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(54) Title: TAILORED HYDROPHOBIC CARBON MOLECULAR SIEVE MEMBRANE

(57) Abstract: It is provided a hydrophobic carbon molecular sieve membrane (CMSM) characterized by comprising pores with a pore size distribution in which at least 20 % of the pores have a pore size from 0.5 to 0.6 nm, measured by perm-porosimetry; and having a C/O ratio higher than 8 and a C/H ratio higher than 20; the membrane being obtainable by dip-coating a support with a dipping solution comprising a carbon precursor, a non-aqueous solvent, a curing agent, and a pore forming agent, wherein the pore forming agent is in an amount from 0.5 wt% to 8 wt% related to the weight of carbon precursor; followed by carbonization at a temperature higher than 700 °C and lower than 1000 °C; and wherein the carbon molecular sieve membrane has a higher hydrophobicity than a membrane prepared by the same process but without the addition of the pore forming agent. It is also provided a method for the preparation of the CMSM, and its use for the selective separation of propionic acid from a mixture with water and acetic acid and as a membrane reactor or part of a membrane reactor.



Tailored hydrophobic carbon molecular sieve membrane

This application claims the benefit of European Patent Application EP23382699.9 filed on July 07, 2023.

Technical Field

- 5 The present invention relates to carbon molecular sieve membranes (CMSMs) having hydrophobic pores of a specific size and size distribution and their uses for the selective separation of some compounds such as propionic acid, or as membrane reactors.

Background Art

- Propionic acid (PA), is intensively used as antimicrobial agent, anti-inflammatory
10 substance, herbicides, preservatives in bakery and cheese products. Industrially, PA is mainly produced through a petrochemical route reaching to a global market size of 1.5 billion USD in 2021 and estimated to grow to about 1.8 billion USD by 2028. Due to the global increasing demand for PA and problems such as global warming associated with petrochemical route production of PA, bio-PA is preferred as a sustainable alternative.
15 Production of PA in bioreactors are studied for decades. Unfortunately, petrochemical production still is more economical than microbial production.

- In the fermentative production of propionic acid, *Propionibacterium ssp.* is a promising genus. However, the specific growth rate usually drops by more than 50% when there is 1% propionic acid present in the medium. The low productivity and low concentration of
20 the PA produced in the conventional propionic acid fermentations seems to be due to the strongly inhibition produced by PA specially when the pH is below 6. Acetic acid is the most important by-product produced during propionic fermentation and it can impair PA production (due to its toxicity) and recovery in downstream processing. Low acid concentration ensures higher product yield and lower amounts of by-products. One way to
25 increase the yield is by in-situ extraction of PA from the fermentation (extractive fermentation processes). Several techniques have been reported to remove PA such as solvent extraction, electrodialysis, and resin adsorption.

- Membrane such as carbon molecular sieve membranes (CMSMs) are potential candidates for PA in-situ separation by pervaporation. In a PA pervaporation separation
30 process, key parameters such as high PA permeance, PA perm-selectivity and stable performance require a tailor-made membrane regarding hydrophobicity, pore size distribution (PSD) and porosity.

CMSMs are product of the carbonization of thermosetting polymers such as polyimides and phenolic resins, offering the mentioned tunable properties, while being inexpensive

(see M.A. Llosa et al., "Composite-alumina-carbon molecular sieve membranes prepared from Novolac resin and boehmite. Part I: Preparation, characterization and gas permeation studies", *Int. J. Hydrogen Energy*. 2015, vol. 40, pp. 5653–5663; M.A. Llosa et al. "Composite-Alumina-Carbon Molecular Sieve Membranes Prepared from Novolac Resin and Boehmite. Part II: Effect of the Carbonization Temperature on the Gas Permeation Properties". *Int J Hydrogen Energy* 2015, Vol. 40, pp. 3485–3496; J. A. Hamm, et al., "Recent advances in the development of supported carbon membranes for gas separation", *Int J Hydrogen Energy*, 2017, Vol. 42, pp. 24830-24845).

CMSMs can be tailored made by modifying their precursor, nano additives in their structure, carbonization atmosphere and temperature, polymerization degree (PD), and post treatment (see A. Rahimalimamaghani, et al. "Ultra-Selective CMSMs Derived from Resorcinol-Formaldehyde Resin for CO₂ Separation". *Membranes* 2022, Vol. 12, Page 847 **2022**, 12, 847; A. Rahimalimamaghani, et al. "Effect of aluminium acetyl acetate on the hydrogen and nitrogen permeation of carbon molecular sieves membranes". *Int J Hydrogen Energy*, 2022, Vol. 47, pp. 14570-14579).

However, enhancing both PA perm-selectivity and permeance faces challenges due to existing problems such as the stability of the membrane, fouling, reproducibility, and tradeoff between perm-selectivity and permeance which hinders from industrial application.

Therefore, from what is known in the state of the art, there is still a need for a stable chemically/physically CMSM for long term performance and efficient in-situ separation of PA from low concentration aqueous phases in membrane bio reactors.

Summary of Invention

The inventors of the present invention have developed a hydrophobic carbon molecular sieve membrane (CMSM) obtained by dip-coating a support with a dipping solution comprising a phenolic resin and a polymer acting as pore forming agent and source of hydrophobic carbon and, then, carrying out a carbonization at a temperature higher than 700 °C and lower than 1000 °C in order to make the membrane hydrophobic. In particular, the inventors have found that the incorporation of a certain amount of a pore forming agent such as polyvinyl butyral (PVB), methylcellulose, poly(vinyl alcohol) (PVOH), and polyvinylpyrrolidone (PVP), among others, to the dipping solution allows obtaining a carbon molecular sieve membrane with a pore diameter in the microporous region (such as from 0.5 to 0.6 nm) and having a higher hydrophobicity than the corresponding CMSMs prepared without the addition of the pore forming agent.

By the use of the pore forming, the inventors not only have achieved a specific pore

diameter but also a narrower pore size distribution in the whole membrane, and a stable porous structure.

Besides, advantageously, the combination of the specific composition of the dipping solution used for the preparation of the CMSM, in particular, comprising the sacrificial pore forming agent defined herein, and the specific process wherein carbonization is carried out at a limited range of temperatures, unexpectedly not only allows obtaining a membrane with the desired pore size and pore size distribution but also having an increased hydrophobicity compared with a membrane obtained without the use of the pore forming agent, that is, compared with the a membrane prepared by the same process but for the addition of the pore forming agent. This combination of specific pore size and pore size distribution, and degree of hydrophobicity allows obtaining a more selective membrane towards PA.

The CMSMs of the present invention show a high selectivity and chemical stability at pervaporation conditions, even in the long-term performance, which makes these CMSMs especially useful for the industrial separation of certain compounds. As an example, PA can be selectively separated from a mixture comprising PA, AA, and water by pervaporation. Besides, the CMSMs of the present invention are prepared from very cheap precursors.

Thus, a first aspect of the present invention relates to a hydrophobic carbon molecular sieve membrane characterized by comprising pores with a pore size distribution in which at least 20 % of the pores have a pore size from 0.5 to 0.6 nm, measured by perm-porosimetry; and having a C/O ratio higher than 8 and a C/H ratio higher than 20; the membrane being obtainable by dip-coating a support with a dipping solution comprising a carbon precursor, a non-aqueous solvent, a curing agent, and a pore forming agent, wherein the pore forming agent is in an amount from 0.5 wt% to 8 wt%, particularly, from higher than 0.5 wt% to 8 wt%, related to the weight of carbon precursor related to the weight of carbon precursor; followed by carbonization at a temperature higher than 700 °C and lower than 1000 °C; and wherein the carbon molecular sieve membrane has a higher hydrophobicity than a membrane prepared by the same process but without the addition of the pore forming agent.

The average pore size and the pore size distribution is measured by perm-porosimetry (see examples section for the measurement methodology).

A second aspect of the present invention relates to a process for the preparation of a hydrophobic carbon molecular sieve membrane as defined above, the process comprising:

- a) providing a porous support;

- 5 b) providing a dipping solution comprising a carbon precursor such as a phenol-formaldehyde resin or a benzoxazine resin, a non-aqueous solvent, a curing agent, and the pore forming agent, wherein the pore forming agent is in an amount from 0.5 wt% to 8 wt%, particularly, higher than 0.5 wt% to 8 wt%, related to the weight of carbon precursor;
- c) dipping the porous support at least once in the dipping solution of step b) to obtain a coated support;
- d) optionally, drying the coated support of step c);
- 10 e) carbonizing the coated support of step c) or of step d) at a temperature higher than 700 °C and lower than 1000 °C in a non-oxidizing atmosphere or vacuum to obtain a hydrophobic carbon molecular sieve membrane; and
- f) cooling the hydrophobic carbon molecular sieve membrane of step e) to room temperature.

Another aspect of the present invention relates to a process for the preparation of a hydrophobic carbon molecular sieve membrane as defined herein, the process comprising:

- 15 a) providing a solution comprising a carbon precursor such as a phenol-formaldehyde resin or a benzoxazine resin, a non-aqueous solvent, a curing agent, and the pore forming agent, wherein the pore forming agent is in an amount from 0.5 wt% to 8 wt%, particularly, higher than 0.5 wt% to 8 wt%, related to the weight of carbon precursor;
- 20 b) casting the solution of step a) on a substrate to obtain a membrane precursor;
- c) carbonizing the membrane precursor of step c) at a temperature higher than 700 °C and lower than 1000 °C in a non-oxidizing atmosphere or vacuum to obtain a self-supported carbon molecular sieve membrane; and
- 25 d) cooling the self-supported carbon molecular sieve membrane of step e) to room temperature.

Another aspect of the present invention relates to a method for the selective separation of propionic acid from a mixture containing propionic acid, acetic acid, and water, the process comprising:

- 30 a) providing a hydrophobic carbon molecular sieve membrane as defined herein; and
- b) contacting a mixture containing propionic acid, water and acetic acid with one side of the membrane while vacuum is applied in the other side of the membrane to produce a permeate gas stream in order to separate PA by pervaporation.

35 Another aspect of the present invention relates to the use of a CMSM as defined above, for the selective separation of propionic acid from a mixture with water and acetic acid.

A fifth aspect of the present invention relates to the use of a CMSM as defined above, as a membrane reactor or part of a membrane reactor.

Brief Description of Drawings

Fig. 1 shows effect of the carbonization temperature and the addition of PVB in the pore size distribution of the CMSMs prepared in Example 1: (a) at 750 °C (CMSMs 750P0, 750P0.5, and 750P1); (b) at 850 °C (CMSMs 850P0, 850P0.5, and 850P1), and (c) all of them for the sake of better comparison.

Fig. 2 shows the effect of the carbonization temperature and the addition of PVB on the water flux of the CMSMs prepared in Example 1.

Fig. 3 shows the effect of the carbonization temperature and of the addition of PVB in CMSMs on the pervaporation (purity and flux) of a feeding solution containing (a) 5% of propionic acid (PA) and (b) 5% of acetic acid. Temperature of 37 °C, permeated at 12 mbar.

Fig. 4 shows the effect of carbonization temperature and introduction of PVB in CMSMs on the purity of PA and AA of a feeding solution containing 5% of propionic acid and 5% acetic acid. Temperature 37 °C, permeated 12 mbar.

Fig. 5 shows the effect of carbonization temperature and introduction of PVB in CMSMs on the purity of PA and AA of a feeding solution containing (a) 10% of propionic acid and 5% acetic acid; and (b) 5% of propionic acid and 10% acetic acid. Temperature 37 °C, permeated 12 mbar.

Detailed description of the invention

All terms as used herein in this application, unless otherwise stated, shall be understood in their ordinary meaning as known in the art. Other more specific definitions terms as used in the present application are as set forth below and are intended to apply uniformly throughout the specification and claims unless an otherwise expressly set out definition provides a broader definition.

The term "phenol formaldehyde resin" and the term "phenolic resin" have been used herein as synonym terms.

As used herein, the term "hydrophobic carbon molecular sieve membrane (CMSM)" refers to a CMSM capable of adsorbing an amount of water (%) equal to or lower than 15 wt% (according to the procedure explained herein below) and, particularly, having a C/O ratio higher than 8 and a C/H ratio higher than 20.

