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# A non-invasive study of flow dynamics in membrane distillation hollow fibre modules using low-field nuclear magnetic resonance imaging (MRI)

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## Abstract

Low-field bench-top nuclear magnetic resonance imaging (MRI) has been applied to investigate the hydrodynamics in novel hollow fibre modules with four different configurations of randomly-packed, spacer-knitted, curly and semi-curly fibres, specifically designed for the membrane distillation (MD) process. Imaging, spatially resolved velocity maps and propagators (probability distributions of displacement/velocity) were all acquired in the modules with flow in the shell side. The MRI data were correlated with overall module performance.

The results have revealed that the curly configuration exhibited more significant transverse flow and hence enhanced mixing, compared to the randomly packed configuration; this was consistent with an enhanced MD performance in terms of permeation flux. Interestingly, the velocity maps of the spacer-knitted fibre design indicated a significant flow channeling in the centre of the module, despite its enhanced MD performance. Fortunately, combined with further investigations on the localized velocity images of this configuration, the acquisition of propagators provided valuable information in revealing the existence of reduced stagnant regions and significant transverse flow at varied operating conditions, which indicated a better overall mixing and hence confirmed its module performance.



**Keywords:** *hollow fibres module, membrane distillation, magnetic resonance imaging, hydrodynamics, propagators*

## 1. Introduction

As an alternative for seawater desalination, membrane distillation (MD) is a promising technique credited with several advantages: low sensitivity to salt concentration and theoretically 100% salt rejection; feasibility to utilize low-grade heat and renewable energy (*e.g.*, waste heat or solar power); low vulnerability to membrane fouling and good performance under mild operating conditions as compared to conventional, multi-stage distillation or reverse osmosis (RO) [1]. Despite many attractive characteristics and extensive lab-scale studies, MD has not been widely implemented in industry due to several major challenges [1, 2]: the development of highly-permeable and anti-wetting membranes [1, 3-7]; design of commercial MD modules with good hydrodynamics, even flow distribution and significantly less local temperature polarization [8-10]; and establishment of reliable energy assessment and heat recovery systems [11-16].

As a preferable configuration for industrial applications, hollow fibre modules present more versatility, larger membrane area per unit volume, reduced vulnerability to temperature polarization [17] and enhanced productivity. Nevertheless, many prior studies on general hollow fibre modules have shown that non-ideal flow distribution could lead to less active membrane area, insufficient mixing and local loss of driving force, and hence low heat-or mass-transfer efficiencies [18-25]. As summarized in a recent review [25], novel design concepts achieving even cross-flow distribution were widely applied for commercial hollow fibre modules as liquid-liquid/liquid-gas membrane contactors (*e.g.*, Celgard Liqui-Cel$^{TM}$ modules [20, 26, 27]). However, investigations on hydrodynamic improvements in MD hollow fibre modules are sparse in the open literature mainly due to fabrication and modeling complications [2, 28-35]. Enhancing strategies such as flow alteration aids or modifying fibre layout to create secondary flows or eddies (such as cross-flow design or turbulence promoters, *e.g.* spacers or baffles) have been proposed for improving MD module performance experimentally [7, 30, 31, 36, 37]. In the MD process employing shell-side feed, the occurrence of significant channeling, bypassing, or dead zones can greatly reduce the local driving force and decrease module performance. Prior studies on hollow fibre module design showed that the fluid flow across the fibre bundles needs to be evenly distributed in order to achieve an effective mitigation of temperature polarization and improvement of the MD process efficiency [7, 18, 38-40]. For a direct understanding of the fluid dynamics fundamentals, in particular the uniformity of flow, physical inspection of the module inner structures/fibre arrangement and flow distribution is essential in providing valuable insights for future optimum module design work.

Traditionally, there are many approaches for characterizing flow distribution [41]: broadly these are invasive or non-invasive. Invasive or quasi-invasive techniques include structural inspection by disassembling the module parts [42], tracer analysis [43], combined X-ray computed tomography (CT) scanner and radio-opaque tracer dye study and/or high-speed tracer photography [44-46]. However, to achieve in-situ real-time monitoring of the flow field inside a confined opaque vessel, non-invasive techniques are preferred. However, optical methods as one of the non-invasive techniques are restricted to special conditions such as transparent membranes [47] or fluorescent tracers. Nuclear magnetic resonance (NMR) has various advantages including being non-invasive, the absence of ionizing radiations, freedom to image any selected plane through a complex sample (or generate a 3-dimensional image of the sample as a whole) and the ability to image non-metallic samples which are optically opaque [48], which is an ideal feature for the MD modules composed of opaque plastics.

