then compressed to 25 bar together with recycled gas composed of gas streams (9) and (10). The gas which has been compressed and cooled to 20°C is applied to the feed stream separation stage (1). The retentate of this stage is passed via the first retentate stream (7) to the retentate separation stage (2). A reducing valve (13) on the retentate side of the retentate separation stage (2) is set to 18.1 bara and thus determines the driving force through the membrane of membrane separation stages (1) and (2). The retentate of the retentate separation stage (2) has a content of 99.7% methane and 0.3% carbon dioxide. 0.499 m³/h of this mixture leaves retentate separation stage (2). The permeate of retentate separation stage (2) has a pressure of 0.2 bara, established by a vacuum pump, and has a volume flow rate of 0.258 m³/h with a methane content of 25.8% and a carbon dioxide content of 74.2%. The gas stream is recycled from the pressure side of the vacuum pump via the second permeate stream (9) into the mixing chamber and compressed again by the compressor (4).

The permeate of the feed stream separation stage (1) has a volume flow rate of 0.608 m³/h with a carbon dioxide content of 93.2% and a methane content of 6.8%, and is passed via the first permeate stream (6) as feed into the permeate separation stage (3). The pressure drop over the membrane of stage (1) does not extend to ambient pressure, but is limited to 4.4 bara by a reducing valve (14) on the retentate side of the permeate separation stage (3). This gives a third permeate stream (11) from permeate separation stage (3) of 0.501 m³/h with a composition of 99.5% carbon dioxide and only 0.5% methane. The third retentate stream (10) from the permeate separation stage (3) is 0.107 m³/h and

has a composition of 36.2% methane and 63.8% carbon dioxide and is recycled into the mixing chamber and compressed again. The sum of recycled streams (9) and (10) is therefore 0.366 m³/h or 36.6% based on the amount of gas to be separated supplied. Pure product streams are obtained with a moderate double compression rate. The membranes used exhibit a high mixed gas selectivity for carbon dioxide over methane of 45. In contrast to the above example 3, use of a vacuum pump on the permeate side of the retentate separation stage (2) gives a much cleaner retentate with the same compressor output (99.7% methane rather than 98.5%).

List of figures:

- 5 **Fig. 1:** Influence of the pressure ratio and of the selectivity on the separation outcome
- Fig. 2:** One-stage membrane separation stage without recycling
- 10 **Fig. 3:** One-stage membrane separation stage with recycling
- Fig. 4:** Two-stage membrane separation stage with recompression and recycling
- 15 **Fig. 5:** Staged arrangement for retentate and permeate with recompression and recycling in the second retentate stage upstream of the first retentate stage
- 20 **Fig. 6:** Staged arrangement for retentate and permeate with recompression and recycling in the second retentate stage upstream of the second retentate stage
- 25 **Fig. 7:** Staged arrangement for permeate with recompression
- Fig. 8:** Staged arrangement for retentate with permeate recycling from the second stage and staged arrangement for permeate with recompression
- 30 **Fig. 9:** Staged arrangement for retentate with permeate recycling from the second stage
- 35 **Fig. 10:** Connection arrangement with internal staged arrangement for permeate

Fig. 11: Illustrative connection arrangement of several membrane modules according to invention

5 **Fig. 12:** Three-stage connection arrangement of membrane modules with a compressor and retentate recycling of the permeate separation stage (3) without total decompression into an elevated compression stage of the compressor (4)

10

Fig. 13: Three-stage connection arrangement of membrane modules with a compressor and retentate recycling of the third stage without total decompression and permeate recycling of the second stage into an elevated compression stage of the compressor (4)

15

20 **List of reference numerals:**

- 1: Feed stream separation stage
- 2: Retentate separation stage
- 3: Permeate separation stage 3
- 25 4: One-stage or multistage compressor
- 5: Feed stream
- 6: First permeate stream
- 7: First retentate stream
- 8: Second retentate stream
- 30 9: Second permeate stream
- 10: Third retentate stream
- 11: Third permeate stream
- 12: Optional pressure-reducing valve in the first retentate stream 7
- 35 13: Optional pressure-reducing valve in the second retentate stream 8
- 14: Optional pressure-reducing valve in the third retentate stream 10

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- 15: Vacuum pump (not reproduced in the figures)
- 16: Mixing chamber (not reproduced in the figures)
- 17: Crude gas stream