The terms "pore size" as used herein refer to the average pore diameter and is measured

by Perm-porosimetry. This technique measures the average active pore size in the CMSMs.

The term “permeation flow” is defined as the volume of the gas passing through the membrane per unit time. This value is determined experimentally with a flow meter.

- 5 The term “permeation flux” is defined as the weight of a compound flowing through the membrane per unit area per unit time. This value is calculated from the “permeation flow” divided by the membrane’s area.

- 10 The term “permeance” is defined as the number of mols of the feed gas passing through a unit area of membrane at unit time and under unit pressure gradient, the common unit used in CMSM is $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. This value is calculated from the “permeation flux” divided by the difference of pressure between the retentate and permeate.

The term “perm-selectivity” or ideal selectivity related to a gas refers to the ratio of the permeance of two single gases at the same temperature.

- 15 Pervaporation (or pervaporative separation) is a processing method for the separation of mixtures of liquids by partial vaporization through a non-porous or porous membrane. The term "pervaporation" derives from the combination of the of the two steps process: (a) permeation through the membrane by the permeate, then (b) its evaporation into the vapor phase. The membrane acts as a selective barrier between the two phases: the liquid-phase feed and the vapor-phase permeate. It allows the desired components of the liquid feed to transfer through it by vaporization. Separation of components is based on a difference in transport rate of individual components through the membrane.
- 20

The term “pressure difference” refers to the difference of the partial pressures of the gas in the retentate and in the permeate.

- 25 The term “partial pressure difference” for a given gas refers to the difference of the gas partial pressure in the retentate and the gas partial pressure in the permeate.

- The term “negligible” refers to a value that either coincides with zero within the context of the measurement accuracy or is less than a defined threshold value, which for example takes into account a deviation from zero, which is hardly avoidable for structural reasons or which do not have any significant effect on the performance in terms of permeance and selectivity of the CMSM.
- 30

The term “room temperature” refers to a temperature of about 20 °C to about 25 °C.

It is noted that, as used in this specification and the appended claims, the singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise.

As mentioned above, an aspect of the present disclosure relates to an hydrophobic carbon molecular sieve membrane, the hydrophobicity being due to the specific percentages of C/O and C/H ratios defined above, the membrane being characterized by comprising pores with a pore size distribution in which at least 20 % of the pores have a pore size from 0.5 to 0.6 nm; and the membrane being obtainable by dip-coating a support with a dipping solution comprising a resin as defined herein, a non-aqueous solvent, a curing agent, and a pore forming agent as defined herein; followed by carbonization at a temperature higher than 700 °C and lower than 1000 °C; wherein the carbon molecular sieve membrane has a higher hydrophobicity than a membrane prepared by the same process but without the addition of the pore forming agent.

In an embodiment, the hydrophobic carbon molecular sieve membrane is characterized by comprising pores with a pore size distribution in which at least 20 % of the pores have a pore size from 0.5 to 0.6 nm, measured by perm-porosimetry; and having a C/O ratio higher than 8 and a C/H ratio higher than 20; the membrane being obtainable by dip-coating a support with a dipping solution comprising a carbon precursor, a non-aqueous solvent, a curing agent, and a pore forming agent, followed by carbonization at a temperature higher than 700 °C and lower than 1000 °C; wherein the pore forming agent is in an amount higher than 0.5 wt% to 8 wt%, particularly, from higher than 0.5 wt% to 5 wt%, related to the weight of carbon precursor; and wherein the carbon molecular sieve membrane has a higher hydrophobicity than a membrane prepared by the same process but without the addition of the pore forming agent; optionally, wherein the membrane comprises a pore size distribution in which less than 20 % of the pores have a pore size from 0.3 to 0.4 nm.

In an embodiment of the carbon molecular sieve membrane of the present disclosure, the C/O ratio is from 10 to 95. In another embodiment, the C/O ratio is from 20 to 70. In another embodiment, the C/O ratio is from 30 to 60. In another embodiment, the C/O ratio is from 40 to 50.

In another embodiment of the carbon molecular sieve membrane of the present disclosure, optionally in combination with the embodiments above, the C/H ratio is from 20 to 1000. In another embodiment, the C/H ratio is from 40 to 1000. In another embodiment, the C/H ratio is from 50 to 800. In another embodiment, the C/H ratio is from 60 to 600. In another embodiment the C/H ratio is from 70 to 400. In another embodiment, the C/H ratio is from 100 to 200.

In a particular embodiment, optionally in combination with the embodiments above, the pore size distribution is that in which at least 25 % of the pores have a pore size from 0.4 to 0.6 nm. In a particular embodiment, optionally in combination with the embodiments

above, the pore size distribution is that in which at least 30 % of the pores have a pore size from 0.4 to 0.6 nm. In a particular embodiment, optionally in combination with the embodiments above, the pore size distribution is that in which at least 50 % of the pores have a pore size from 0.4 to 0.6 nm. In a particular embodiment, optionally in combination with the embodiments above, the pore size distribution is that in which at least 80 % of the pores have a pore size from 0.4 to 0.6 nm.

In a particular embodiment, optionally in combination with the embodiments above, the pore size distribution is that in which at least 20 % of the pores have a pore size from 0.5 to 0.6 nm. In a particular embodiment, optionally in combination with the embodiments above, the pore size distribution is that in which at least 25 % of the pores have a pore size from 0.5 to 0.6 nm. In a particular embodiment, optionally in combination with the embodiments above, the pore size distribution is that in which at least 40 % of the pores have a pore size from 0.5 to 0.6 nm. In a particular embodiment, optionally in combination with the embodiments above, the pore size distribution is that in which at least 75 % of the pores have a pore size from 0.5 to 0.6 nm.

In another embodiment, the CMSM of the present disclosure comprises pores with a pore size distribution in which at least 30 % of the pores have a pore size from 0.5 to 0.6 nm, measured by perm-porosimetry; and has a C/O ratio higher than 15 and a C/H ratio higher than 30. In a particular embodiment, the CMSM comprises pores with a pore size distribution in which at least 35 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry. In another particular embodiment, in the dipping solution used for preparing the CMSM the pore forming agent is in an amount from 0.5 wt% to lower than 1 wt% related to the weight of carbon precursor and the carbonization temperature is from 750 °C to lower than 850 °C.

Accordingly, in an embodiment, the CMSM of the present disclosure comprises pores with a pore size distribution in which at least 30 % of the pores have a pore size from 0.5 to 0.6 nm and at least 35 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry; has a C/O ratio higher than 15 and a C/H ratio higher than 30; in the dipping solution used for preparing the CMSM, the pore forming agent is in an amount from 0.5 wt% to lower than 1 wt% related to the weight of carbon precursor; and the carbonization temperature is from 750 °C to lower than 850 °C.

In another embodiment, the CMSM of the present disclosure comprises pores with a pore size distribution in which at least 40 % of the pores have a pore size from 0.5 to 0.6 nm, measured by perm-porosimetry, and has a C/O ratio higher than 18 and a C/H ratio higher than 50. In a particular embodiment, the CMSM comprises pores with a pore size distribution in which at least 55 % of the pores have a pore size from 0.4 to 0.6 nm,

measured by perm-porosimetry. In another particular embodiment, in the dipping solution used for preparing the CMSM the pore forming agent is in an amount from 1 wt% to 5 wt% related to the weight of carbon precursor and the carbonization temperature is from 750 °C to lower than 850 °C.

- 5 Accordingly, in an embodiment, the CMSM of the present disclosure comprises pores with a pore size distribution in which at least 40 % of the pores have a pore size from 0.5 to 0.6 nm and at least 55 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry; has a C/O ratio higher than 18 and a C/H ratio higher than 50; in the dipping solution used for preparing the CMSM the pore forming agent is in an amount
10 from 1 wt% to 5 wt% related to the weight of carbon precursor; and the carbonization temperature is from 750 °C to lower than 850 °C.

- In another embodiment, the CMSM of the present disclosure comprises pores with a pore size distribution in which at least 65 % of the pores have a pore size from 0.5 to 0.6 nm, measured by perm-porosimetry; and has a C/O ratio higher than 25 and a C/H ratio higher
15 than 150. In a particular embodiment, the CMSM comprises pores with a pore size distribution in which at least 80 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry. In another particular embodiment, in the dipping solution used for preparing the CMSM the pore forming agent is in an amount from 0.5 wt% to lower than 1 wt% related to the weight of carbon precursor and the carbonization
20 temperature is from 850 °C to lower than 900 °C.

- Accordingly, in an embodiment, the CMSM of the present disclosure comprises pores with a pore size distribution in which at least 65 % of the pores have a pore size from 0.5 to 0.6 nm and at least 80 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry; has a C/O ratio higher than 25 and a C/H ratio higher than 150; in the
25 dipping solution used for preparing the CMSM the pore forming agent is in an amount from 0.5 wt% to lower than 1 wt% related to the weight of carbon precursor; and the carbonization temperature is from 850 °C to lower than 900 °C.

- In another embodiment, the CMSM of the present disclosure comprises pores with a pore size distribution in which at least 75 % of the pores have a pore size from 0.5 to 0.6 nm, measured by perm-porosimetry, and has a C/O ratio higher than 35 and a C/H ratio higher
30 than 200. In a particular embodiment, the CMSM comprises pores with a pore size distribution in which at least 82 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry. In another particular embodiment, in the dipping solution used for preparing the CMSM the pore forming agent is in an amount from 0.7 wt% to
35 lower than 1 wt% related to the weight of carbon precursor and the carbonization temperature is from 850 °C to lower than 900 °C.

Accordingly, in an embodiment, the CMSM of the present disclosure comprises pores with a pore size distribution in which at least 75 % of the pores have a pore size from 0.5 to 0.6 nm and at least 82 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry; has a C/O ratio higher than 35 and a C/H ratio higher than 200; in the
5 dipping solution used for preparing the CMSM the pore forming agent is in an amount from 0.7 wt% to lower than 1 wt% related to the weight of carbon precursor; and the carbonization temperature is from 850 °C to lower than 900 °C.

In another embodiment, the CMSM of the present disclosure comprises pores with a pore size distribution in which at least 80 % of the pores have a pore size from 0.5 to 0.6 nm,
10 measured by perm-porosimetry, and has a C/O ratio higher than 40 and a C/H ratio higher than 300. In a particular embodiment, the CMSM comprises pores with a pore size distribution in which at least 85 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry. In another particular embodiment, in the dipping solution used for preparing the CMSM the pore forming agent is in an amount 1 wt% to 5 wt%
15 related to the weight of carbon precursor and the carbonization temperature is from 850 °C to lower than 900 °C.

Accordingly, in an embodiment, the CMSM of the present disclosure comprises pores with a pore size distribution in which at least 80 % of the pores have a pore size from 0.5 to 0.6 nm and at least 85 % of the pores have a pore size from 0.4 to 0.6 nm, measured by
20 perm-porosimetry; has a C/O ratio higher than 40 and a C/H ratio higher than 300; in the dipping solution used for preparing the CMSM the pore forming agent is in an amount 1 wt% to 5 wt% related to the weight of carbon precursor; and the carbonization temperature is from 850 °C to lower than 900 °C.

The content of C, H, and O are as determined using an elemental analyzer equipment
25 such as Flash smart Thermo Scientific.

In another particular embodiment, the carbon molecular sieve membrane comprises a negligible amount of pores larger than 1 nm.

In another particular embodiment, the carbon molecular sieve membrane comprises a pore size distribution in which less than 20 % of the pores have a pore size from 0.3 to 0.4
30 nm. In another particular embodiment, the carbon molecular sieve membrane comprises a pore size distribution in which less than 10 % of the pores have a pore size from 0.3 to 0.4 nm. In another particular embodiment, the carbon molecular sieve membrane comprises a pore size distribution in which less than 5 % of the pores have a pore size from 0.3 to 0.4 nm.

35 In an embodiment, optionally in combination with the embodiments above, the carbon

molecular sieve membrane is a supported membrane. The supported carbon molecular sieve membrane of the present invention has a support and a carbon molecular sieve membrane which can also be named as carbon selective layer.