NMR involves the excitation and relaxation of various nuclei under the influence of a magnetic field [49]. The signal strength depends on the number of spins in a sample and depends on the gyromagnetic ratio of the nuclei. In general, the proton ($^1$H nucleus) is considered as the most prevailing and hence the targeting nuclei in NMR signal detection, which originates predominately from the water content of our modules. The signal strength is proportional to $^1$H density modulated by various signal relaxation processes. The application of magnetic field gradients allows both imaging and displacement (self-diffusion and velocity) measurement. These can be combined to deliver velocity maps, in which velocity is measured for each pixel in the image [50-54]; alternatively spatially unresolved probability distributions of displacement (readily converted to velocity) can be measured, these are known as propagators [44, 45, 48, 55-58].

Early module studies used NMR flow imaging to elucidate flow distribution in inorganic tubular configurations by mapping the axial flow velocities and verifying with theoretical modeling results [59, 60]. Membrane bioreactor researchers also explored the capability of NMR imaging technique for observing Starling flows in the shell side of hollow fibre modules [61, 62]. Studies using both structural and velocity imaging for flow analysis have been conducted in both hollow fibre [63] as well as spiral wound membrane modules [64, 65]. Applications of MRI to hemodialyzer modules containing thousands of fibres revealed significant flow mal-distribution despite the presence of turbulence promoters [66-68].

Despite its clear advantages and ability to inform module development, the use of MRI in such a capacity is limited. This is undoubtedly due to geometric constraints on the modules as well as comparatively poor signal relative to other metrology techniques. Moreover, all above-mentioned studies have adopted super-conductive magnet, high-field NMR techniques with $^1$H resonance frequencies up to 600 MHz. This is understandable given the greater signal-to-noise ratio (SNR) available; SNR $\propto(B_0)^{7/4}$, where $B_0$ is the magnetic field strength. However, these systems are expensive, consequently limited in availability, immobile and generally require expert operators. Thus far, low-field bench-top NMR/MRI systems (< 50 MHz) have rarely been adopted for flow investigations and imaging, not to mention MD related studies. Although restricted by low SNR characteristics and hence limited spatial resolution (or large voxel size) for imaging purpose due to time constraints, low field NMR apparatuses are capable of performing non-spatially resolved NMR displacement experiments to obtain flow-field statistics [44, 45, 48, 55-58]. Moreover, with simpler operational procedures, easier maintenance, significantly lower cost and smaller footprint, low-field NMR/MRI systems are both more accessible to a broader range of scientists/engineers as well as showing much greater potential for industrial application.

Therefore, in the current study we employ a bench-top NMR spectrometer featuring a 0.3 T permanent magnet (corresponding to a $^{1}H$ resonance frequency of 12.7 MHz) and 3D magnetic field gradients for imaging and motion measurements. Using this apparatus, we measure the flow field with a focus on the homogeneity in four MD hollow fibre module designs (*i.e.,* conventional randomly-packed, spacer-knitted, semi-curly and curly fibre modules [18]). Combined with 2D structural and velocity images, the displacement/velocity propagators, which are significantly less influenced by signal-to-noise ratio (SNR), are acquired and correlated against membrane performance and the interplay of hydrodynamics for the first time in the literature. The compromise involved in applying this bench-top apparatus compared to a high-field super-conducting system is also briefly discussed.

## 2. Experimental protocol

### *2.1 Hollow fibre module preparation and MD performance tests*

In this study Polyvinylidenefluoride (PVDF) hollow fibre membranes developed by a commercial supplier [36], with outer and inner diameters of 1.45 – 1.50 and 0.97 –1.03 mm, respectively, were used to fabricate lab-scale multi-fibre MD modules. A brief summary of membrane and module specifications are listed in Table 1. The detailed measurements of the PVDF membrane characteristics (*i.e.,* wall thickness, porosity, and pore size/pore size distribution, etc) can be found in the literature [36]. During module fabrication, the fibres were potted into the housings made from transparent Acrylic material to facilitate direct surface observation of the fibre bundles, as shown in Fig. 1. Four different module configurations (Fig. 1) were assembled in various ways, *i.e.*, modules with 51 randomly-packed, spacer-knitted, curly and semi-curly (mixture of straight and curly) fibres, with a module inner diameter 19 mm and effective length 450 mm; packing density of 30%; and membrane area of 0.1−0.11 $m^2$. The randomly packed module was used as the conventional module benchmark. Besides the semi-curly fibre configuration, which is considered as a compromise design to reduce the fabrication complexity, the assembly procedures for modules of different patterns can be found in our previous work [18]. In the module fabrication process, care must be taken to avoid damaging the membrane surface.