Claims

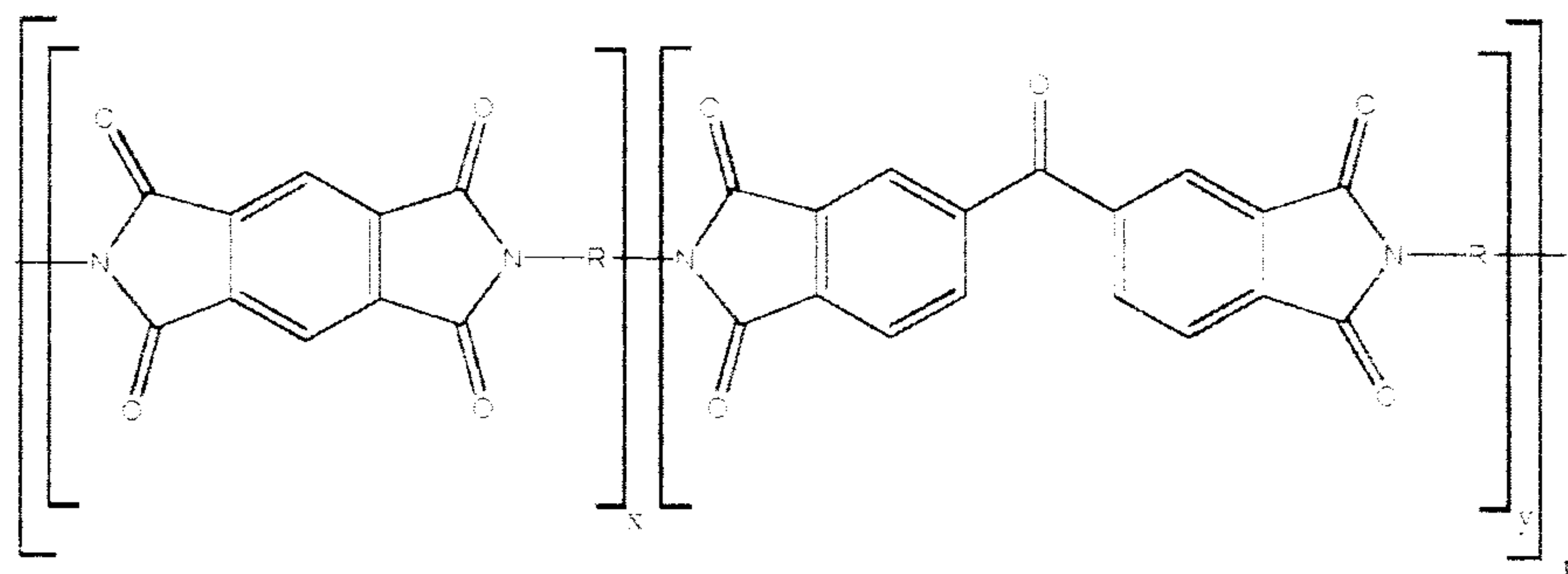
1. An apparatus for separating gases, comprising membrane separation stages (1) to (3), at least one compressor (4) and/or at least one, preferably one or two, vacuum pump(s) (15), the feed stream separation stage (1) separating a feed stream (5) consisting of at least two components into a first permeate stream (6) and a first retentate stream (7), the retentate separation stage (2) dividing the first retentate stream (7) into a second permeate stream (9) which is supplied to the feed stream (5), and a second retentate stream (8) which is withdrawn as a product, and the permeate separation stage (3) dividing the first permeate stream (6) into a third retentate stream (10) which is supplied to the feed stream (5), and a third permeate stream (11) which is withdrawn as a product, characterized in that
- the first permeate stream (6) is not subjected to any recompression,
 - at least in the feed stream separation stage (1), but preferably in all three membrane separation stages (1) to (3), gas separation membrane modules having a mixed gas selectivity of at least 30 are used,
 - the apparatus is configured such that the gas volume recycled in the second permeate stream (9) and in the third retentate stream (10) totals less than 60% by volume of the volume of the crude gas stream (17),
 - the concentration of at least one permeate gas of the feed stream separation stage (1), after recycling of the second permeate stream (9) and of the third retentate stream (10), is increased in the feed stream (5), preferably increased by at least 2%, more preferably by at least 3% and more preferably by 3 to 40%, in each case

compared to the concentration in the crude gas stream (17).

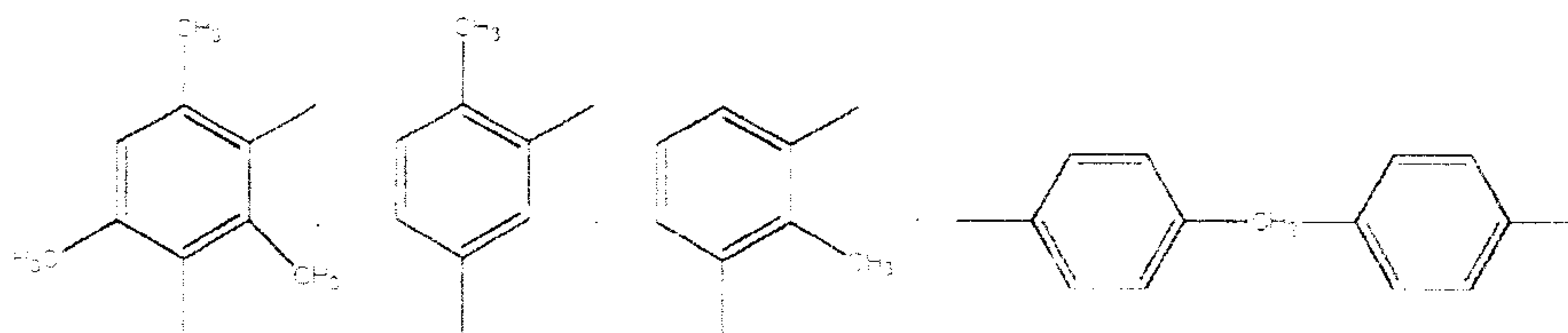
2. The apparatus as claimed in claim 1,
5 characterized in that
the second permeate stream (9) and the third retentate stream (10) are passed along the suction side of the compressor (4) for reprocessing.
- 10 3. The apparatus as claimed in claim 1 or 2,
characterized in that
a multistage compressor (4) is used.
- 15 4. The apparatus as claimed in claim 3,
characterized in that
the second permeate stream (9) and/or the third retentate stream (10) is/are introduced into the compressor (4) between two compression stages.
- 20 5. The apparatus as claimed in any of claims 1 to 4,
characterized in that
the first retentate stream (7) and/or the second retentate stream (8) and/or the third retentate stream (10) is/are passed through a pressure-
25 reducing valve.
6. The apparatus as claimed in any of claims 1 to 5,
characterized in that
a gas separation membrane module having a mixed
30 gas selectivity of at least 35, preferably at least 40 and more preferably at least 45 is used
in at least one of the membrane separation stages
(1) to (3).
- 35 7. The apparatus as claimed in any of claims 1 to 6,
characterized in that
at least one of the membrane separation stages (1)
to (3) comprises more than one gas separation

membrane module, which are connected in parallel and/or in series.

8. The apparatus as claimed in any of claims 1 to 7,
5 characterized in that
the gas separation membrane module(s) consist(s)
of hollow fiber membranes and/or flat membranes.
9. The apparatus as claimed in any of claims 1 to 8,
10 characterized in that
the materials used for the separation-active layer
of the membranes are amorphous or semicrystalline
polymers, for example but not exclusively
15 polyimides, polyamides, polysulfones, cellulose
acetates and derivatives, polyphenylene oxides,
polysiloxanes, polymers with intrinsic
microporosity, mixed matrix membranes, facilitated
transport membranes, polyethylene oxides,
polypropylene oxides or mixtures thereof.
- 20
10. The apparatus as claimed in claim 9,
characterized in that
the material used for the separation-active layer
of the membranes is a polyimide of the general
25 formula



R is selected from the group consisting of



x, y : mol fraction where $0 < x < 0.5$ and $1 > y > 0.5$.