5 In another embodiment of the supported carbon molecular sieve membrane, the support is a porous support. In a particular embodiment, the porous support is a metallic support. In another particular embodiment the porous support is an inorganic, non-metallic solid, based on an oxide, nitride, boride, or carbide, preferably selected from the group of alpha alumina, titanium oxide, zirconium oxide, ceria, and gamma alumina. In another particular
10 embodiment, the supported carbon molecular sieve membrane is that where the support is a porous carbon support.

In another particular embodiment, the supported carbon molecular sieve membrane is that where the support is a porous zirconia support. In another particular embodiment, the supported carbon molecular sieve membrane is that where the support is a porous alumina support.

15 In another embodiment, optionally in combination with the embodiments above, the supported carbon molecular sieve membrane has a shape that can be tubular, hollow fiber, or planar.

In a particular embodiment, the supported CMSM of the present invention comprises a single selective layer on a surface of the porous support. Depending on the support, the
20 selective layer could be on the outer or in the inner surface (i.e. in the case of a tubular support).

All the particular embodiments disclosed above and bellow for the supported carbon molecular sieve membrane in any combination are also particular embodiments of the present invention.

25 As mentioned above, the supported carbon molecular sieve membrane of the present invention can be prepared by dip-dry (polymerization)-carbonization method. The process comprises a) providing a porous support; b) providing a dipping solution comprising a carbon precursor such as a phenol-formaldehyde resin or a benzoxazine resin, a non-aqueous solvent, a curing agent, and a pore forming agent as defined herein in an amount
30 from 0.5 wt% to 8 wt%, particularly, higher than 0.5 wt% to 8 wt%, related to the weight of carbon precursor, c) dipping the porous support at least once in the dipping solution of step b) to obtain a coated support; d) optionally, drying the coated support of step c); e) carbonizing the coated support of step c) or of step d) at a temperature higher than 700 °C and lower than 1000 °C in a non-oxidizing atmosphere or vacuum to obtain a supported
35 carbon molecular sieve membrane; and f) cooling the supported carbon molecular sieve membrane of step e) to room temperature.

In another embodiment, optionally in combination with the embodiments above, the carbon molecular sieve membrane is a self-supported membrane. In the self-supported membrane the support is the same carbon material.

Thus, in another embodiment, the hydrophobic carbon molecular sieve membrane of the present invention can be prepared by a process comprising: a) providing a solution comprising a carbon precursor such as a phenol-formaldehyde resin or a benzoxazine resin, a non-aqueous solvent, a curing agent, and the pore forming agent, wherein the pore forming agent is in an amount from 0.5 wt% to 8 wt%, particularly, higher than 0.5 wt% to 8 wt%, related to the weight of carbon precursor; b) casting the solution of step a) on a substrate to obtain a membrane precursor; c) carbonizing the membrane precursor of step b) at a temperature higher than 700 °C and lower than 1000 °C in a non-oxidizing atmosphere or vacuum to obtain a self-supported carbon molecular sieve membrane; and d) cooling the self-supported carbon molecular sieve membrane of step c) to room temperature. The casting of the solution of step a) on the substrate can be performed by using a doctor blade.

In another particular embodiment, the self-supported carbon molecular sieve membrane can be prepared by dry-wet spinning the solution comprising carbon precursor such as a phenol-formaldehyde resin or a benzoxazine resin, a non-aqueous solvent, a curing agent, and the pore forming agent in order to obtain hollow fibers (of about 0.5-3 mm diameter) and, then, carrying out the carbonization step as defined above (cf. Huang, Yaoqing et al. "Progress on polymeric hollow fiber membrane preparation technique from the perspective of green and sustainable development." *Chemical Engineering Journal* 403 (2021): 126295).

Examples of curing agents include, without being limited to, a combination of formaldehyde and an amine such as ethylenediamine, 1,3-diaminopropane (propane-1,3-diamine), putrescine (butane-1,4-diamine), cadaverine (pentane-1,5-diamine, 1,2 diamino propne, or diphenylethylenediamine; a combination of formaldehyde and an acid such as oxalic acid, phosphoric acid, acetic acid, or sulfuric acid; a combination of formaldehyde and an alkali metal or alkaline earth hydroxide (e.g. KOH, NaOH, Ba(OH)₂, or Ca(OH)₂); hexamethylenetetramine; a combination of formaldehyde and a metal salt of Zn, Mg, Cd, Pb, Cu, Co, Ni, in particular, the metal salt is an acetate salt; and hexamethylenetetramine. Instead of formaldehyde, paraformaldehyde can be used.

In another embodiment, the non-aqueous solvent has a boiling point equal to or higher than 60 °C. In a particular embodiment, the solvent has a boiling point equal to or higher than 100 °C. Examples of appropriate solvents include N-methyl 2-pyrrolidone, water, ethanol, methanol, 2-propanol, ethyl propionate, 2-methoxyethanol, 4-methyl-2-pentanone, dioxane, and chloroform.

In an embodiment, the carbon precursor is in an amount from 2 wt% to 30 wt% of the dipping solution, in particular from 5 wt% to 20 wt% of the dipping solution.

5 Examples of carbon precursors include, without being limited to, phenolic resins, polyimides, polyfurfuryl alcohol, cellulose, cellulosic derivatives, and poly(vinylidene chloride).

10 In an embodiment, the carbon precursor is a phenol-formaldehyde resin, also known as phenolic resin. Phenols or phenolic compounds have in the structure at least one hydroxyl attached to an aromatic hydrocarbon group. Phenolic resins, such as resols and novolac resins, are desirable precursors to prepare CMSMs, since they present the advantage of being inexpensive and possess high carbon yield, withstanding elevated temperatures without losing their shape.

15 Phenolic resins are the product of the poly-condensation reaction of phenol-type compound with formaldehyde, their structure and properties depending on the formaldehyde/phenol-type compound ratio (F/P), catalyst, pH and temperature. There are two forms of phenolic resins: resol and novolac. Resol resins are the product of basic catalysis in excess of formaldehyde (F/P >1). Novolac resins are obtained in acidic media and the amount of formaldehyde is lower, usually with an F/P of ca. 0.75-0.85, for instance at a temperature from 80 to 110 °C. The acidic media may be for instance provided by an acid such as oxalic acid.

20 Examples of phenol-type compounds used in the preparation of phenolic resins include, without being limited to, phenol (hydroxybenzene), dihydroxyphenyl such as catechol, resorcinol, or hydroquinone and p-tert-butyl phenol. Other phenolic resins can also be used. Further examples of appropriate phenolic resins are phenol-urea-formaldehyde, phenol-melamine-formaldehyde, dicyclopentadiene-phenol, phenol and formaldehyde derivatives such as resol-formaldehyde, hydroquinone derivatives, or polybenzoxazine. In
25 an embodiment, the phenolic resin is a novolac resin.

In a particular embodiment, the phenol-formaldehyde resin is a phenolic resin, in particular a resorcinol-formaldehyde resin, more particularly, a resorcinol-formaldehyde novolac resin.

30 In another embodiment, the resin is a benzoxazine resin. Benzoxazine resins can be obtained by polycondensation of a phenol-type compound, an amine and formaldehyde (cf. Tiwari, I. et al., "Polybenzoxazine-an enticing precursor for engineering heteroatom-doped porous carbon materials with applications beyond energy, environment and catalysis". *Materials Today Chemistry*, 2022, vol. 23, p. 100734).

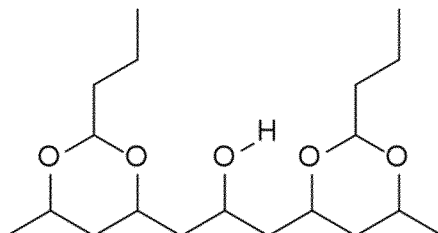
35 As mentioned above, the dipping solution also contains a pore forming agent. The pore

forming agent is such that it is soluble in the dipping solution.

In another embodiment, optionally in combination with one or more features of the particular embodiments defined above, the pore forming agent is selected from the group consisting of polyvinyl butyral (PVB), cellulose ethers such as methylcellulose (MC) and cellulose esters such as cellulose acetate, poly(vinyl alcohol) (PVOH), polyvinylpyrrolidone (PVP), polylactic acid (PLA); and poloxamers. In particular, the pore forming agent is selected from the group consisting of polyvinyl butyral (PVB), methylcellulose, poly(vinyl alcohol) (PVOH), and polyvinylpyrrolidone (PVP). In a particular embodiment, the pore forming agent is PVB. In another particular embodiment, the pore forming agent is methylcellulose. In another particular embodiment, the pore forming agent is cellulose acetate. In another particular embodiment, the pore forming agent is PVOH. In another particular embodiment, the pore forming agent is PVP. In another particular embodiment, the pore forming agent is PLA. In another particular embodiment, the pore forming agent is a poloxamer.

Polyvinylbutyral is a polymer containing polar and non-polar chemical domains enabling the formation of flexible green films with high tensile strength and good elongation behaviour. Chemical structure of PVB is the following:

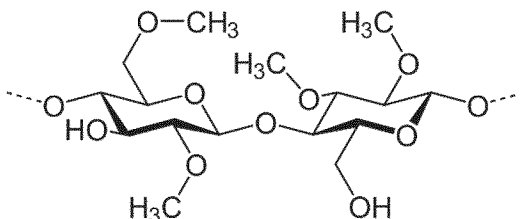
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PVB has many oxygen groups making it more reactive to decomposition at high temperatures.

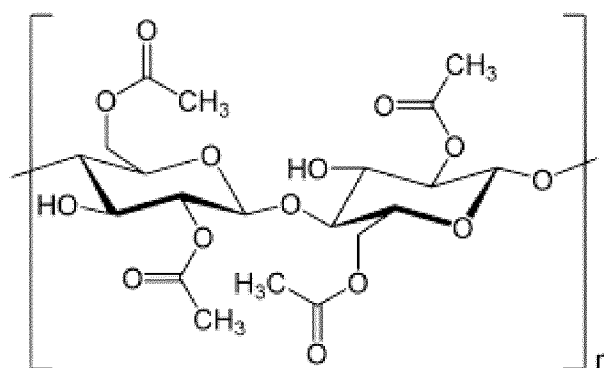
Methylcellulose is a synthetic polymer having the following chemical structure:

25



Cellulose acetate is partially acetylated cellulose, in which the acetyl content ranges from 29.0% to 44.8%, corresponding to mono-, di-, and triacetate. It has the following chemical structure:

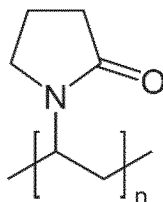
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Poly(vinyl alcohol) (PVOH), is a water-soluble synthetic polymer having the chemical formula $[\text{CH}_2\text{CH}(\text{OH})]_n$.

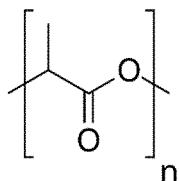
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Polyvinylpyrrolidone (PVP) is a water-soluble polymer having the following chemical structure:



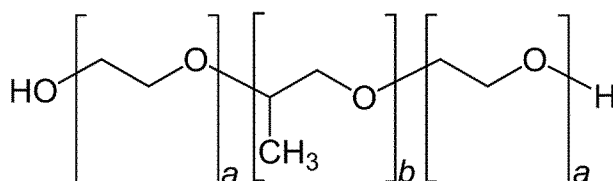
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Poly(lactic acid) also known as poly(lactic acid) poly, lactic, acid or polylactide (PLA), is a thermoplastic polyester with backbone formula $(\text{C}_3\text{H}_4\text{O}_2)_n$ or $[-\text{C}(\text{CH}_3)\text{HC}(=\text{O})\text{O}-]_n$



20

Poloxamers are non-ionic triblock copolymers composed of a central hydrophobic chain of polyoxypropylene (poly(propylene oxide)) flanked by two hydrophilic chains of polyoxyethylene (poly(ethylene oxide))



25

hydrophilic hydrophobic hydrophilic

After carbonization, the pore forming agent are almost completely decomposed, although a residue of them remains, what increases the hydrophobicity of the resulting membrane.