The membrane distillation (MD) performance for all hollow fibre modules was evaluated in terms of attainable flux using the experimental setup (DCMD system) shown previously [18], in which the feed temperature was varied while holding the permeate temperature and other operating conditions constant; All the experiments were conducted using the DCMD system and synthetic seawater (3.5 wt % sodium chloride solution) as feed. Both the feed and permeate solutions were cycled through the hollow fibre module in countercurrent mode. On the shell side, the feed solution (synthetic seawater: conductivity around 60 $ms\cdot cm^{-1}$), was heated (in the range 313K – 343K) and circulated by a peristaltic pump (0 – 12 $L\cdot min^{-1}$). On the lumen side, the permeate (Deionized (DI) water with conductivity around 0.5 $\mu s\cdot cm^{-1}$) was cooled down to 298K by a cooling circulator and cycled by another peristaltic pump (0 – 4 $L\cdot min^{-1}$). The distillate was collected in an overflow tank sitting on a balance (± 0.1 g).

*2.2 NMR experimental protocol*

The NMR experiments were conducted using an Oxford MARAN low-field bench-top MRI system employing a 0.3 Tesla permanent magnet with a ($^{1}H$) resonance frequency of 12.7 MHz. The system features a sample access of 53 mm in diameter, any practical length and accommodates 3D magnetic field gradients for spatial encoding. The experimental setup for flowing experiments through the shell side of the multi-fibre membrane modules is shown in Fig. 2.

In this experiment each membrane module was installed and tested individually in the 5.3-cm i.d. resonator RF probe. De-ionized water (DI) was used as the flowing fluid and circulated through the shell side of the module using a peristaltic pump, which was calibrated using NMR velocity imaging of water in an equivalent pipe. The imaging planes were chosen as both parallel- and perpendicular-to-flow directions, *i.e.*, module's axial Y and transverse Z directions, respectively, allowing the cross section and side view of a module to be analyzed. Conventional MRI pulse sequences were used to acquire images, velocity images/maps and propagators [57]. 2D Images were acquired over a field of view of 30 mm × 30 mm employing 256 pixels in each dimension (in-plane resolution of 117 μm) and a slice thickness of 5 cm. In terms of velocity encoding, magnetic field gradient strength was varied in 128 increments for propagator acquisition ($g_{max}$ = 64 mT·m$^{-1}$, $\delta$ = 4 ms, $\Delta$ = 100 ms) whilst the strength employed for velocity imaging was varied depending on the velocity to avoid signal phase fold-over ($\delta$= 4 ms, $\Delta$ = 20 ms). Total acquisition times of propagators, 2D images and 2D velocity maps were 34, 54 and 68 minutes respectively.

*2.3 Flow calibration and error assessment*

All experiments were repeated to check reproducibility. The flow rate of the pump was calibrated using NMR velocity imaging and volumetric throughput measurements of water, which showed excellent agreement (error within ±5%). In the MD performance experiments, the results for the water-flux fluctuations were also within ±5% (illustrated as error bars in the figures). The temperature and flow rate variations were strictly controlled within ±0.2°C and ± 10 $mL\cdot min^{-1}$.

## 3. Theoretical basis for NMR signal analysis

NMR signal is caused by the interaction of the nuclear spin (or quantized angular momentum) of a nuclei (*e.g.*, $^1H$ in this paper) with an external static magnetic field ($B_0$), causing spin resonance at the Larmor frequency ($\omega_0$). The basic principle of MRI (and displacement measurements) is to spatially encode the spins by superposition of constant magnetic field gradient applied across the sample, *G*, onto a static magnetic field [57]. In the case of displacement measurements, the consequential change in phase ($\varphi$) of the NMR signal is proportional to the spin displacement ($\mathbf{r}'(t)$) according to:

$$\frac{d\varphi}{dt} = \gamma G \mathbf{r}'(t) \tag{1}$$

where $\gamma$ is the gyromagnetic ratio of the nuclei (*e.g.*, $^1H$).