5

11. The apparatus as claimed in any of claims 1 to 10, characterized in that at least 95%, preferably at least 97%, more preferably at least 99% and most preferably at least 99.5% of the retentate component of the feed stream separation stage (1) which has been introduced into the apparatus with the crude gas stream (17) is discharged via the second retentate stream (8).

15

12. The apparatus as claimed in any of claims 1 to 11, characterized in that not more than 5%, preferably not more than 3%, more preferably not more than 1% and most preferably not more than 0.5% of the retentate component of the feed stream separation stage (1) introduced into the apparatus with the crude gas stream (17) is discharged via the third permeate stream (11).

25

13. A process for separating gas mixtures, characterized in that an apparatus according to any of claims 1 to 12 is used.

30

14. The process as claimed in claim 13, characterized in that the gas mixture used is a mixture of predominantly but not exclusively carbon dioxide and methane or predominantly but not exclusively hydrogen and

35

methane or predominantly but not exclusively carbon monoxide and hydrogen or crude biogas or crude natural gas.

- 5 15. The process as claimed in either of claims 13 and 14,
characterized in that
the pressure on the permeate side (6) of the feed
stream separation stage (1) is adjusted,
10 preferably by means of a pressure-reducing valve (14) on the retentate side of the permeate separation stage (3), to 1 to 30 bar, preferably to 2 to 20 bar and more preferably to 3 and 10 bar.
- 15 16. The process as claimed in any of claims 13 to 15, characterized in that
the pressure of the first and second retentate stream (7) and (8) is adjusted, preferably by
20 means of a pressure-reducing valve (13) in the second retentate stream (8), to 1 to 100 bar, preferably to 5 to 80 bar and more preferably to 10 to 70 bar.
- 25 17. The process as claimed in any of claims 13 to 16, characterized in that
the driving force used for the separation task is a partial pressure differential between the retentate side and the permeate side in the
30 respective membrane separation stages, the partial pressure differential being generated by a compressor in the feed stream (5) and/or by a vacuum pump (15) in the second and/or third permeate stream (9) and/or (11) and/or by a
35 permeate-side purge gas stream.
18. The process as claimed in claim 16 or 17, characterized in that

5 the pressure of the permeate of the feed stream separation stage (1) is the same or increased relative to the ambient pressure, such that a partial pressure differential still exists between retentate and permeate of the permeate separation stage (3), and hence there is a driving force in the case that the permeate of the permeate separation stage (3) is at ambient pressure or reduced pressure is applied.

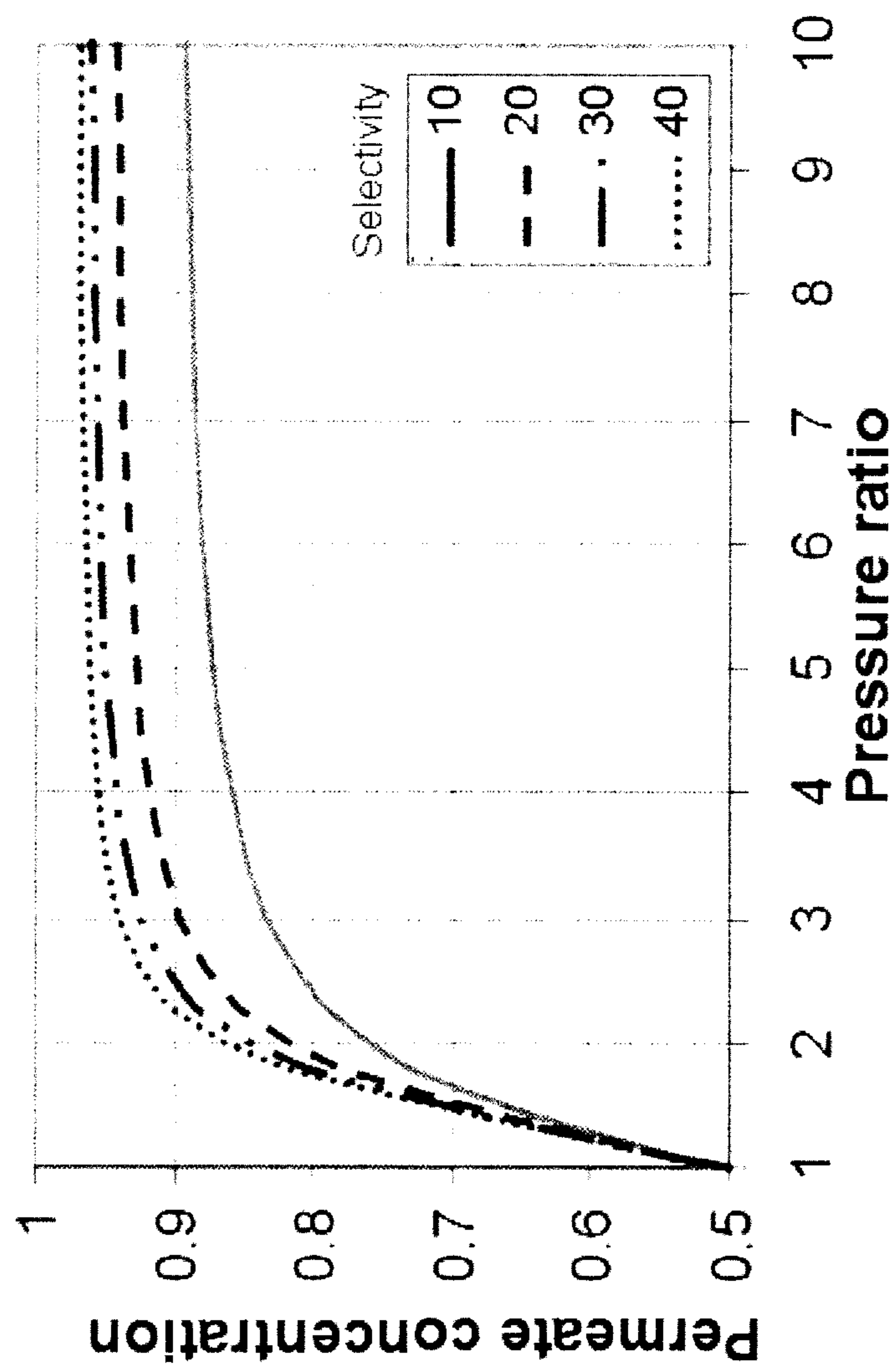


Fig. 1: Influence of the pressure ratio and of the selectivity on the separation outcome

