Modeling of a water vapor selective membrane unit to increase the energy efficiency of humidity harvesting

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Abstract. Air humidity is a promising source of clean and safe drinking water. However, in conventional systems a lot of energy is wasted on the production of cold air, rather than the condensation of water vapor. This study examines the possibility of using a hollow fiber membrane module to make this process more energy efficient, by separating the vapor from other gases, prior to the cooling process with the help of selective membranes. The water vapor concentration within a fiber has been modeled using a random walker approach, and the membrane permeability has been implemented as a re-bounce probability for simulation particles interacting with the membrane. Considering the additional work requirement for driving a feed flow through the membrane section and the computed water vapor permeation it could be shown that the energy demand per unit water is lowest for slow flow speeds and favors short and thin fibers. The total energy requirement was estimated to be less than half of the conventional one. Comparison with other CFD simulations and a real life module has shown a good level of agreement, indicating that a membrane section could improve the energy efficiency of humidity harvesting significantly.

1. Introduction
Increasing water scarcity and the demand for safe drinking water have led to necessity to exploit new sources of fresh water. A huge reservoir of fresh water is the water vapor present in the atmosphere. Technologies exploiting this source (Atmospheric Water Vapor Processing; AWVP) mostly consist of a main cooling cycle in which a stream of moist air is cooled down below its dew point and the condensate is collected [1].

The efficiency of this process is mainly determined by the coefficient of performance (COP) of the cooling cycle as well as the temperature and relative humidity of the air. In such a system however, a huge part of the energy is wasted on the byproduct of cold air, rather than being used for water production (see figure 1)

The objective of this study is to increase the efficiency of a wind driven AWVP system by means of a water vapor selective membrane unit. With such a membrane, water vapor can be separated from the air [2] prior to the cooling, so that the heat is used for the condensation process only. However, mechanical energy is now needed to drive the air flow through the membrane module which consists of a number of hollow fibers (long and very thin tube coated with a membrane layer on the inside). Membrane technology has already found a wide use in
gas dehydration processes [3], yet these applications focus more on the outcome of the product, than on the efficiency of the process.

The mechanical work needed to drive the feed flow, is determined by the fibers dimensions (length and radius) and the flow speed. To find the optimum range for those working parameters, simulations were run that estimate the water vapor permeation through the membrane section, while calculating the workload needed to drive the feed flow. Although there is already a number of numerical approaches towards modeling the mass transport in hollow fiber membranes (using either self-made finite volume methods [4], commercial CFD (Computational Fluid Dynamics) software [5], or solving the differential equations using orthogonal collocation [6], a new one has been chosen in this work, as the above mentioned have their limitations in either the permeability simulations according to the solution-diffusion model [7], the computational power demand, or the lack of possibility to scan over a wide range of parameters.

With the help of the random-walker approach it was now possible to draw a map of the sets of parameters over orders of magnitude, and for each triplet of radius, length and feedspeed the according work requirements to produce 1 ml of permeate could be calculated.

2. Methods

2.1. The random walker approach

2.1.1. The concentration distribution within a fiber The random-walker approach uses a number of $N_0$ simulation particles to represent the water vapor molecules in the air. Each particle is, like an individual molecule, subject to molecular diffusion, which means that its likelihood to change it’s position is governed by a normal distribution around 0, with a standard deviation that is equal to its mean step size. The direction of movement is totally arbitrary (random), and the distance it moved from it’s initial position is governed by it’s step size (walker) which is a function of the interval time and the diffusion constant.

Water vapor transport within a fiber is determined by 2 main contributions: convection and diffusion. As this work focuses on the laminar region ($Re \leq 2300$), no turbulence occur, and therefore the convective mixing in radial direction is neglected in these simulations. This means that for the radial movement only the diffusion driven displacement needs to be considered.