As mentioned above, the pore forming agent is in an amount from 0.5 wt% to 8 wt%

related to the weight of carbon precursor. In another embodiment, the pore forming agent is in an amount from 0.5 wt% to 8 wt% related to the weight of carbon precursor. In another embodiment, the pore forming agent is in an amount from 0.8 wt% to 8 wt% related to the weight of carbon precursor. In another embodiment, the pore forming agent is in an amount from 0.8 wt% to 5 wt% related to the weight of carbon precursor. In another embodiment, the pore forming agent is in an amount from 0.8 wt% to 3 wt% related to the weight of carbon precursor. In another embodiment, the pore forming agent is in an amount from 0.8 wt% to 2 wt% related to the weight of carbon precursor. In another embodiment, the pore forming agent is in an amount from 0.8 wt% to 1.2 wt% related to the weight of carbon precursor.

In another embodiment, the pore forming agent is in an amount from higher than 0.5 wt% to lower than 1 wt% related to the weight of carbon precursor. In another particular embodiment, the pore forming agent is in an amount of a 1 wt.% related to the weight of carbon precursor.

In a particular embodiment, the pore forming agent is PVB, in particular, an amount from 0.8 wt% to 1.2 wt% related to the weight of carbon precursor. In another particular embodiment, the PVB is in an amount of a 1 wt.% related to the weight of carbon precursor.

In another particular embodiment, the pore forming agent is PVP, in particular, in an amount from 0.8 wt% to 1.2 wt% related to the weight of carbon precursor. In another particular embodiment, the PVP is in an amount of a 1 wt.% related to the weight of carbon precursor.

In another particular embodiment, the pore forming agent is methylcellulose, in particular, in an amount from 0.8 wt% to 1.2 wt% related to the weight of carbon precursor. In another particular embodiment, the methylcellulose is in an amount of a 1 wt.% related to the weight of carbon precursor.

In another particular embodiment, the pore forming agent is polylactic acid, in particular an amount from 0.8 wt% to 1.2 wt% related to the weight of carbon precursor. In another particular embodiment, the polylactic acid is in an amount of a 1 wt.% related to the weight of carbon precursor.

In another particular embodiment, the pore forming agent is poloxamer, in particular an amount from 0.8 wt% to 1.2 wt% related to the weight of carbon precursor. In another particular embodiment, the poloxamer is in an amount of a 1 wt.% related to the weight of carbon precursor.

The treatment of immersing the porous alumina support in the dipping solution can be

performed from 1 to 10 times. In a particular embodiment, the process is that where the dipping step is carried out only once. In another particular embodiment, the process is that where the dipping step is repeated between 2-6 times. In another particular embodiment, the process is that where the dipping step is repeated between 3-5 times. In another particular embodiment, the process is that where the dipping step is repeated 5 times.

This treatment is generally carried out at room temperature for an appropriate time. An appropriate time can be 5-120 seconds. Generally, it is sufficient to maintain porous support in the dipping solution for 5-120 seconds, in particular around 30 s. Generally, it is carried out under agitation, for example, at a speed of 5 mm/s. The dipping coating is generally repeated several times with an interval that can be for instance of 5 min, generally it is sufficient a time of around 10-40 s between cycles, in particular around 20 s.

In a particular embodiment, the drying step of the coated support is carried out at a temperature below the boiling point of the solvent used in the dipping solution. For instance, if N-methyl-2-pyrrolidone is used, the temperature is between 90 to 110 °C. More particularly it is carried out under argon atmosphere.

In another particular embodiment, the process is that wherein the carbonizing temperature is from 750 °C to 950 °C. In another particular embodiment, the process is that wherein the carbonizing temperature is from 800 °C to 900 °C. In another particular embodiment, the process is that where the carbonizing temperature is 850 °C.

In another particular embodiment, the process is that where the step e) of carbonization is carried out under a non-oxidant atmosphere or vacuum. In another particular embodiment, the inert atmosphere is selected from the group consisting of argon atmosphere, nitrogen atmosphere, helium atmosphere, H₂ atmosphere, and NH₃ atmosphere. In another particular embodiment, the non-oxidant atmosphere is argon atmosphere. The carbonization pressure ranges from 2 mbar to 6 bars.

In another particular embodiment, the process is that where the step e) of carbonization is carried out at a heating rate of from 0.2 °C/min to 10 °C/min and a dwell time from 1 to 40 h. In a more particular embodiment, the carbonization is carried in a tubular oven, with heating ramp 1 °C /min until 850 °C and then is maintained at 850 °C for 2 h.

All the particular embodiments disclosed above for the process in any combination are also particular embodiments of the present invention.

The carbon molecular sieve membrane of the present invention can also be defined by its preparation process. Thus, it is part of the present invention a carbon molecular sieve membrane obtainable by the process defined herein above and below.

In the present disclosure, it is noted that when discussing the carbon molecular sieve membrane, process for its preparation, or its use, each one of the embodiments or features defined for any one of the mentioned aspects can be considered applicable to any other one of the other aspects, whether they are explicitly discussed in the context of that other aspect or not.

As commented above, fermentation production of propionic acid is a sustainable alternative to the production of PA through a petrochemical rout. In the bacterial fermentation production of propionic acid, acetic acid is the most important by-product. Acetic acid can impair PA production. Thus, one effective method to increase the yield of PA is by its in-situ extraction from the fermentation medium by pervaporation. In this process, a membrane is in contact with the fermentation liquid in one side, while vacuum is applied in the other side to produce a permeate gas stream. Since the fermentation liquid is not subject a harsh condition, this technique has little impact in microorganisms, fermentation nutrients and substrates

As commented above, surprisingly, the CMSM of the present disclosure is useful for the selective separation of propionic acid. Propionic acid can be prepared from glycerol in a fermentation media. In particular, the CMSM of the present disclosure is useful for the selective separation of propionic acid from a mixture containing propionic acid, acetic acid, and water. In an embodiment, the CMSM of the present disclosure is useful for the selective separation of propionic acid from fermentative processes, particularly, from a fermentation medium containing propionic acid, acetic acid, and water.

In an embodiment, the CMSM of the present disclosure is useful for the selective separation of propionic acid from a mixture containing also other carboxylic acids.

In another embodiment, the CMSM of the present disclosure is useful for the selective separation of propionic acid from a mixture containing also alcohols

This aspect can also be defined as a method for the selective separation of propionic acid, in particular, from a mixture comprising propionic acid, acetic acid, and water, the process comprising: a) providing a carbon molecular sieve membrane as defined above; and b) contacting a mixture comprising propionic acid, in particular, a mixture comprising propionic acid, water and acetic acid, with one side of the membrane while vacuum is applied in the other side of the membrane to produce a permeate gas stream in order to separate propionic acid by pervaporation. As an example, in the pervaporation process, the solution can be at a temperature from 30 to 50 °C such as of 37 °C and the pressure of the permeate can be from 10 mbar to 20 mbar such as of 12 mbar.

In a particular embodiment, the aqueous mixture contains from 2 wt.% to 95 wt.% of

propionic acid, and from 0.5wt.% to 50wt.% acetic acid. In another embodiment, the aqueous mixture contains from 2 wt.% to 30 wt.% of propionic acid, and from 2 wt.% to 15wt.% acetic acid. In another embodiment, the aqueous mixture contains from 5wt.% to 10 wt.% of propionic acid, and from 5 wt.% to 10 wt.% acetic acid.

- 5 In a particular embodiment, step b) of this aspect of the invention is carried out at a temperature from 5°C to 95 °C, from 15 °C to 70 °C, from 20 °C to 50 °C, or from 20 °C to 40 °C, or at room temperature.

- 10 CMSM known in the art, being designed to separate gases with sizes smaller than CH₄ (0.34 nm), are not suitable for the separation of PA separation, for which bigger pores are needed. The CMSMs of the present disclosure, by combining the required hydrophobicity in the pores (given by the specific C/O, C/H ratios) and a pore size distribution wherein at least 20% of the pores have a pore size from 0.5 to 0.6 nm, allows the selective separation of PA from a mixture with water and AA.

- 15 In particular, in the fermentative production of PA, the CMSM of the present disclosure can be used as a membrane bioreactors for PA in-situ separation by pervaporation, allowing to effectively separate PA with high concentration on the permeate from a low concentration feed through pervaporation. Advantageously, the method of the invention is scalable, compact, and energetically efficient.

- 20 Thus, one application of a CMSM as defined above is its use as a membrane bioreactor. The CMSM of the invention has high potential because it is easier to prepare, cheaper, and has better permeation properties than other potential membranes that are currently investigated in the field of membrane bioreactors.

- 25 Throughout the description and claims the word "comprise" and variations of the word, are not intended to exclude other technical features, additives, components, or steps. Furthermore, the word "comprise" encompasses the case of "consisting of".

The following examples and drawings are provided by way of illustration, and they are not intended to be limiting of the present invention. Furthermore, the present invention covers all possible combinations of particular and preferred embodiments described herein.

Examples

- 30 Materials and methods

Formaldehyde (37%), propionic acid (PA) (99%) and acetic acid (AA)(99-100%) from VWR chemicals, and KOH pellets, N-methyl-2-pyrrolidone (NMP, 99.5%), polyvinyl butyral (PVB) (Mw 50-80K), and resorcinol (99%) from Merck (Sigma-Aldrich) were used without further purification. Asymmetric tubular zirconia supports with an average pore

size of 120 nm, outer diameter of 10 mm, and inner diameter of 7 mm were supplied by Inopore GMBH.

EXAMPLE 1

Novolac precursor synthesis

- 5 65 g of phenol was placed inside a three neck round bottom flask equipped with a reflux condenser and heated to 50 °C for 60 min, then 1 g oxalic acid was added while mixing at 500 rpm with magnetic stirrer for 30 min; the temperature was increased to 85 °C and 46 g of formaldehyde was added dropwise in a period of 60 min. After 10 h of reaction, the solution was centrifuged three times at 4400 rpm and 10 °C to separate water and
- 10 unreacted reactants. In the final step, the precursor was dried under vacuum at 50 °C and 4 mbar for 24h. The resulted Novolac powder was used as carbon precursor in the synthesis of CMSMs.

Dipping solution preparation

- 20 g of the prepared Novolac was mixed with 78 g of NMP in a high shear force mixer
- 15 (Thinky ARE-310) at 2000 rpm for 30 min; then, the equipment was left to rest for 10 min to prevent the overheating of the solution; this cycle was repeated 3 times. Next, 1.6 g of formaldehyde was introduced to the solution and mixed at 2000 rpm for 30 min. Then, 0.4 g of oxalic acid was added and mixed at 2000 rpm for another 30 min. This mixture was used to prepare dipping solutions with various contents of PVB (0, 0.5, and 1 wt% related
- 20 to the weight of carbon precursor). PVB has added to the dipping solution solution via high shear mixing for 30 min with 2000 rpm for two cycles (Thinky 250).

Preparacion of the CMSM

- The CMSMs were prepared using resorcinol-formaldehyde resin by the dip-dry
- (polymerize)- carbonization method. In short, the membranes shown in Table 1 below
- 25 were prepared. For each membrane, the support was dipped at room temperature for 30 s in the dipping solution using a custom-made dip-coating machine and withdrawal at speed of 5 mm/s. This dipping cycle was repeated five times with an interval of 20 s between cycles. Next, the membrane was immediately moved to a rotary dryer oven where the coated supports were dried under argon atmosphere at 140 °C for 6 hr. Then, the tubes
- 30 were carbonized in a tubular oven (Nabertherm R 170/1000/12) using a heating ramp of 1 °C /min and dwell time of 3 h at the required temperature in a flowing argon atmosphere (100 l/h). After the carbonization, the CMSMs were stored in a humidification chamber with a 100 % Relative Humidity (RH) to stabilize the hydrophilic sites in the CMSMs for one month.