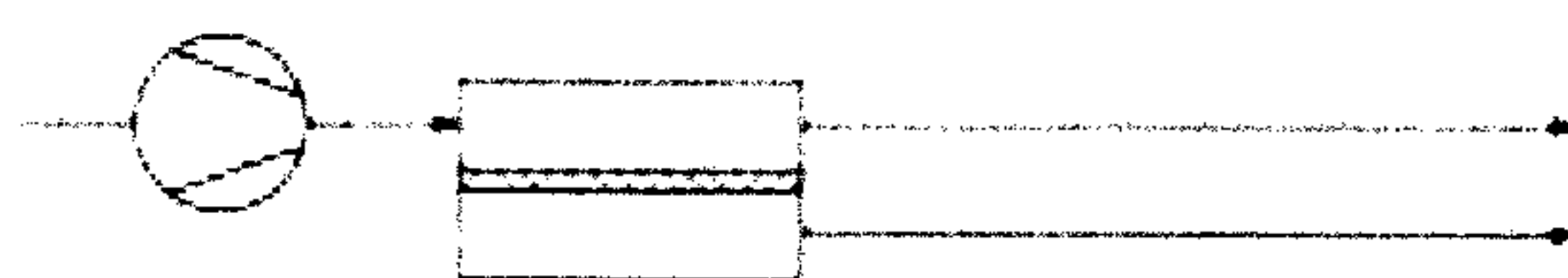


Fig. 2: One-stage membrane separation stage without recycling

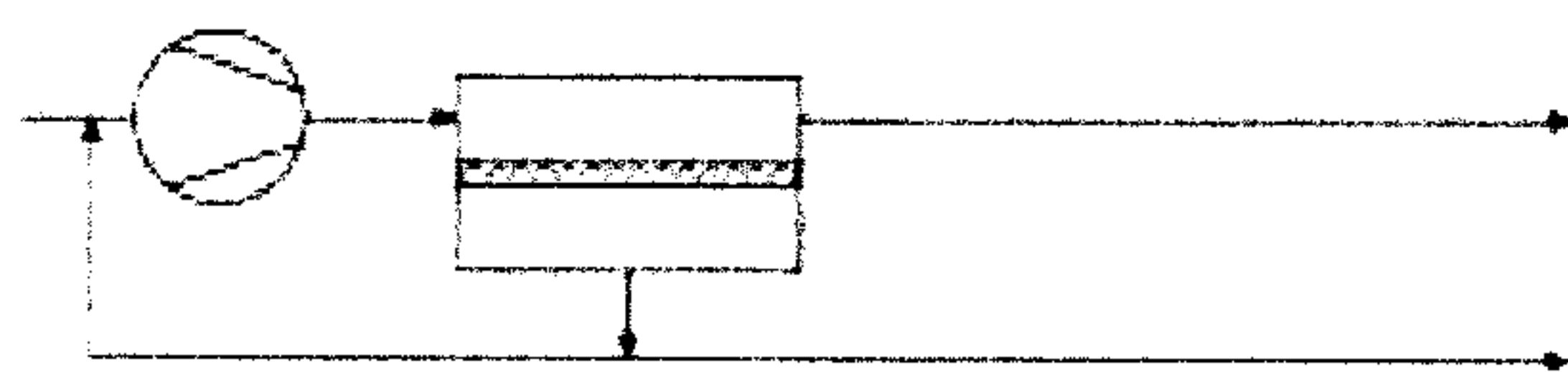


Fig. 3: One-stage membrane separation stage with recycling

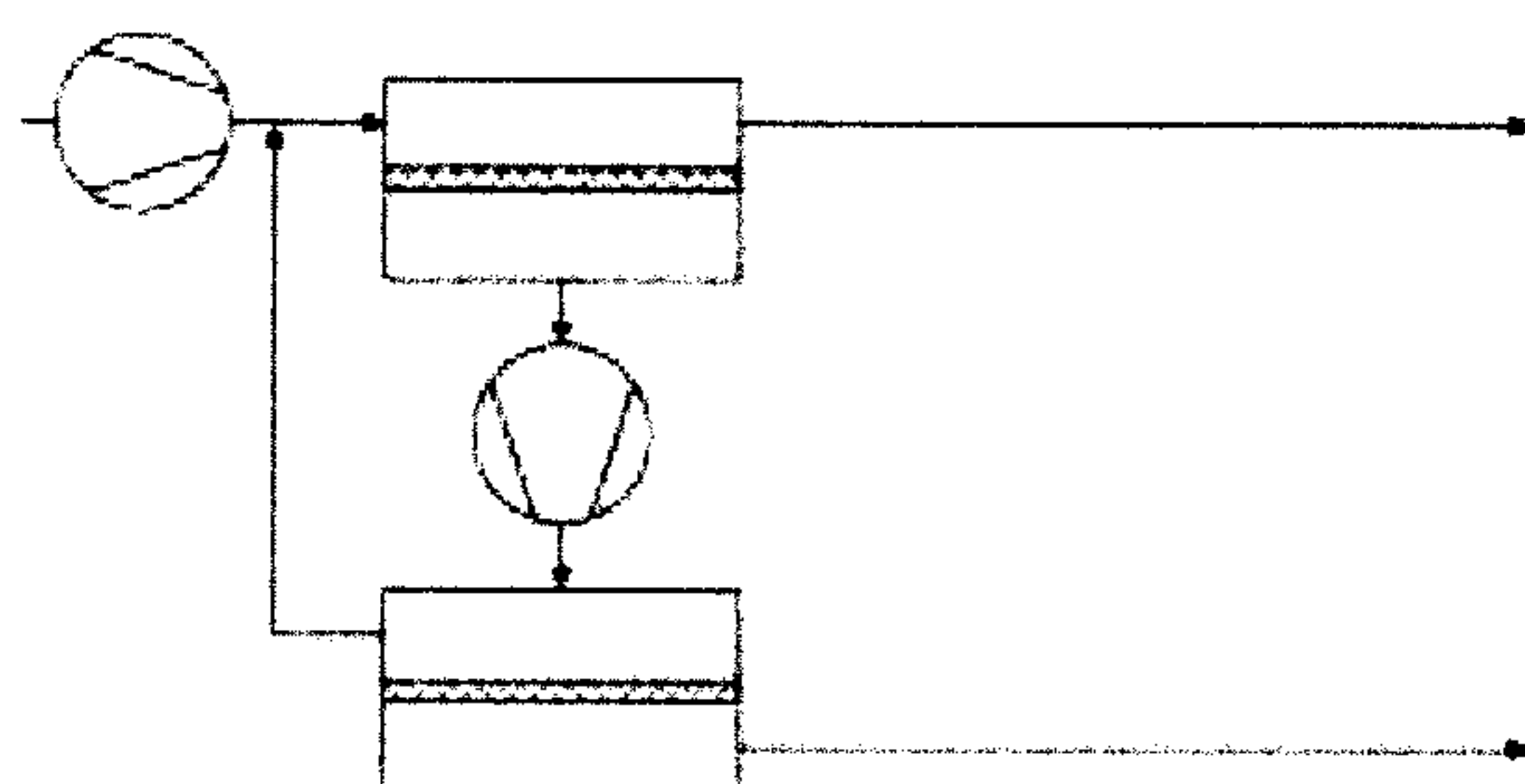


