Ceramic hollow fibre membrane, membrane module and method for producing the membrane

BACKGROUND OF THE INVENTION:

Field of the invention.

The invention relates to a ceramic hollow fibre membrane for microfiltration, ultrafiltration and gas separation, having a porosity of at least 10%. Membrane modules with ceramic hollow fibre membranes are for instance being employed in separation and concentration processes for separating and concentrating gasses and liquids.

Background of the invention.

Such a ceramic hollow fibre membrane is known from the international patent application with publication No. WO 94/23829. Because the surface area/volume ratio of this known fibre membrane is relatively high, the efficiency of the concentration or separation process will be high. In this document is noticed that the high surface area/volume ratio is of vital importance to be able to compete with other types of membranes. These known hollow fibre membranes have an external diameter of 0,5-3 mm and a wall thickness of 30-500 micrometer. There is a constant development to increase the surface area/volume ratio in order to improve the efficiency.

Summary of the invention.

An objective of the invention is to provide a ceramic hollow fibre membrane of the type described in the preamble of claim 1 with which a higher efficiency of the concentration or separation process will be possible than with the known fibre membrane. For this purpose, the fibre membrane according to the invention is characterized in that said membrane has an external diameter of 3,1-10 mm and a wall thickness of 0,51-4,9 mm.

Although the existing direction of development is to increase the surface area/volume ratio in order to improve the efficiency, the present invention is based on the insight that a higher efficiency can be obtained with fibre membranes with a less surface area/volume ratio than that of the known fibre membranes. The explanation for this is that hollow fibre membranes having a greater external diameter and a greater wall thickness are stronger and the separation or concentration processes can be carried out at higher pressures and higher flow rates which leads to a high increase in efficiency which is more than necessary to compensate the decrease in efficiency due to the lower surface area/volume ratio. In case no higher pressures will be used less drop in pressure will occur, because the membranes according to the invention also have a greater internal diameter than the known membranes, and thus a lower pressure will be sufficient which results in a higher energetic efficiency.

Preferably the ceramic hollow fibre membrane has an external diameter of 3,5-4,5 mm and a wall thickness of 0,51-0,55 mm and more preferably an external diameter of 4 mm and a wall thickness of 0,52-0,54 mm.

An embodiment of the fibre membrane according to the invention is characterized in that on the inside and/or outside of the wall of the fibre membrane a thin ceramic coating is present. Preferably a ceramic coating is applied either on the inside or on the outside of the wall of the fibre membrane. Using such a fibre membrane the efficiency of a concentration or separation process can further be increased. When a substrate with large pores is used and a thin layer with the actual membrane pores is coated on that substrate the resistance of the flow is reduced which greatly enhances the flux. This allows the usage of larger diameter fibres in case stronger fibres are requested, for example when high viscosity fluids or high solids contents fluids are being used as feed in the separation or concentration process.

The invention also relates to a membrane module comprising a bundle of ceramic hollow fibre membranes according to the invention, which membranes have a porosity of at least 10% and which membrane module has a flange on each end of the bundle fibre membranes.

With respect to the membrane module, the invention is characterized in that said membranes each have an external diameter of 3,5-4,5 mm and a wall thickness of 0,51-0,55 mm, preferably an external diameter of 3,5-4,5 mm and a wall thickness of 0,51-0,55 mm and more preferably an external diameter of 4 mm and a wall thickness of 0,52-0,54

mm.

An embodiment of the membrane module according to the invention is characterized in that said membranes each have an internal or external ceramic membrane coating.

The invention also relates to a method for producing a ceramic hollow fibre membranes for microfiltration, ultrafiltration and gas separation according to the invention, which membranes each have an external diameter of 3,1-10 mm and a wall thickness of 0,51-4,9 mm, said method comprising:

- making a paste by filling a thermoplastic polymer binder system with a ceramic powder;
- making said thermoplastic binder system plastic by heating;
- melt extruding the paste through a spinneret to produce ceramic hollow fibre membranes;
- heating the membranes to remove the binder system by thermal diffusion; and
- sintering the powder particles to each other to obtain single layer hollow fibre membranes being free of an additional micro-porous layer, said fibre membranes having a porosity of at least 10%.