The membranes were named with the temperature of carbonization followed by the concentration of PVB in the dipping solution as defined above; thus, 750P0 (Comp. Ex. 1), 750P0.5 (Ex. 1.1), 750P1 (Ex. 1.2) correspond to the CMSMs obtained by using a dipping solution without the addition of PVB, with 0.5 wt.% of PVB, and with 1 wt.% of PVB, respectively, and carbonized at 750 °C; and 850P0 (Comp. Ex. 2), 850P0.5 (Ex. 1.3), and 850P1 (Ex. 1.4) correspond to the CMSMs obtained by using a dipping solution without the addition of PVB, with 0.5 wt.% of PVB, and with 1 wt.% of PVB, respectively, and carbonized at 850 °C.

For physicochemical characterization, non-supported membranes were obtained from the dipping solution remaining after the dipping; by pouring in Teflon evaporating dishes and heating at the same condition of carbonization of the supported membranes. The obtained films were carbonized at the same conditions of the respective supported CMSM.

EXAMPLE 2: CMSMs characterization

Carbon, hydrogen and oxygen elemental analysis

The CHO composition of non-supported CMSMs samples prepared as in Example 1 was determined by elemental analysis (C, H and O) using an automatic Micro analyzer (Thermo Scientific™ , Flash smart elemental analyzer).

Before the analysis, the samples were dried at 300 °C under N₂ for 24 h to remove any adsorbed water molecules from the pores.

For each sample, from observed values, the lowest molecular weight of the formula in which the number of CHN were positive integer numbers and best fitted the observed values was found (Obs). Then, the composition of this compound was re-calculated (Calc). The results are listed in Table 1, while the ratio of carbon to oxygen (C/O) and carbon to hydrogen (C/H) atoms in the membranes are shown in Table 2 below.

Table 1

	Elemental análisis (wt%)		Number atoms	Elemental análisis (wt%)		Number atoms
	Obs	Calc		Obs	Calc	
750 P0			850 P0			
C	89.2	89.2	94	95.1	95.1	91
H	3.2	3.2	40	0.7	0.7	8
O	7.6	7.6	6	4.2	4.2	3
MW			1265			1148

750P05				850P05		
C	92.1	92.1	95	96.3	96.3	83
H	2.7	2.7	33	0.6	0.59	6
O	5.2	5.2	4	3.1	3.1	2
MW			1239			1034
750P1				850P1		
C	93.3	93.3	98	97.4	97.4	113
H	1.6	1.59	20	0.3	0.29	4
O	5.1	5.1	4	2.3	2.3	2
MW			1260			1392

It can be observed that the composition of the observed and calculated structure matches very well.

For the membranes carbonized at 750 °C, the molecular weights were similar, and the number of carbons and hydrogen increased slightly with the quantity of the PVB added.

- 5 The membranes carbonized at 850 °C had more wt% of carbon than those carbonized at 750 °C, and the opposite was observed for hydrogen and oxygen. This is an indication that at higher temperatures of carbonization, the number of functional groups is reduced.

For the membranes without PVB and with 0.5 of PVB, the molecular weight of the basic structural unit decreased with the temperature. However, when the content of PVB

- 10 increases to 1, the opposite was observed, suggesting that some PVB was not completely removed, increasing the carbon content in the 850P1 membrane.

Hydrophobicity/Hydrophilicity analysis

In previous works concerning to hydrophilic CMSM prepared from phenolic resins for selective extraction of water gas (see the two articles of A. Llosa et al., and the two

- 15 articles of A. Rahimalimamaghani, *et al.*, *ibid*) the inventors reported that the pore size, pore size distribution and hydrophilicity/hydrophobicity of these CMSM could be tuned by changing the temperature of carbonization and the addition of hydrophilic nanoparticles.

FTIR analysis indicated that between 550-650 °C there was a sharp decrease in the oxygen content and above 650 cross linking between carbon chains are produced

- 20 increasing the hydrophobicity. NMR relaxations and pore size distribution analysis shown that an increase in carbonization temperature during the preparation of composite Al-CMSMs caused i) the densification of the structure forming smaller pores and ii) the removal of hydrophilic functional groups making the pores more hydrophobic.

Non-supported CMSMs samples prepared as in Example 1 were powdered and sieved to

20-40 μm particle size, weighted (1 gram) and placed inside a 100 Relative Humidity (RH) chamber for 7 days.

- The hydrophilicity of the membranes was estimated by measuring the weight gained by the dry membrane after it was stored in an environment saturated with water. After saturation with water vapor, the samples were weighted again, and the amount of water adsorbed calculated. Table 2 shows the water adsorbed (wt %) and relation of the number of C/O and C/H for the non-supported membranes carbonized at 750 °C and 850 °C and having various contents of PVB.

Table 2

	Comp. Ex. 1	Ex. 1.1	Ex. 1.2	Comp. Ex. 2	Ex. 1.3	Ex. 1.4
	750P0	750P0.5	750P1	850P0	850P0.5	850P1
Water adsorbed (%)	17	15	13	7	5	4
C/O ratio	11.7	17.7	18.3	22.6	31	42.3
C/H ratio	27.9	34.1	58.3	135.9	160.5	324.7

- By increasing the carbonization temperature from 750 °C to 850 °C, the capacity to adsorb water was drastically reduced, indicating the membrane was more hydrophobic. This was also reflected in the C/O ratio (the presence of O makes the membrane more hydrophilic). The water adsorbed decreased with the addition of PVB, what is related to the C/O ratio, the highest being for 850P1. The C/H ratio was an indication of the graphitization of the carbon structure and, consequently, of the hydrophobicity.

Example 2.3.- Pore size distribution (PSD) analysis of the supported CMSM

- The pore size distribution of the CMSMs was determined by perm-porosimetry using the equipment and methodology reported in A. Rahimalimamaghani, *et al.* "Effect of aluminium acetyl acetate on the hydrogen and nitrogen permeation of carbon molecular sieves membranes". *Int J Hydrogen Energy*, 2022, Vol. 47, pp. 14570-14579. Before the PSD measurement, the CMSM was dried under N₂ atmosphere at 3 bar and 300 °C for 24 h. For PSD measurement, He was used as carrier gas at 2 bar operational pressure and 70 °C, and water as condensable liquid. The results are shown in Tabla 3 below and Fig. 1:

Table 3

Pore size distr.	750 P0	750P0.5	750P1	850 P0	850P0.5	850P1
0.5-0.6 nm (%)	26	31	46	44	70	81
0.4-0.6 nm (%)	29	36	62	76	85	87

The CMSM carbonized at 750 °C show that the pore size distribution is not uniform, the addition of PVB shifts the peaks to smaller pores; those carbonized at 850 °C show more uniform pore distribution having a mean peak at 0.5 nm; at higher temperatures, the condensation in polymeric chains are higher, resulting in a reduction of the size of the pores. Pores bigger than 1 nm disappear with the addition of PVB, which fills the bigger pores of the membrane, while increasing the pores smaller than 0.5 nm. As can be seen in Fig. 1, in the 850P1 CMSM, 81 % of the pores are between 0.5 and 0.6 nm.

Example 3: Pervaporation measurements

Pervaporation characterization of the CMSMs was carried out using the custom-made pervaporation setup reported in A. Rahimalimamaghani, *et al.*. "New Hydrophilic Carbon Molecular Sieve Membranes for Bioethanol Dehydration via Pervaporation". *Chemical Engineering Journal*, 2022, Vol. 435, pp.134891. Each CMSM was tested with 10 L of fresh feed at 37 °C and permeate pressure of 12 mbar. Each experiment was carried out for 6h, and every hour the permeated was weighted and the composition determined by HPLC (Shimadzu, UFLC XR). For most of the cases, the average of the 6 samples measured at each hour is reported. Pervaporation of a) water; b) binary samples of 5% of PA in water (PA 5%), and 5% of AA in water (AA 5%), and c) ternary samples containing PA and AA in water (PA5%+AA5%, PA10%+AA5%, and PA5%+AA10%), were performed.

Fig. 2 shows the pervaporation of only water. It was observed that the water flux was almost constant in all the cases. The membranes carbonized at 750 °C exhibited higher water flux than those at 850 °C, what was the expected for a more hydrophilic membrane, and the flux increased with the addition of PVB probably due to the increase of the porosity produced by the decomposition of the polymer.

Pervaporation studies were performed in water solutions containing PA at 5% wt% or AA at 5% wt%. In Table 4 and Fig. 3 the effect of the carbonization temperature and the PVB on the pervaporation properties of both solutions is shown.

Table 4

CMSM	PA 5%			AA 5%		
	Flux [g m ⁻² h ⁻¹]		PA purity [%]	Flux [g m ⁻² h ⁻¹]		PA purity [%]
	H ₂ O	PA		H ₂ O	PA	
750P	14.3	15.1	51.5	17.0	3.1	15.4
750P05	15.0	21.8	59.2	17.0	3.9	18.5
750P1	15.8	28.4	64.2	18.2	5.5	23.2
850P0	4.4	5.0	52.9	5.2	0.8	12.8

850P05	5.4	7.5	58.1	6.0	1.7	21.6
850P1	5.6	16.1	73.9	6.7	2.8	29.0

Without wishing to be bound by theory, the inventors believe that the highest purity obtained by 850P1 (73.9%) is due to the combined effect of the higher hydrophobicity of the membrane and the narrow pore size distribution, in the range of 0.5-0.6 nm; and that for the same membrane, the AA purity is 29.0% is mainly due to their higher dipolar moment 1.74 D than PA (0.63 D); for the same reasons, the purity for PA and AA are lower for 750P1 than 850 P1. The inventors believe that the the increase of purity of PA and AA with the addition of PVB is mainly due to the increase in their fluxes since water flux is not dependent on the amount of PVB, but, the flux increase considerably going from 0.5 to 1% of PVD, which is attributed to the increase of porosity by the free space left by PVB during carbonization.

Permeation studies were also carried out with samples containing a 5% of PA and a 5% of AA. Fig. 4 and Table 5 show the effect of the carbonization temperature and the introduction of PVB in CMSMs on the pervaporation properties of water solutions containing mixtures of 5% of propionic acid (PA) and 5% of acetic acid (AA).

Table 5

CMSM	PA 5%+ AA 5%				
	Flux [g m ⁻² h ⁻¹]			Purity [%]	
	H ₂ O	PA	AA	PA	AA
750P	9.7	40.2	9.2	68.0	31.8
750P05	10.4	44.9	10.0	68.7	33.5
750P1	12.3	46.5	10.5	67.1	34.1
850P0	2.8	52.3	9.3	81.3	36.4
850P05	3.4	60.6	6.4	86.1	39.1
850P1	5.0	67.1	3.9	88.3	41.1

The results show that the highest purity is obtained with 850P1 (88.3 %), which is higher than that from a solution containing only a 5% of PA (73.9% , Figure 3). Without wishing to be bound by theory, the inventors believe that PA is adsorbed on the hydrophobic pores and permeated by adsorption diffusion, at the same time blocking the pores to the passage of the more hydrophilic and smaller AA and, consequently, the flux is smaller with 750P1. It is also observed that there is an increase of the purity in function of the PVB added but less marked than with only PA; the purity is lower for the membranes carbonized at 750 °C; and for AA, the lowest purity is for 850P1 and decrease with the PVB added.

Table 6 shows the effect of carbonization temperature and introduction of PVB in CMSMs on pervaporation properties of water solutions containing mixtures of 5% of propionic acid (PA) and 5% of acetic acid (AA). The pervaporation results of a solutions containing the double of PA (10%PA+5%AA) are shown in Table 6 and Figure 5a. The PA purity is similar to (5%PA+5%AA), but for AA, the lowest is for 750P1. Without wishing to be bound by theory, the inventors believe that the higher the concentration of AA, the higher the blockage of the hydrophobic pores. For the solution with double concentration of AA (5%PA+10%AA) (Figure 5b), PA purity for 850P1 is lower than the other cases (61.9%) probably due to the higher competition of AA with PA for the pores, and the purity increases almost linearly with the PVB where the porosity and the hydrophobicity are larger.