Fig. 4: Two-stage membrane separation stage with recompression and recycling

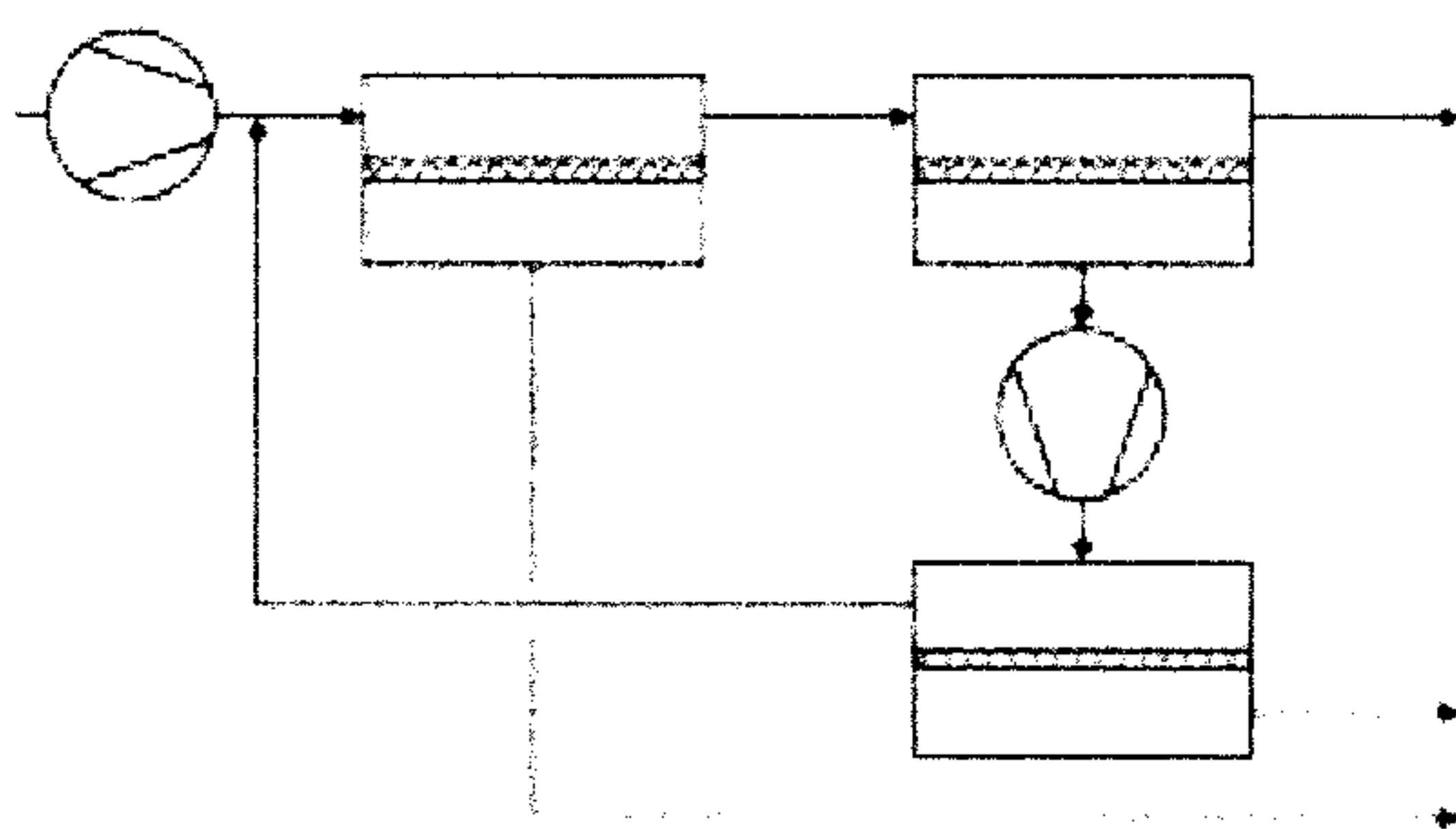


Fig. 5: Staged arrangement for retentate and permeate with recompression and recycling in the second retentate stage upstream of the first retentate stage