Along the axial direction ($z$-dimension) a convective stream is formed due to an applied pressure drop over the fiber. As the average flow speed of air is several orders of magnitude
larger than the diffusive transport, the initial assumption, that the latter contribution can be neglected for the wanted accuracy, was then proven. This would leave the convection as the only transport mechanism along the z-axis.

As previously mentioned, one of the main advantages of this method is the range over which the permeation can be observed. Therefore triplets of radius, length and pressure drop (and therefore the resulting mean flow velocity according to the Hagen-Poiseuille equations: $\bar{u} = \Delta P R^2 / 8 \mu L$) were being scanned for, that satisfy the criterion of laminar flow, as well as some other restrictions of practical feasibility that were applied: (a) the length was varied in a range between 0.01 m and 1 m in steps of 0.01 m; (b) the minimal radius was set as 0.25 mm and was observed in steps of 0.05 mm to a maximum of 2 mm; (c) the applied (uncorrected) pressure drop for the calculation of the average feed speed was restricted to a range of 1 hPa to 200 hPa (due to the estimated pressure range of standard fans) (d) the flow profile was restricted to laminar flow ($Re \leq 2300$).

The velocity profile in a fiber with laminar flow forms a parabolic shape determined by its radial position $r$ and the fiber radius $R$:

$$u(r) = 2\bar{u} \left(1 - \frac{r^2}{R^2}\right)$$

(1)

As such a flow profile rockets up the computational expenses, the simulations were performed using a plug flow (a homogenous speed distribution with a value $\bar{u}$, independent of the radial position) and then compared to the CFD simulations to estimate the goodness of that approach. These evaluations have shown that the outcome is precise enough for its purpose, and that the plug flow approach is a reasonable simplification (see figure 2c).

This approach now allows for a completely separated treatment of the diffusive and the convective transport. It leaves the diffusion as a subsequent series of two-dimensional cross-sections, and the convection as mean speed, that determines the residual time within the fiber.

2.1.2. Diffusion in radial direction

Fick’s second law of diffusion (expressed in terms of the probability $P$ to find a particle in the interval $[\vec{x}, \vec{x} + d\vec{x}]$ at a point of time $t$) states:

$$\frac{\partial P(\vec{x}, t)}{\partial t} = D \frac{\partial^2 P(\vec{x}, t)}{\partial x^2}$$

(2)

The solution to this equation is

$$P(\vec{x}, t)d\vec{x} = \frac{1}{(4\pi D t)^{n/2}} e^{-\frac{\vec{x}^2}{4nDt}} d\vec{x}$$

(3)

where $D$ is the diffusion constant in $m^2/s$ of a particle in a medium, and $n$ is the number of observed dimensions.

Equation 3 shows, that the position of any particle after a certain time $t$ is determined by a Gaussian distribution with a mean value of 0 and a standard deviation of $\sqrt{2nDt}$. This also leads to a mean-squared-displacement (MSD) of $2nDt$.

In the routine written in Matlab, a uniform 2d-distribution of a number of $N_0 = 10^6$ particles was prescribed in a region confined by a circle determined by the fiber radius $R$. The situation was modeled again after a given time interval $t_{int}$ of $10^{-5}$ sec. These values were chosen after series of simulation that showed, that the outcomes were sufficiently stable (within 1% of a converging value), while the computing time was held relatively low.

The second simulation step was achieved by adding a random displacement to every simulation particle, determined by equation 3. All those particles were chosen for the next
iteration step, that were still located within the bounds of the defined region. After a number of \( t/\bar{u}_{t_{int}} \) simulation steps, the number of the particles still remaining in the confined region were compared to the initial number, and therefore the fraction of particles that interacted with the boundary could be calculated.