Table 6

CMSM	PA 10%+ AA 5%					PA 5%+ AA 10%				
	Flux [$\text{g m}^{-2}\text{h}^{-1}$]			Purity [%]		Flux [$\text{g m}^{-2}\text{h}^{-1}$]			Purity [%]	
	H ₂ O	PA	AA	PA	AA	H ₂ O	PA	AA	PA	AA
750P	7.0	12.3	0.8	61.4	3.8	8.3	5.0	4.8	27.6	26.4
750P05	7.0	14.9	0.7	66.2	2.9	10.3	6.9	5.3	30.5	23.7
750P1	8.3	18.6	1.0	66.7	3.6	11.1	11.4	6.6	39.2	22.8
850P0	1.4	6.4	0.7	75.3	7.8	2.1	3.2	1.7	46.2	23.7
850P05	1.4	11.5	0.7	84.6	4.9	2.5	5.2	1.9	54.2	19.4
850P1	2.2	20.7	0.7	87.8	2.8	3.6	9.8	2.4	61.9	15.2

As can be seen from the results, the combination of the specific composition of the dipping solution used for the preparation of the CMSM, the dipping solution comprising a sacrificial pore forming agent in relatively low amounts, and a specific range of carbonization temperature, unexpectedly allows obtaining a membrane with the desired pore size and pore size distribution and hydrophobicity, the later being higher than the one of a membrane obtained from the same dipping solution and carbonized at the same temperature but without the pore forming agent. This combination of specific pore size, pore size distribution, and degree of hydrophobicity allows increasing the desired permeation properties, that is obtaining a more selective membrane towards PA.

Citation List

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2. M.A. Llosa *et al.* "Composite-Alumina-Carbon Molecular Sieve Membranes Prepared

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 8. A. Rahimalimamaghani, *et al.* "New Hydrophilic Carbon Molecular Sieve Membranes for Bioethanol Dehydration via Pervaporation". *Chemical Engineering Journal* 2022, 435, 134891.
- For reasons of completeness, various aspects of the invention are set out in the following numbered clauses:
- Clause 1. An hydrophobic carbon molecular sieve membrane characterized by comprising pores with a pore size distribution in which at least 20 % of the pores have a pore size from 0.5 to 0.6 nm, measured by perm-porosimetry; and having a C/O ratio higher than 8 and a C/H ratio higher than 20; the membrane being obtainable by dip-coating a support with a dipping solution comprising a carbon precursor, a non-aqueous solvent, a curing agent, and a pore forming agent, wherein the pore forming agent is in an amount higher than 0.5 wt% to 15 wt% related to the weight of carbon precursor; followed by carbonization at a temperature higher than 700 °C and lower than 1000 °C.
- Clause 2. The hydrophobic carbon molecular sieve membrane according to clause 1, wherein the membrane comprises a pore size distribution in which less than 20 % of the pores have a pore size from 0.3 to 0.4 nm.

Clause 3. A process for the preparation of a hydrophobic carbon molecular sieve membrane as defined in clauses 1 or 2, the process comprising:

- a) providing a porous support;
- b) providing a dipping solution comprising a phenol-formaldehyde resin or a
5 benzoxazine resin as carbon precursor, a non-aqueous solvent, a curing agent, and the pore forming agent, wherein the pore forming agent is in an amount higher than 0.5 wt% to 15 wt% related to the weight of carbon precursor;
- c) dipping the porous support at least once in the dipping solution of step b) to obtain a coated support;
- 10 d) optionally, drying the coated support of step c);
- e) carbonizing the coated support of step c) or of step d) at a temperature higher than 700 °C and lower than 1000 °C in a non-oxidizing atmosphere or vacuum to obtain a supported carbon molecular sieve membrane; and
- 15 f) cooling the supported carbon molecular sieve membrane of step e) to room temperature.

Clause 4. A process for the preparation of a hydrophobic carbon molecular sieve membrane as defined in clauses 1 or 2, the process comprising:

- a) providing a solution comprising a phenol-formaldehyde resin or a benzoxazine resin
20 as carbon precursor, a non-aqueous solvent, a curing agent, and the pore forming agent, wherein the pore forming agent is in an amount higher than 0.5 wt% to 15 wt% related to the weight of carbon precursor;
- b) casting the solution of step a) on a substrate to obtain a membrane precursor;
- c) carbonizing the membrane precursor of step c) at a temperature higher than 700 °C and lower than 1000 °C in a non-oxidizing atmosphere or vacuum to obtain a self-
25 supported carbon molecular sieve membrane; and
- d) cooling the self-supported carbon molecular sieve membrane of step e) to room temperature.

Clause 5. The process according to clauses 3 or 4, wherein the carbon precursor is in an amount from 2 wt% to 30 wt% of the dipping solution.

30 Clause 6. The process according to clauses 3 to 5, wherein the carbon precursor is a phenolic resin, in particular, a resorcinol-formaldehyde resin.

Clause 7. The process according to clauses 3 to 6, wherein the pore forming agent is selected from the group consisting polyvinyl butyral, cellulose ethers such as methylcellulose, cellulose esters such as cellulose acetate, poly(vinyl alcohol), and
35 polyvinylpyrrolidone, polylactic acid; and poloxamers.

Clause 8. The process according to any one of clauses 3 to 7, wherein the pore forming agent is in an amount from 0.5 wt% to 10 wt% related to the weight of carbon precursor.

5 Clause 9. The process according to any one of clauses 3 to 8, wherein the pore forming agent is polyvinyl butyral.

Clause 10. The process according to clauses 9, wherein polyvinyl butyral is in an amount from 0.8 wt% to 1.2 wt% related to the weight of carbon precursor.

Clause 11. The process according to any one of clauses 3 to 10, wherein the carbonizing temperature is from 750 °C to 950 °C or from 800 °C to 900 °C.

10 Clause 12. The process according to any one of clauses 3 to 11, wherein the carbonization is carried out at a heating rate of from 0.2 °C/min to 10 °C/min and a dwell time from 1 to 40 h.

Clause 13. A method for the selective separation of propionic acid from an aqueous mixture comprising propionic acid, in particular, from an aqueous mixture comprising propionic acid and acetic acid, the process comprising:

15 a) providing a hydrophobic carbon molecular sieve membrane as defined in any one of clauses 1 to 4; and

b) contacting an aqueous mixture comprising propionic acid, in particular, the aqueous mixture comprising propionic acid and acetic acid, with one side of the membrane

20 while vacuum is applied in the other side of the membrane to produce a permeate gas stream in order to separate propionic acid by pervaporation.

Clause 14. Use of a hydrophobic CMSM as defined in any one of clauses 1 to 4 for the selective separation of propionic acid, in particular, from a mixture containing propionic acid, water and acetic acid.

25 Clause 15. Use of a hydrophobic CMSM as defined in any one of clauses 1 to 4, as a membrane reactor or part of a membrane reactor.

Claims

1. An hydrophobic carbon molecular sieve membrane characterized by comprising pores with a pore size distribution in which at least 20 % of the pores have a pore size from 0.5 to 0.6 nm, measured by perm-porosimetry; and having a C/O ratio higher than 8 and a C/H ratio higher than 20; the membrane being obtainable by dip-coating a support with a dipping solution comprising a carbon precursor, a non-aqueous solvent, a curing agent, and a pore forming agent, followed by carbonization at a temperature higher than 700 °C and lower than 1000 °C; wherein the pore forming agent is in an amount from 0.5 wt% to 8 wt% related to the weight of carbon precursor; and wherein the carbon molecular sieve membrane has a higher hydrophobicity than a membrane prepared by the same process but without the addition of the pore forming agent; optionally, wherein the membrane comprises a pore size distribution in which less than 20 % of the pores have a pore size from 0.3 to 0.4 nm.
2. The hydrophobic carbon molecular sieve membrane according to claim 1, wherein at least 30 % of the pores have a pore size from 0.5 to 0.6 nm and at least 35 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry; the C/O ratio is higher than 15 and the C/H ratio is higher than 30; the pore forming agent is in an amount from 0.5 wt% to lower than 1 wt% related to the weight of carbon precursor; and the carbonization at a temperature is from 750 °C to lower than 850 °C; or, alternatively, wherein at least 65 % of the pores have a pore size from 0.5 to 0.6 nm and at least 80 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry; and having a C/O ratio higher than 25 and a C/H ratio higher than 150; the membrane being obtainable by dip-coating a support with a dipping solution comprising a phenol-formaldehyde resin or a benzoxazine resin as a carbon precursor, a non-aqueous solvent, a curing agent, and a pore forming agent, wherein the pore forming agent is in an amount from 0.5 wt% to lower than 1 wt% related to the weight of carbon precursor; followed by carbonization at a temperature from 850 °C to lower than 900 °C; or, alternatively, wherein at least 40 % of the pores have a pore size from 0.5 to 0.6 nm and at least 55 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry; the C/O ratio is higher than 18 and the C/H ratio higher than 50; the pore forming agent is in an amount from 1 wt% to 5 wt% related to the weight of carbon precursor; and the carbonization temperature is from 750 °C to lower than 850 °C;

or, alternatively,

wherein at least 75 % of the pores have a pore size from 0.5 to 0.6 nm and at least 82 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry; the C/O ratio higher than 35 and the C/H ratio higher than 200; the pore forming agent is in an amount from 0.7 wt% to lower than 1 wt% related to the weight of carbon precursor; and
5 the carbonization temperature is from 850 °C to lower than 900 °C;

or, alternatively,

wherein at least 80 % of the pores have a pore size from 0.5 to 0.6 nm and at least 85 % of the pores have a pore size from 0.4 to 0.6 nm, measured by perm-porosimetry; the C/O
10 ratio higher than 40 and the C/H ratio higher than 300; the pore forming agent is in an amount from 1 wt% to 5 wt% related to the weight of carbon precursor; and the carbonization temperature is from 850 °C to lower than 900 °C.

3. The hydrophobic carbon molecular sieve membrane according to claims 1 or 2, wherein
15 the pore forming agent is selected from the group consisting polyvinyl butyral, cellulose ethers such as methylcellulose, cellulose esters such as cellulose acetate, poly(vinyl alcohol), polyvinylpyrrolidone, polylactic acid; and poloxamers, particularly polyvinyl butyral;
optionally, wherein the a carbon precursor is a phenol-formaldehyde resin or a
20 benzoxazine resin.

4. A process for the preparation of a hydrophobic carbon molecular sieve membrane as defined in claim 1, the process comprising:
a) providing a porous support;
25 b) providing a dipping solution comprising a carbon precursor such as a phenol-formaldehyde resin or a benzoxazine resin, a non-aqueous solvent, a curing agent, and the pore forming agent, wherein the pore forming agent is in an amount from 0.5 wt% to 8 wt%, particularly, higher than 0.5 wt% to 8 wt%, related to the weight of carbon precursor;
30 c) dipping the porous support at least once in the dipping solution of step b) to obtain a coated support;
d) optionally, drying the coated support of step c);
e) carbonizing the coated support of step c) or of step d) at a temperature higher than 700 °C and lower than 1000 °C in a non-oxidizing atmosphere or vacuum to obtain a
35 supported carbon molecular sieve membrane; and
f) cooling the supported carbon molecular sieve membrane of step e) to room temperature;

or, alternatively,

- a) providing a solution comprising a phenol-formaldehyde resin or a benzoxazine resin as carbon precursor, a non-aqueous solvent, a curing agent, and the pore forming agent, wherein the pore forming agent is in an amount from 0.5 wt% to 8 wt%, particularly, higher than 0.5 wt% to 8 wt%, related to the weight of carbon precursor;
- b) casting the solution of step a) on a substrate to obtain a membrane precursor;
- c) carbonizing the membrane precursor of step c) at a temperature higher than 700 °C and lower than 1000 °C in a non-oxidizing atmosphere or vacuum to obtain a self-supported carbon molecular sieve membrane; and
- d) cooling the self-supported carbon molecular sieve membrane of step e) to room temperature.

5. The process according to claim 4, wherein the carbon precursor is in an amount from 2 wt% to 30 wt% of the dipping solution.

6. The process according to claims 4 or 5, wherein the carbon precursor is a phenol formaldehyde resin, in particular, a resorcinol-formaldehyde resin.

7. The process according to claims 4 to 6, wherein the pore forming agent is selected from the group consisting polyvinyl butyral, cellulose ethers such as methylcellulose, cellulose esters such as cellulose acetate, poly(vinyl alcohol), polyvinylpyrrolidone, polylactic acid; and poloxamers.