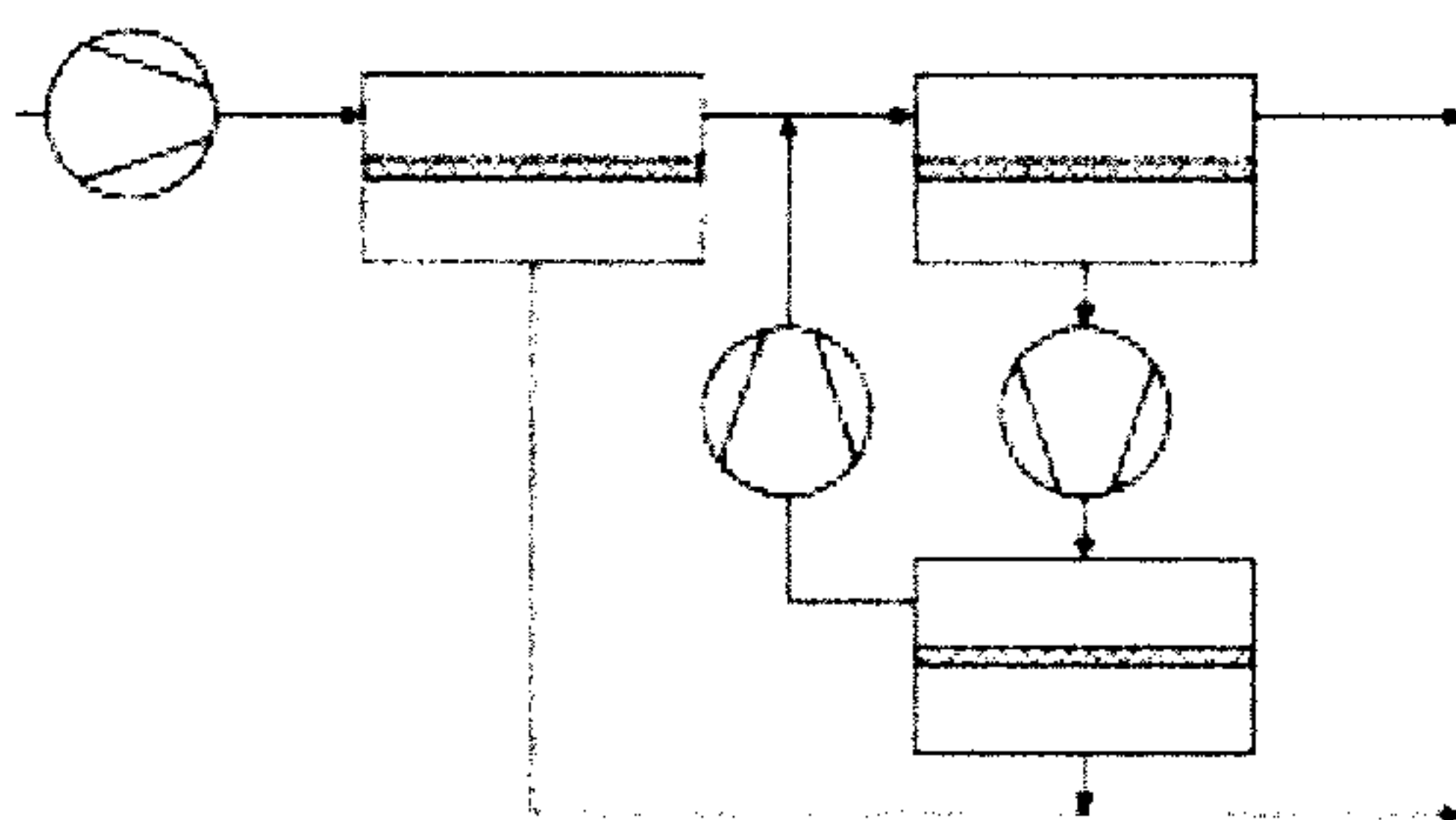


Fig. 6: Staged arrangement for retentate and permeate with recompression and recycling in the second retentate stage upstream of the second retentate stage