With respect to the method, the invention is characterized in that a ceramic powder coating is applied on the inside and/or outside of the fibre membrane, and then the coating is dried and sintered. Preferably a ceramic coating is applied either on the inside or on the outside of the fibre membrane.

It is noticed that this method can also be used to produce fibre membranes having other dimensions (external diameter, wall thickness) than those mentioned.

An embodiment of the method according to the invention is characterized in that to remove the binder system the membranes are placed in a burn-off furnace in which hot air is circulated. Due to this circulation of hot air the process of removing the binder system is improved which results is a stronger membrane of a higher quality. Because the membranes obtained by this method are stronger higher pressures can be allowed during the separation or concentration processes which results in a higher efficiency.

A further embodiment of the method according to the invention is characterized in that during sintering the membranes are lying and stacked. With the

method according to the invention it is possible that the membranes contact each other during sintering without getting fixed to each other. By lying and stacking the membranes the membranes require less area and therefore a more economic sintering process is achievable.

Yet a further embodiment of the method according to the invention is characterized in that after melt extrusion the membranes are laid against each other on a heating plate in a furnace to keep the membranes at a constant temperature. Due to this the membranes will be of a better quality (for example: more straight, free of internal stresses). It is possible to lay the membranes against each other because the type of binder used. The binder used is a thermoplastic binder with the tradename Licomont from the firm Clariant.

Brief description of the drawings.

The invention will be elucidated more fully below on the basis of a drawing in which an embodiment of the method according to the invention is shown. In this drawing the figure is a schematic of an apparatus for practicing the present method.

Detailed description of the drawings.

In the figure, an extruder 1 can be seen, which introduces the paste to be spun into three spinnerets 3 by means of a spinning pump 2. The spinnerets 3 produce three continuous fibres. Then the hollow fibres are cut at desired lengths at a cutting station 4. Subsequently, the fibres 5 are laid against each other on a heating plate 6 in a furnace 7 to keep the fibres at a constant temperature of about 50 degrees Celsius to remove internal stresses. Next, the fibres 5 are placed in a burn-off furnace 8 in which hot air is circulated by means of a fan 9 to remove the binder system. Subsequently, the fibres 5 are laid down and stacked in a sintering installation 10 in which they are sintered.

After that or before sintering or even before putting the fibres in the burn-off furnace a ceramic powder coating is applied either on the inside or outside of the fibre membrane, and then the coating is dried and sintered. The thickness of the coating layer can be between 10 nanometer and 5000 nanometer and the material of the coating is typically aluminium oxide (alumina), but can also be other type of ceramics/inorganic materials,

including gamma alumina, titania, zirconia, silica, zeolite, carbon, microporous carbon, amorphous carbon, etc. and mixtures thereof.

The paste which is spun to give hollow fibre membranes consists of a thermoplastic polymer binder system and a ceramic powder. The thermoplastic polymer system becomes plastic at a temperature of between 50 and 220 degrees Celsius and serves as an aid during shaping (and sintering). The percentage of ceramic powder is between 30 and 70% V/V, preferably between 45 and 55% V/V. The paste is mixed in a mixer and granulated after cooling. The granules are then introduced into the extruder 1, where they melt again and, via the spinning pump 2 and spinnerets 3 are formed into hollow fibre membranes. The polymer binder system is removed in the burn-off furnace 8, after which the residual shape is sintered in a sintering installation 10.

The thermoplastic binder in the paste is preferably a binder from the firm Clariant available under the tradename Licomont. The ceramic powder in the paste preferably consists of aluminium oxide, although silicon nitride (Si_3N_4), silicon carbide, sialon and other ceramic powders can also be used. In the case of material based on silicon nitride, a certain amount of sinter aid, for example itrium oxide or aluminium oxide, can be added to the paste to control the porosity. The temperature in the burn-off furnace is about 500 degrees Celsius and that in the sintering furnace is about 1300 degrees Celsius in the case of aluminium oxide powder and about 1650 degrees Celsius in the case of silicon nitride powder. Sintering takes about 2 hours. The hollow fibre membranes obtained are able to withstand a corrosive environment and a relatively high temperature.