8. The process according to any one of claims 4 to 7, wherein the pore forming agent is in an amount from 0.5 wt% to 10 wt% related to the weight of carbon precursor.

9. The process according to any one of claims 4 to 8, wherein the pore forming agent is polyvinyl butyral.

10. The process according to claim 9, wherein polyvinyl butyral is in an amount from 0.8 wt% to 1.2 wt% related to the weight of carbon precursor.

11. The process according to any one of claims 4 to 10, wherein the carbonizing temperature is from 750 °C to 950 °C or from 800 °C to 900 °C.

12. The process according to any one of claims 4 to 11, wherein the carbonization is carried out at a heating rate of from 0.2 °C/min to 10 °C/min and a dwell time from 1 to 40 h.

13. A method for the selective separation of propionic acid from an aqueous mixture comprising propionic acid, in particular, from an aqueous mixture comprising propionic acid and acetic acid, the process comprising:

- 5 a) providing a hydrophobic carbon molecular sieve membrane as defined in any one of claims 1 to 3; and
- b) contacting an aqueous mixture comprising propionic acid, in particular, the aqueous mixture comprising propionic acid and acetic acid, with one side of the membrane while vacuum is applied in the other side of the membrane to produce a permeate
- 10 gas stream in order to separate propionic acid by pervaporation.

14. Use of a hydrophobic CMSM as defined in any one of claims 1 to 3 for the selective separation of propionic acid, in particular, from a mixture containing propionic acid, water and acetic acid.

15

15. Use of a hydrophobic CMSM as defined in any one of claims 1 to 3, as a membrane reactor or part of a membrane reactor.

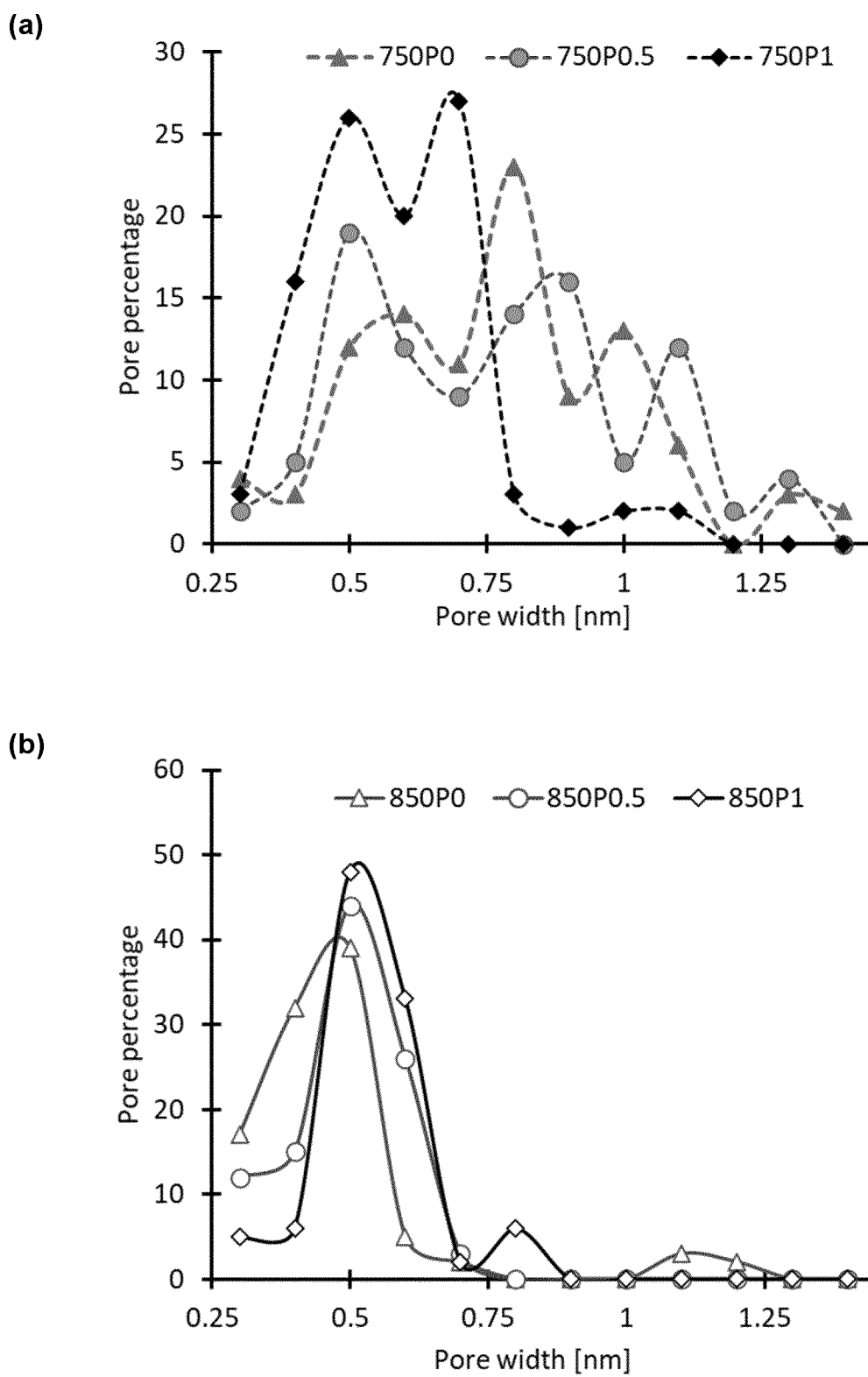


Fig. 1 (cont.)

(c)