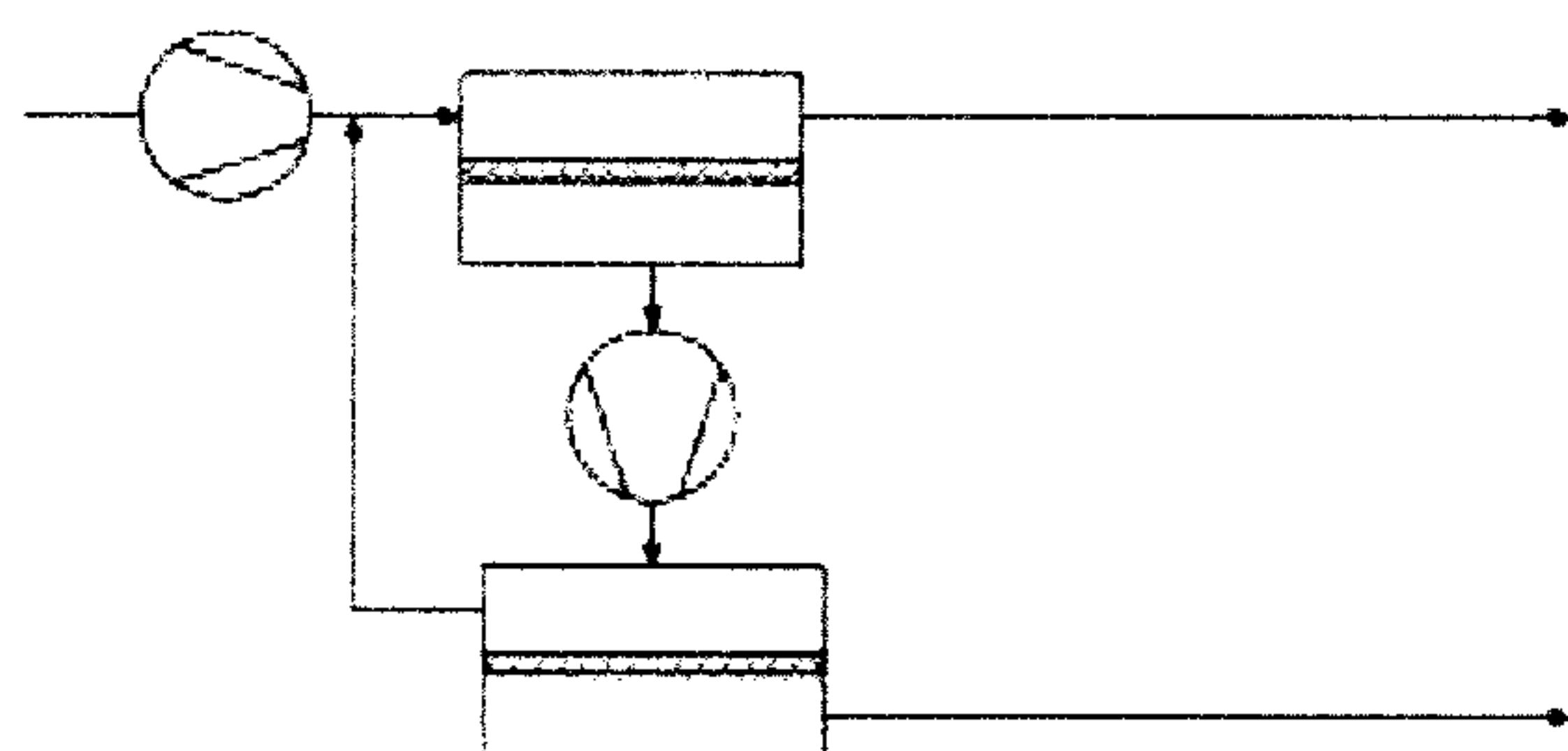


Fig. 7: Staged arrangement for permeate with recompression

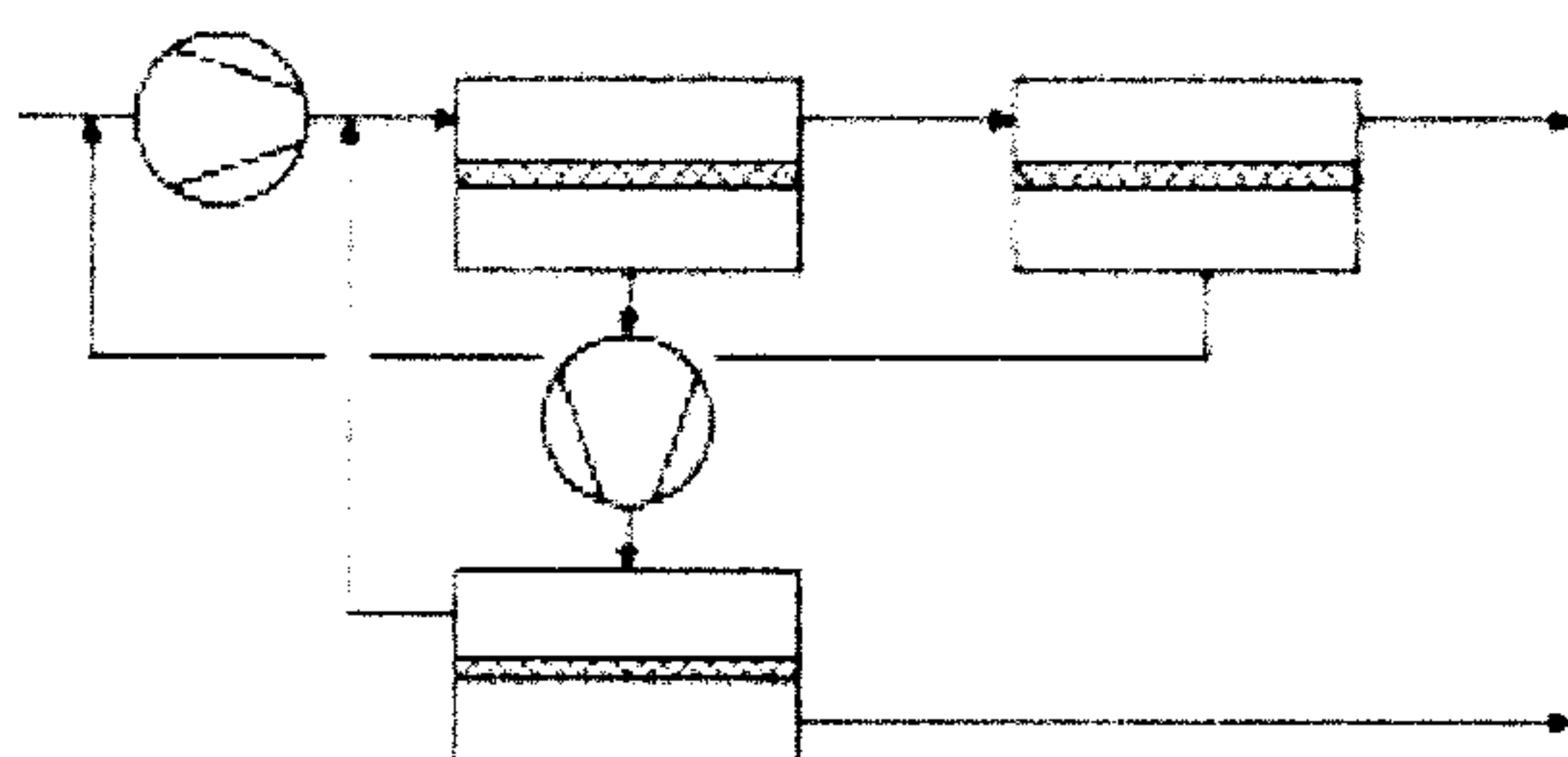


Fig. 8: Staged arrangement for retentate with permeate recycling from the second stage and staged arrangement for permeate with recompression