Pulsed Field Gradient (PFG) NMR techniques [57], via appropriate application of Eq. (1), can be used to measure distribution of NMR signal phase and hence the probability distribution of displacement (*i.e.*, propagator). The propagator ($\overline{P}(R, \Delta)$) is defined as the probability distribution of (in our case water) molecules being displaced (by both advection and diffusion) a distance *R* over a time interval Δ (*e.g.*, starting at *t*=0 and location *r* and propagating to *r*+*R* after time *t*=*Δ*).

As an inverse Fourier transform of the acquired PFG NMR signal, the averaged propagator $\overline{P}$ is given as:

$$\overline{P}(R,\Delta) = \int_V P(r|r+R,\Delta)\, p_0(r)\, dr \qquad (2)$$

where $p_0(r)$ is the initial signal probability distribution as a function of initial position *r*.

For a given time interval, *Δ*, useful comparative statistics regards propagators focus on the moments of the propagator:

$$\mu_n = \left\langle (x-\mu)^n \right\rangle = \int_{-\infty}^{\infty} (x-\mu)^n P(x)\, dx \qquad (3)$$

where $\mu_n$ is the n$^{th}$ central moment, $\mu_1$ is the first raw moment (*i.e.* mean), *P(x)* is the normalized probability distribution as function of displacement (*x*) in one direction defined by the applied gradient. The second central moment, $\mu_2$, (directly related to the variance, $\sigma^2$, or standard deviation, $\sigma$, of displacement) is used to quantify the uniformity of flow, and the spread of the residence time distribution (RTD). Its magnitude generally scales with increasing heterogeneity corresponding to wider distributions (*e.g.* long break-through tails).

## 4. Results and discussion

*4.1 Water molecule contrast NMR imaging*

To acquire a direct display of the fibre arrangements, 2D images of the different designs (*i.e.*, randomly packed, spacer-knitted, semicurly- and curly-fibre modules) filled with stationary DI water were acquired transverse and parallel to the module axis. These are presented in Fig. 3. The thickness of the excited slice is 5 cm. With the signal originating from the water content on the shell side of the module, the fibre matrix is revealed. Well-defined fibres in the transverse plane are aligned perpendicular to the slice direction; as expected these are most prominent in the randomly-packed module (Fig. 3a) and least prominent in the curly-fibre design (Fig. 3d). From the axial direction images (side-view), undulating flow paths are most obvious in the curly-fibre module (Fig. 3d) and partially evident in the semicurly-fibre modules (Fig. 3c), consistent with its compromised pattern between the randomly-packed and curly-fibre designs.

*4.2 MD performance of various module designs*

Fig. 4 shows a comparison of module performance for four designs in terms of the effect of feed temperature on the water permeation flux, at feed and permeate flow rates of $Q_f$ = 3 L·min$^{-1}$ and $Q_p$ = 0.4 L·min$^{-1}$, respectively. It is noted that apart from the semi-curly fibre configuration, the performance results for other modules of different patterns can be found in our previous work [36]. Undoubtedly, the permeation fluxes of all MD modules follow a classical exponential increase with increasing feed temperature based on the

Antoine equation [69]. Compared to the randomly-packed module, significant flux enhancement is achieved by the modified configurations. The highest improvement of up to 92 % is observed by the modules with extensive undulating membrane surface (curly fibres and spacer-knitted) at a feed temperature of 343 K. Intermediate behavior is observed for the semi-curly membrane design. As discussed in our previous MD studies [36], the heat-transfer process could be enhanced by modifying the flow channel and/or increasing the velocity to reduce the thermal boundary layer on the membrane surface. *i.e.,* when the temperature at the membrane surface approaches the temperature in the bulk permeate, the driving force for vapor transport through the membrane can be maximized. Therefore, the modules with undulating membrane surface (in particular the curly and spacer-knitted fibres) show advantages by achieving higher vapor permeability and mitigating the temperature polarization effect with reasonably lower energy losses; this is mainly due to the improved shell-side hydrodynamics induced by altered fibre geometries and relatively uniform shell-side flow distribution – these are now explored and quantified using NMR techniques.