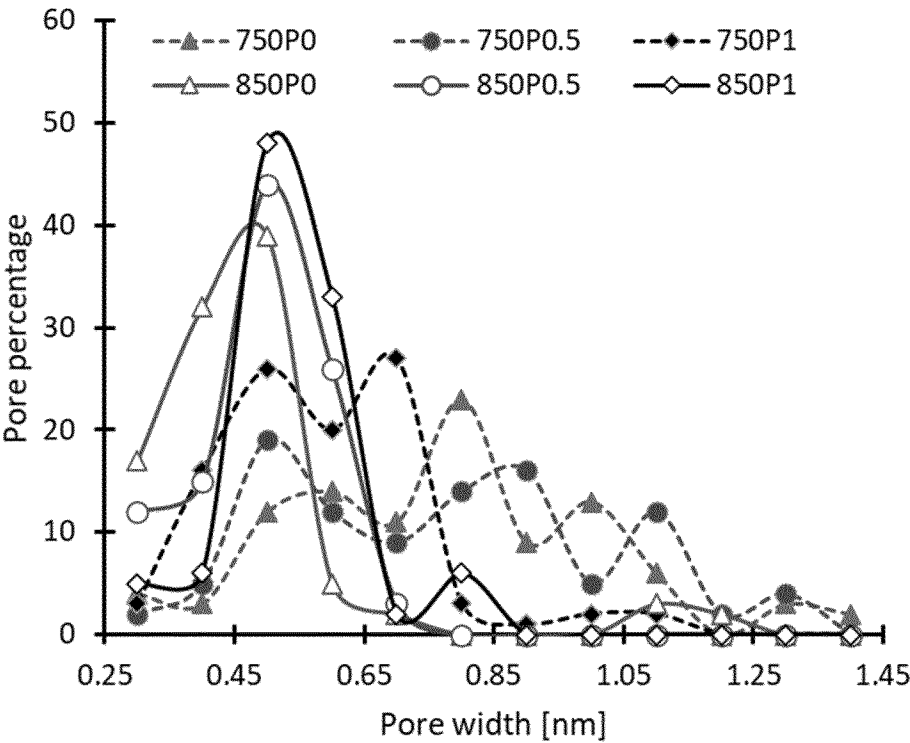


Fig. 1

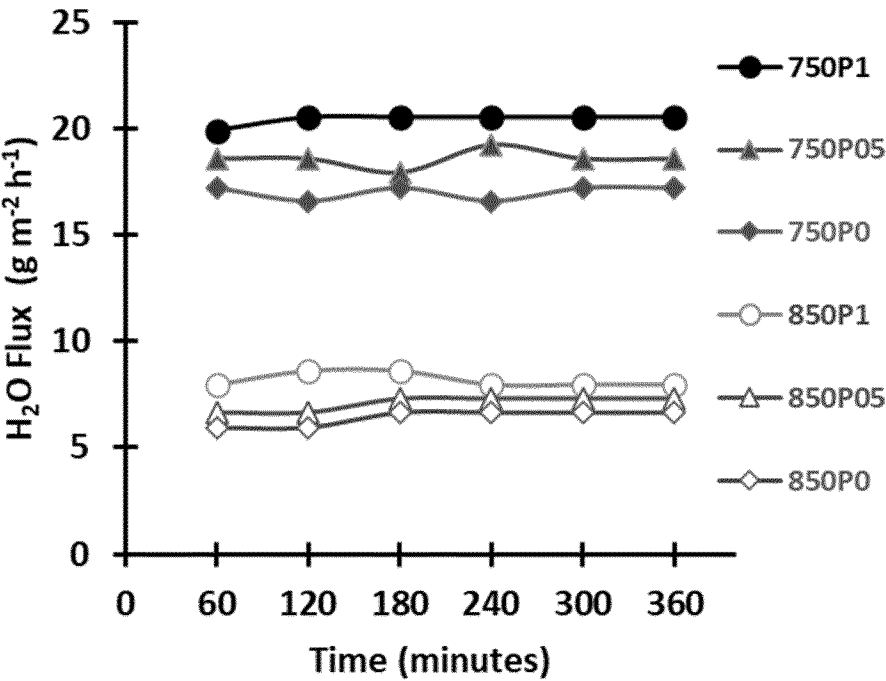


Fig. 2

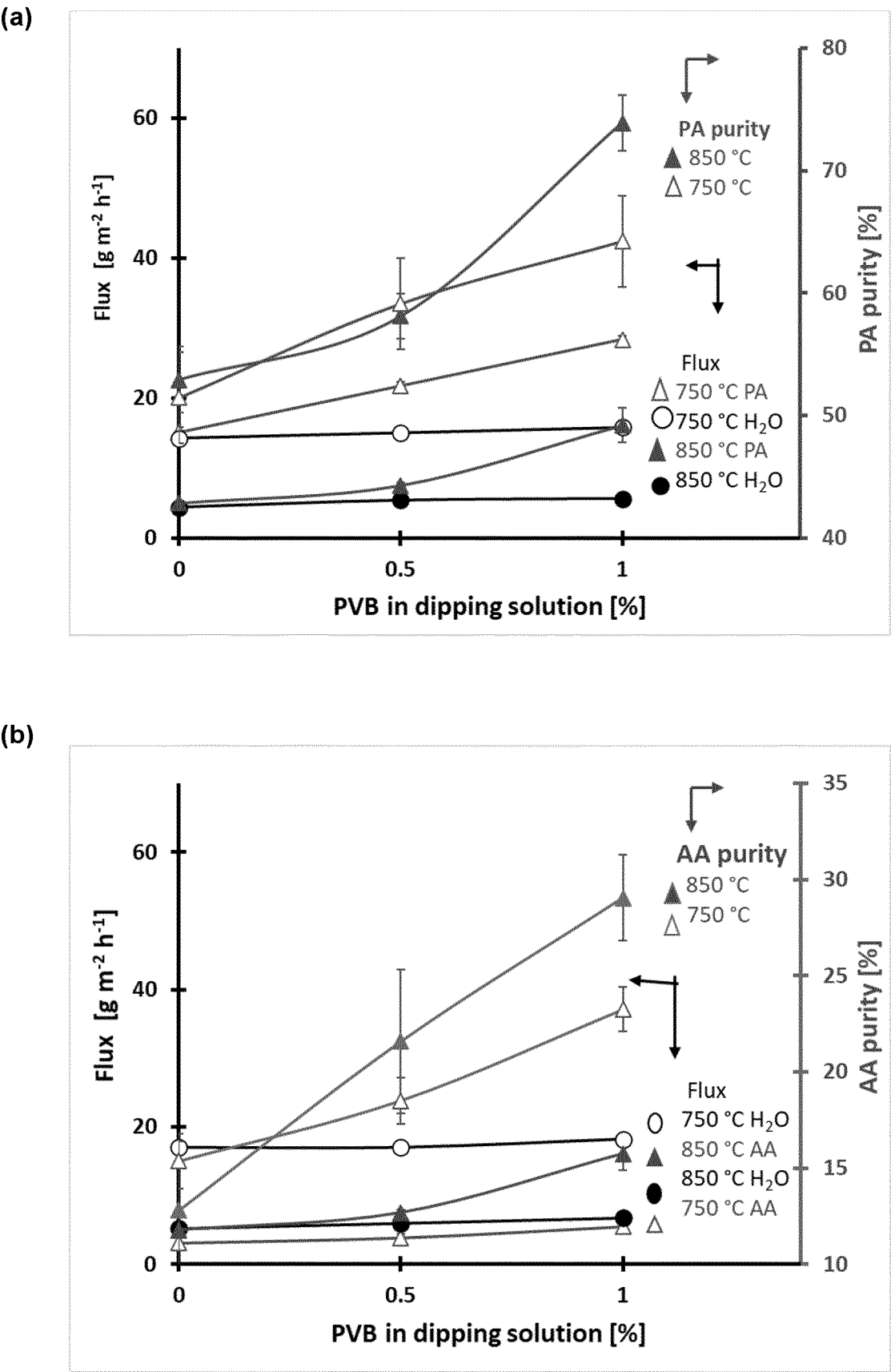


Fig. 3

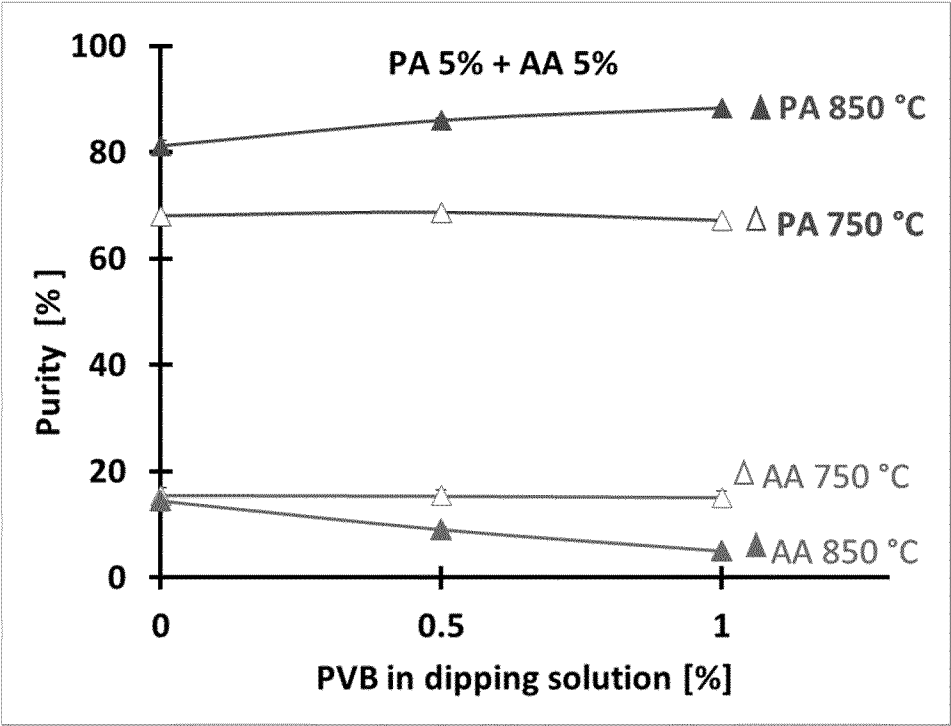


Fig. 4

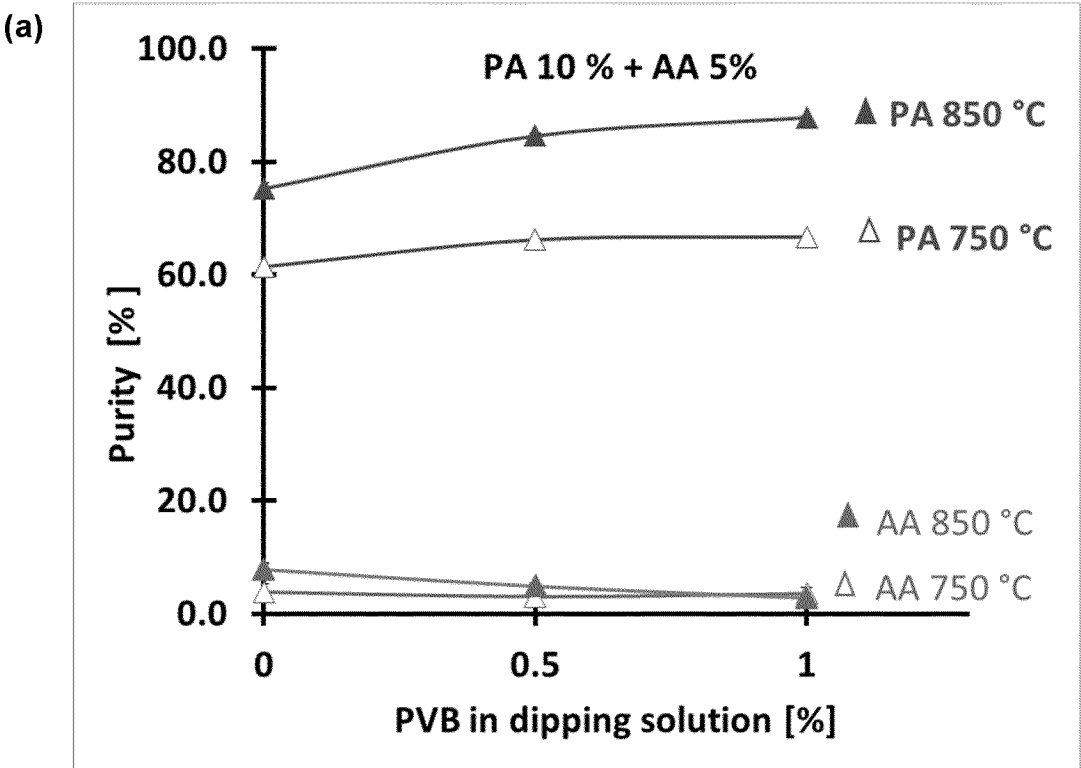


Fig. 5 (cont.)

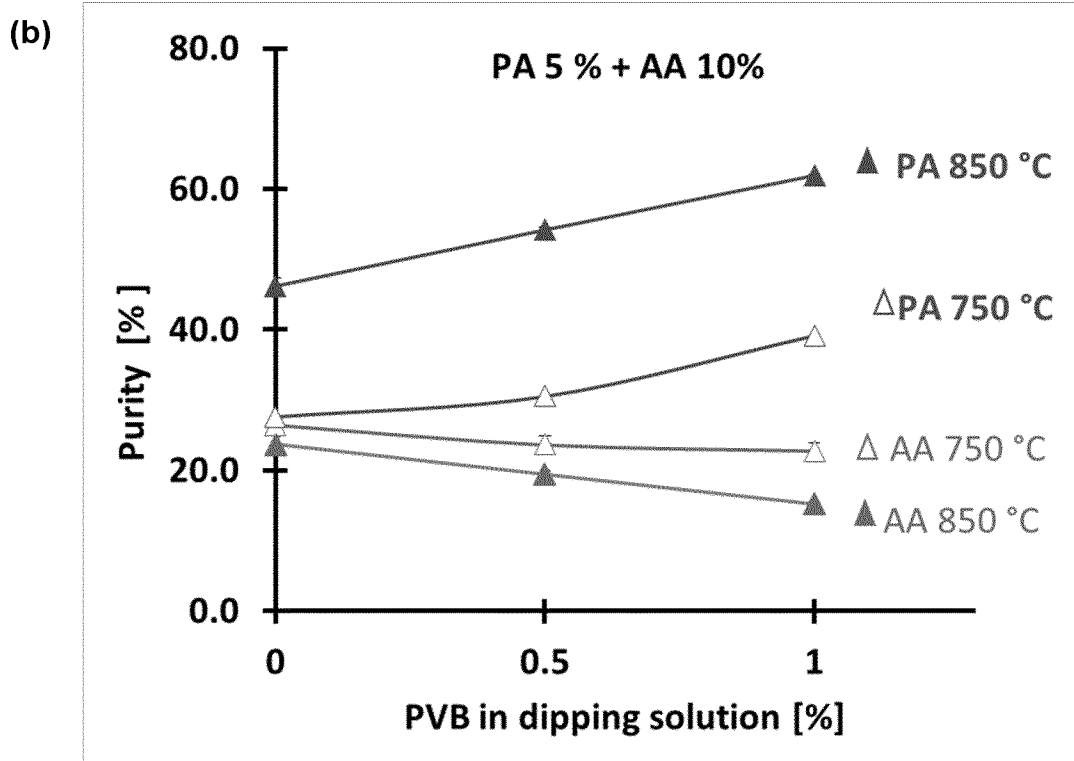


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/068974

A. CLASSIFICATION OF SUBJECT MATTER		
INV. B01D67/00 B01D71/02 B01D61/36 B01D69/02		
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) B01D G01N		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SHUNSUKE TANAKA ET AL: "Pervaporation dehydration performance of microporous carbon membranes prepared from resorcinol/formaldehyde polymer", JOURNAL OF MEMBRANE SCIENCE, ELSEVIER BV, NL, vol. 379, no. 1, 22 May 2011 (2011-05-22), pages 52-59, XP028249667, ISSN: 0376-7388, DOI: 10.1016/J.MEMSCI.2011.05.046 [retrieved on 2011-05-27]	1 - 3
Y	Section 2.2; page 55, column 2; example 1 ----- - / - -	1 - 8, 11 - 15
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 17 September 2024		Date of mailing of the international search report 01/10/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Williams, Jennifer

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/068974

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Balys M. ET AL: "Evaluation of microporous structure of carbon molecular sieves using the pycnometric method" In: "Characterization of Porous Solids VI", 1 January 2002 (2002-01-01), Elsevier Science & Technology, The Netherlands, XP093072812, ISSN: 0167-2991 ISBN: 978-0-444-51261-1 vol. 144, pages 225-230, DOI: 10.1016/S0167-2991(02)80138-0, page 226, paragraph 2 -----	1
Y	CN 109 179 369 A (ZHENGZHOU INST OF MULTIPURPOSE UTILIZATION OF MINERAL RESOURCES CHINES) 11 January 2019 (2019-01-11) claim 4; figure 1; examples 1,2,3 -----	1-8, 11-15
X	US 6 024 899 A (PENG Y LISA [US] ET AL) 15 February 2000 (2000-02-15) column 6, line 42 - line 54; example 1 -----	1-12
A	Huda W.Z. ET AL: "A Comparison of Carbon Molecular Sieve (CMS) Membranes with Polymer Blend CMS Membranes for Gas Permeation Applications", ASEAN Journal of Chemical Engineering, 6 August 2012 (2012-08-06), pages 51-58, XP093073271, DOI: 10.22146/ajche.49755 Retrieved from the Internet: URL:https://www.researchgate.net/publication/288706001_A_Comparison_of_Carbon_Molecular_Sieve_CMS_Membranes_with_Polymer_Blend_CMS_Membranes_for_Gas_Permeation_Applications [retrieved on 2023-08-14] page 52 - column 2 -----	1-15
A	OZAKI J ET AL: "Novel preparation method for the production of mesoporous carbon fiber from a polymer blend", CARBON, ELSEVIER OXFORD, GB, vol. 35, no. 7, 1 January 1997 (1997-01-01), pages 1031-1033, XP004083053, ISSN: 0008-6223, DOI: 10.1016/S0008-6223(97)89878-8 page 1 - page 2 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/068974

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 109179369	A	11-01-2019	NONE

US 6024899	A	15-02-2000	CN 1309620 A 22-08-2001
			EP 1109738 A1 27-06-2001
			JP 2002521296 A 16-07-2002
			US 6024899 A 15-02-2000
			WO 0005172 A1 03-02-2000