The external diameter is preferably about 4 mm and the wall thickness is preferably between 0,52-0,54 mm. The porosity is 30 to 50%. Silicon nitride in particular has a high strength and density and, moreover, a very high temperature resistance and corrosion resistance. The pore size can be adjusted between 0,02 and 3 micrometer and the density and the pore size can be controlled with the aid of the sinter aid and with the aid of the sintering temperature.

Obviously, various modifications and additions are possible within the scope of the invention. The ceramic powder chosen can also be hydroxyapatite, a ceramic powder that is biocompatible and that is used in artificial ossicles or as bone-replacement material. The particle size distribution of the powder can be important. A broad distribution leads to a higher degree of filling. The absolute particle size is important for the binder system

removal process. The smaller the particles, the smaller will be the pores of the product formed and the more difficult it will be to remove the binder system. By adding relatively large amounts of sinter additives and/or by using a higher sintering temperature and longer sintering time, it should be possible to dense-sinter the hollow fibres produced by means of the invention.

Although in the above the invention is explained on the basis of the drawings, it should be noted that the invention is in no way limited to the embodiments shown in the drawings. The invention also extends to all embodiments deviating from the embodiments shown in the drawings within the context defined by the claims. Instead of using three spinnerets also any other number of spinnerets can be used to increase the production speed.

CLAIMS:

1. Ceramic hollow fibre membrane for microfiltration, ultrafiltration and gas separation, having a porosity of at least 10%, characterized in that, said membrane has an external diameter of 3,1-10 mm and a wall thickness of 0,51-4,9 mm.

2. Ceramic hollow fibre membrane according to claim 1, characterized in that, said membrane has an external diameter of 3,5-4,5 mm and a wall thickness of 0,51-0,55 mm.

3. Ceramic hollow fibre membrane according to claim 2, characterized in that said membrane has an external diameter of 4 mm and a wall thickness of 0,52-0,54 mm.

4. Ceramic hollow fibre membrane according to claim 1, 2 or 3, characterized in that on the inside and/or outside of the wall of the fibre membrane a thin ceramic coating is present.

5. Membrane module comprising a bundle of ceramic hollow fibre membranes according to claim 1, 2, 3 or 4, which membranes have a porosity of at least 10% and which membrane module has a flange on each end of the bundle fibre membranes, characterized in that each of said membranes have an external diameter of 3,1-10 mm and a wall thickness of 0,51-4,9 mm.

6. Membrane module according to claim 5, characterized in that said membranes each have an external diameter of 3,5-4,5 mm and a wall thickness of 0,51-0,55 mm.

7. Membrane module according to claim 6, characterized in that said membranes each have an external diameter of 4 mm and a wall thickness of 0,52-0,54 mm.

8. Membrane module according to claim 5, 6 or 7, characterized in that said membranes each have an internal or external ceramic membrane coating.

9. Method for producing ceramic hollow fibre membranes for microfiltration, ultrafiltration and gas separation according to claim 1, 2, 3 or 4, which membranes each have an external diameter of 3,1-10 mm and a wall thickness of 0,51-4,9 mm, said method comprising:

- making a paste by filling a thermoplastic polymer binder system with a ceramic powder;
- making said thermoplastic binder system plastic by heating;
- melt extruding the paste through a spinneret to produce ceramic hollow fibre

membranes;

- heating the membranes to remove the binder system by thermal diffusion; and
- sintering the powder particles to each other to obtain single layer hollow fibre membranes being free of an additional micro-porous layer, said fibre membranes having a porosity of at least 10%,

characterized in that a ceramic powder coating is applied on the inside and/or outside of the fibre membrane, and then the coating is dried and sintered.

10. Method according to claim 9, characterized in that to remove the binder system the membranes are placed in a burn-off furnace in which hot air is circulated.

11. Method according to claim 9 or 10, characterized in that during sintering the membranes are lying and stacked.

12. Method according to claim 9, 10 or 11, characterized in that after melt extrusion the membranes are laid against each other on a heating plate in a furnace to keep the membranes at a constant temperature.