### 2.1.3. Coupling the model to nature

In order to make usable results from this interacting fraction, the parameters have to be chose in such a way that they resemble the conditions of the model environment. For this environment the following parameters are assumed: \( T=30^\circ C \); relative humidity (r.h.) = 50% (those two factors cause a partial pressure of water vapor in the air of \( p_{part} = 21.7 \) hPa, or a concentration of \( 0.8406 \) \( mol/m^3 \)); according to [8] this results in a diffusion constant of \( D_{H_2O}(303.15 K, 1 \) atm\) = \( 0.2630 \cdot 10^{-4} \) \( m^2/s \). The permeate side pressure is kept with a vacuum pump at 10 hPa, and assuming a negligible contribution of other gases than water vapor due to the membrane selectivity, the concentration of water vapor in the air that would exert this pressure is equivalent to \( 0.4034 \) \( mol/m^3 \).

Thus the initial condition of \( N_0 \) uniformly distributed particles within a volume element \((A_{cross} \bar{u} t_{int})\) represents the outside concentration, whereas a situation where no more simulation particles are left within the fiber represents the equilibrium condition with the permeate side, and thus also the same concentration. Any fraction of diffused particles in between would therefore represent the according fraction of concentration difference.

### 2.2. CFD simulations

#### 2.2.1. Pressure drop

To compare analytical pressure drop estimations according to the Hagen-Poiseuille equations and the pressure drop corrections according to ref. [9], resulting in

\[
\Delta p = \begin{cases} 
\frac{1}{\left( 1 - \left( \frac{L}{L_e} \right)^{1.0878} + \frac{1}{\left( \frac{L}{L_e} \right)^{1.0878}} \right)^2} - 1 \frac{\rho \bar{u}^2}{2} & \text{for } L \leq L_e \\
\left( \frac{64 L}{Re d} + 1.1568 \right) \frac{\rho \bar{u}^2}{2} & \text{for } L > L_e 
\end{cases}
\]

(4)

as well as the random walker approach for the water vapor concentration distribution within a fiber (see section 2.1), various sets of radius, length and feed speed were simulated with the commercial finite element CFD software Comsol.

A 2d-axisymmetric geometry was built with a length of 5 cm and 3 cm (for an uncorrected pressure drop of 100 Pa and 500 Pa respectively) that models the cross-section of a fiber. For the inlet condition a uniform inlet speed (plug flow) was fixed according to the above mentioned pressure drops. The outlet boundary conditions were set to atmospheric pressure without viscous stress and for the wall the no-slip condition was applied. The radius was varied in steps between 0.2 mm and 0.5 mm with a stepsize of 0.05 mm.

The mesh was built according to the built in physics controlled mesh (finer mesh sizes at inlet, outlet and wall) with the predefined element size: fine (see figure 2a). Refinement of the mesh has shown independence of the mesh size with these settings.

The mass-flow averaged pressure has been plotted in figure 2b. Each line represents a pressure change of 1 Pa and the pressure build up at the wall (bottom right) due to the no-slip condition and the uniform inlet velocity can be clearly seen.

The pressure drop calculated analytically according to equation 4 predict the results with an error of less than 4% as compared to the CFD simulations (see figure 2c). This outcome shows that the calculated pressure drop is in good agreement with the CFD results, and is precise enough to give good estimations of the work requirements to drive the feed flow.
2.2.2. The concentration distribution within a fiber

For the modelling of the concentration distribution within the fiber, an infinitely permeable membrane has been assumed in the CFD simulations. The velocity fields of the previous simulation (see section 2.2.1) have been used and superimposed with a diffusion process, where the concentrations at the inlet and the wall have been fixed according to the inlet and permeate concentration (see section 2.1.3).