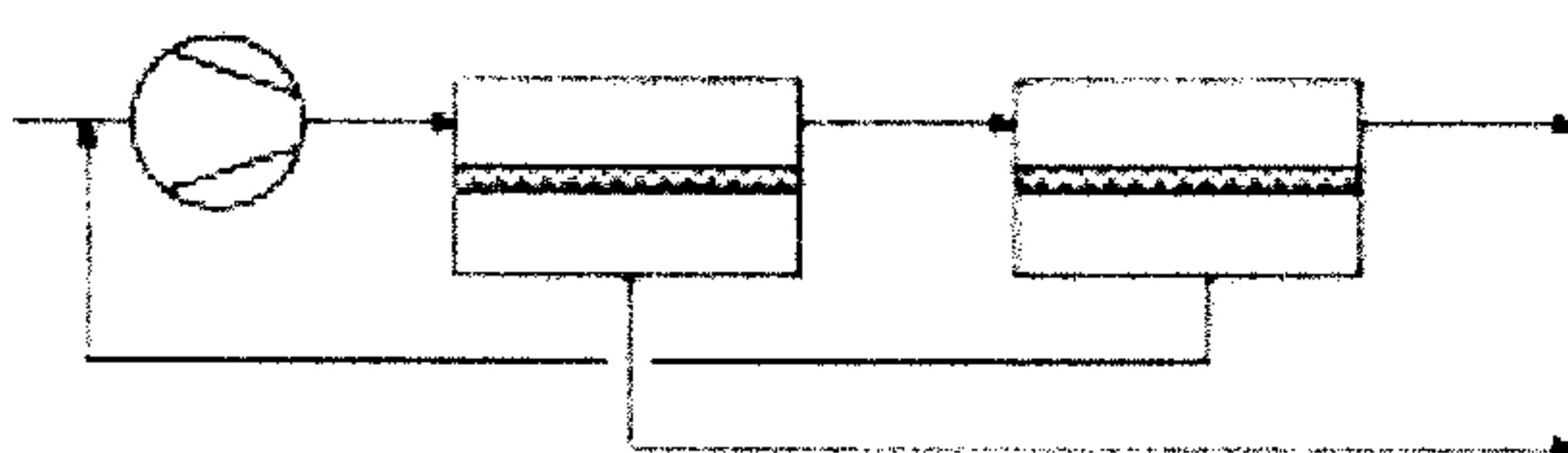


Fig. 9: Staged arrangement for retentate with permeate recycling from the second stage

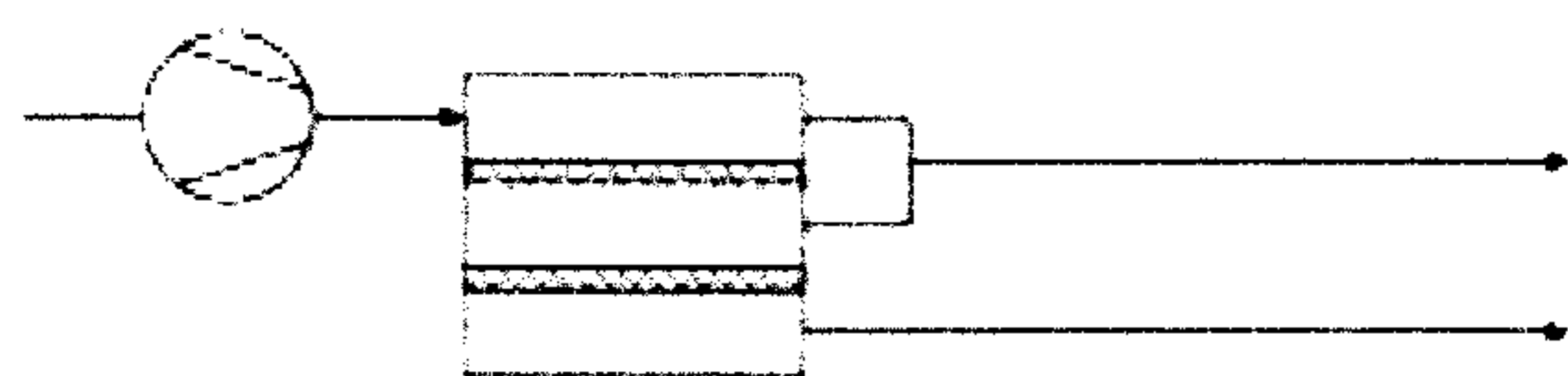


Fig. 10: Connection arrangement with internal staged arrangement for permeate

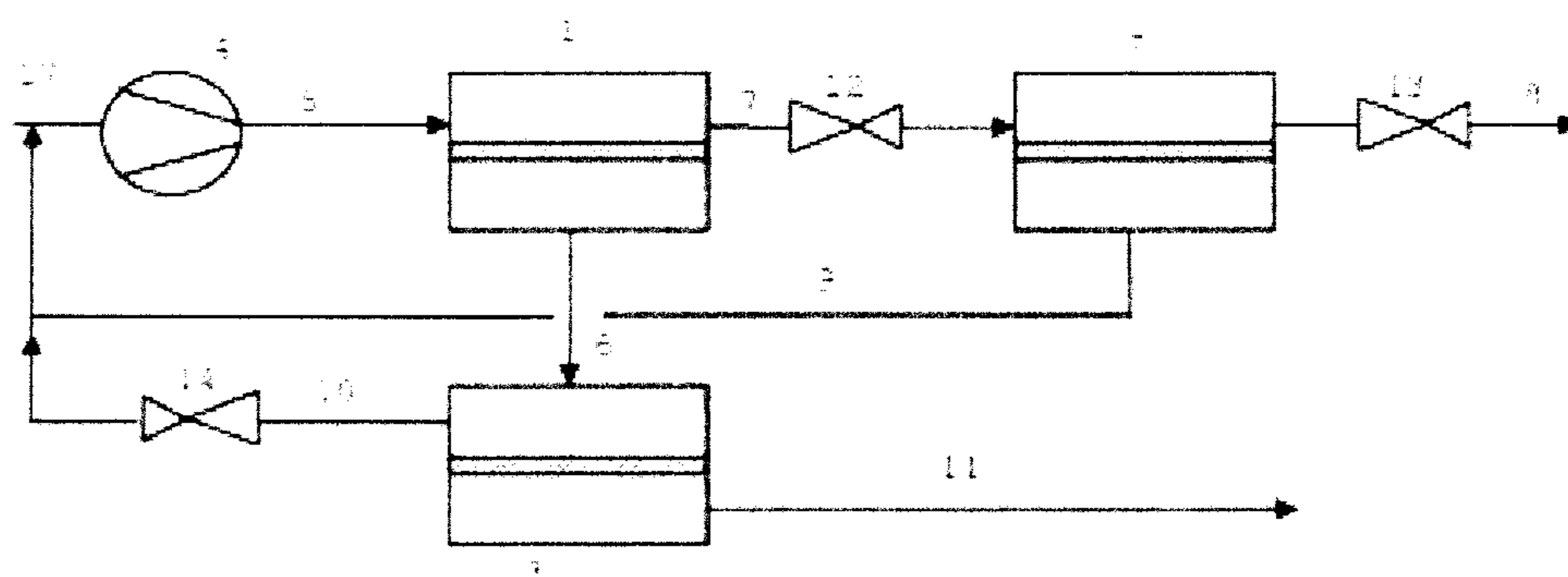


Fig. 11: Illustrative connection arrangement of several membrane modules according to invention