2.3. The implementation of the membrane permeability

As a real membrane has a transport resistance, it is crucial that this permeability is also implemented in the model. This was achieved by converting the permeability properties of a membrane to a re-bounce probability for a simulation particle whenever its random movement should let it interact with the membrane. From the membrane permeability (usually given in the units of barrer which is (at atmospheric pressure, and 30°C) equal to $3.0122 \cdot 10^{-16} \text{mol} \cdot \text{m}^2 \cdot \text{s} \cdot \text{Pa}$) it can be seen that the mass flow through the membrane is dependent on the membrane area, the time and the pressure gradient. Each of the simulation particles represents a number of molecules within a volume element, and as such, a concentration that exerts a partial pressure. Therefore the number of molecules permeating within a certain interval time due to this pressure can be calculated. The decision whether the simulation particle is then taken out of the system or is reflected back, depends on the fraction of the number of molecules theoretically permeating, and the number of molecules one particle represents. This fraction makes up the probability that is employed to every particle hitting the wall.

Considering the relations between the concentration and the pressure gradient (depending on the gas constant $R$ and the absolute temperature $T = 303.15 \text{K}$, the first simulation step in which a number of $\nu_0$ particles hit the wall (that therefore represent the initial total pressure difference over the membrane), and the thickness of the membrane $\delta_{\text{memb}}$, it can be shown (see...
Appendix A) that this permeation probability can be calculated to be

$$ P = \frac{2N_0}{v_0} \frac{P R T \tau_{int}}{\delta_{memb} R} $$

for each particle hitting the wall. ($R$ still being the fiber radius, $N_0$ the number of simulation particles, and $P$ the initial partial pressure difference).

With the implementation of this probability factor a hollow fiber module can now be modeled that takes the decreasing partial pressure gradient along the fiber length into account, and allows for the estimation of the water vapor permeating per unit time and area.

3. Results and Discussion

The concentration distributions within a fiber and the difference between the simulations performed with the commercial CFD software and the random-walker approach can be seen in figure 3. Although the colorcoded images in figures 3a and 3b differ (due to the different flow profiles that have been assumed), figure 3c shows, that the resulting fraction of diffusing molecules seem to level out at about 20% overestimation. It can be clearly seen, that for lengths smaller than the entrance length- where the flow profile resembles more a plug flow than a parabolic profile- the agreement between the different simulation approaches is higher. For fully developed flow profiles at the outlet ($L_e \geq L$) the deviation gets larger, but seems to level out, and so the total error can be estimated to be within a range of 20%, which is an acceptable error for the estimation of a suitable working range.

Under this pretext an evaluation of the membrane permeability according to section 2.3 could be employed. As data could not be compared to the previous CFD simulations, the results were compared to a commercial membrane module that has a length of 0.3 m, an inner diameter of 0.7 µm and a total area of 0.47 m² (with 700 fibers). The manufacturer provides a performance
of approx 2500 GPU which is equivalent to \(8.6 \cdot 10^{-7} \text{mol/s Pa-m}^2\) (the flow speed at which this was measured is unknown to the author) and which is also in agreement with reported literature data [10]. In the above described simulations, varying applied pressure drops, and therefore different mean velocities results in membrane performances in the range of \(6.0 \cdot 10^{-8}\) to \(6.7 \cdot 10^{-6} \text{mol/s Pa m}^2\). This suggest that the simulations resemble real life circumstances, as the value of the module is within the range of the simulation outcome.

Although the exact membrane material and the thickness of the membrane is not known to the author, it can be estimated, that neither the permeability of the membrane will be much higher than the estimated permeability of 104000 barrer, nor will the thickness vary much. And as the simulations consider the feed side and membrane resistance to mass transport only and thus neglect the permeate side resistance (caused by the limited vapor transport away from the membrane) the total performance of the simulated membrane module is still expected to decrease, and therefore even give a better match with the commercial module.

Using not only the data for the 30 cm and the given diameter, but scanning over a wide range of values one can plot the energy requirement for the permeation of 1 ml of water vapor for each triplet of radius, fiber length and applied pressure drop to drive the feed flow (see figure 4). It can be seen that the work requirement to drive the feed flow for the permeation of 1 ml of water vapor is mostly dependent on the pressure drop as driving force (only low range of energy requirement shown here), but also is more favorable for smaller radii (due to shorter entrance lengths, and therefore less pressure loss). Although the work load here does not seem to depend so much on the variation of length, one has to consider that in this operational window most of the vapor has permeated after the first centimetres already, which means the extra length would not be a gain in vapor permeation any more.

This data also allows for the calculation of the total energy requirement. If one assumes a COP (Coefficient of performance) of 5, and considers the energy demand for the condensation process as well as the feed flow one can calculate the total energy requirement for the production of 1 ml of water. For comparison: the energy requirements for the conventional condensation of 1 ml of water out of an air package with 30°C at a relative humidity of 50% cooled down to 4°C are estimated to be 1.2 kJ/ml. For the lowest energy demands the estimated work requirements are less than 50% of the work requirement of an AWVP system without a membrane unit.

4. Conclusion

The random walker approach to the simulation of the water vapor transport through a hollow fiber module shows results that are in good agreement with commercial CFD software and a real life module. The simulation outcome can therefore be used to find the ideal working conditions for a membrane module that can be installed into an atmospheric water vapor processing system.
Furthermore it could be shown, that the energy demand for the water production could be reduced by more than 50% when using the optimal working window, making AWVP systems more energy efficient and therefore also more attractive as a source of fresh and clean drinking water.

Acknowledgments
This work was performed in the TTIW-cooperation framework of Wetsus, centre of excellence for sustainable water technology (www.wetsus.nl). Wetsus is funded by the Dutch Ministry of Economic Affairs, the European Union Regional Development Fund, the Province of Frysln the City of Leeuwarden and the EZ/Kompas program of the Samenwerkingsverband Noord-Nederland. The authors like to thank the participants of the research theme for the fruitful discussions and their financial support.

Appendix A. Permeation probability

One simulation particle $\alpha_i$ stands for

$$\alpha_i = \frac{\Delta c_0 \Delta V}{N_0} \text{[mol]}$$

(A.1)

moles with $\Delta c_0$ the concentration difference between the feed and the permeate side, and $\Delta V$ the volume element of the cross section of the fiber and the distance a particle travels in an simulation time interval ($\Delta z$).

If in the first simulation step $\nu_0$ particles hit the wall, this means that this represents the initial partial pressure difference $\Delta p_0$. Therefore, in any simulation step, one particle hitting the wall means that the membrane sees a partial pressure difference of

$$\Delta p_i = \frac{\Delta p_0}{\nu_0} \text{[Pa]}$$

(A.2)

Knowing the membrane permeability ($P$) and thickness ($\delta_{memb}$), a partial pressure difference of $\Delta p_i$ causes a flux according to $J_i = \frac{P \delta_{memb}}{\nu_0} t \frac{\Delta p_0}{\nu_0} \Delta z$ [mol]

(A.3)

$$\Delta \alpha_i = J_i t \frac{2 R \pi \Delta z}{\nu_0} = \frac{P \delta_{memb}}{\nu_0} \frac{\Delta p_0}{\nu_0} \frac{t}{\nu_0} \frac{2 R \pi \Delta z}{\nu_0}$$

(A.4)

The chance ($P$) that a simulation particle permeates when it hits the membrane, is therefore given by the mass transport that occurs if one particle hits the wall ($\Delta \alpha_i$) and the number of moles one particle represents ($\alpha_i$). Using the ideal gas law ($\Delta p = \Delta c R T$) (R...gas constant; T...abs. Temperature) and substituting for the volume element one gets:

$$P = \frac{\Delta \alpha_i}{\alpha_i} = \frac{\Delta p_0}{\nu_0} \frac{t \frac{2 R \pi \Delta z}{\nu_0}}{\frac{\Delta c_0 \Delta V}{N_0}} = \frac{2 N_0 P \frac{\pi}{\nu_0} \frac{t \frac{t_{int}}{1}}{\delta_{memb} \frac{R}{\nu_0}}}$$

(A.4)

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