*4.3 NMR velocity mapping and flow distribution analysis*

The velocity maps in a transverse slice (for velocity in the superficial flow direction) are shown in Fig. 5 for the four module designs over a slice thickness of 5 cm at a flow rate of 100 $mL \cdot min^{-1}$ over an observation time $\Delta$ of 100 ms. What is immediately obvious is the loss of signal from the centre of the spacer-knitted design – this is a rapid flowing fibre-free channel causing signal loss, and will be discussed further in section 4.5. All other three designs present mean velocities consistent with gravimetric measurements to within 5%. Visually it appears that the most homogeneous flow-field is evident for the semi-curly-fibre design, followed by the curly-fibre and then the randomly packed modules. This is consistent with quantitative standard deviations (σ) calculated for the spatial velocity distributions in Fig. 5: semi-curly fibre – 3.9 $mm \cdot s^{-1}$; curly-fibre – 7.7 $mm \cdot s^{-1}$ and random packing – 8.2 $mm \cdot s^{-1}$. Excessive channeling of the flow is only observed in the spacer-knitted design.

*4.4 Propagator Analysis*

In general, propagators can be more rapidly acquired compared to the velocity images. Unlike the acquisition of imaging information only over a limited slice thickness, displacement probability provides sufficient and accurate statistics at molecular level and interprets NMR signal over the entire detected zone of the module [44, 45, 48, 55-58]. The velocity images (Fig. 5) and their statistics represent only a portion (5 cm slice) of the module volume. To access the mixing intensity and fluid dynamics induced by different designed channels, propagators were measured parallel (Y) and perpendicular (Z) to the superficial flow directions with flowing fluid (DI water) at 100 $mL \cdot min^{-1}$ for an observation time (Δ) of 100 ms; these are presented in Fig. 6 (a) and (b) respectively (converted from displacement probability distributions to velocity distributions by simply dividing by Δ).

In general, the Y-direction (superficial flow direction) propagators (Fig. 6a) present an asymmetric distribution with the greatest probability of finding water molecules around zero velocity, indicative of stagnant fluid. It is evident that the spacer-knitted module shows reduced holdup and comparatively better hydrodynamics with a lower distribution curve; while the three other designs present similar results. In the transverse Z direction (Fig. 6b), the greatest probability is for zero velocity, which is consistent with the minimal transverse flow and significant stagnant zones as evidenced in Fig 6a. The greatest transverse flow is observed for the curly-fibre design, corroborated with the undulating configuration and its intention of promoting mixing. Broadly, the propagator measurements serve to be a useful insight into the internal hydrodynamics and hence mixing in the modules.

For a quantitative analysis of these displacement propagators for the 4 membrane designs, moments (mean displacement $<x>$, mm, and variance $\sigma^2$, $mm^2$) are determined using Eq. 3 and are reported in Table 2. With respect to the mean displacement, the expected mean displacement ($<x>$) value of 0.71 mm is measured for the curly, semi-curly and random designs (within experimental error); while the spacer-knitted design has an $<x>$ of 5% smaller. This minor reduction is a consequence of the partial loss of signal in the centre of this module design (as discussed above for Figure 5(b)). However, the effect is significantly reduced in the case of the propagator acquisition relative to the corresponding velocity image at the exact same flow conditions, due to a reduced NMR echo time for the propagators, as no imaging gradients are required.

Turning to the variance, ideal module behavior would constitute a single consistent speed (not velocity given in the tortuous flow paths) for the water flow through the module shell, which would correspond to a reduced value of variance for displacement. With respect to the Y (superficial flow) direction propagators, the variance for all four module designs is broadly equivalent varying by at most 20% from the average. Nevertheless, it is again noted that there is an obvious reduced hold-up (proportion of velocity around zero velocity) for the spacer-knitted design, which is inconsistent with its superior MD performance results (Fig. 4). In general, the magnitude of the variance in the Z (transverse) propagator indicates greater flow in this direction. In Table 2, the variance increases significantly (in excess of 100%) from the random design to the semi-curly design to the curly design; indicating more intense transverse flow and mirroring their relative MD performance (Fig 4) — implying the existence of fast flowing fluid facilitated by undulating paths and subsequent secondary flows. The data supports the conjecture that module design resulting in enhanced transverse flow improves mixing and hence enhances module performance. However, the spacer-knitted design shows contradictory results. Thus, we proceed to explore this design more thoroughly in the next section.

*4.5 NMR flow analysis for spacer-knitted module*

To further elucidate the hydrodynamics of the shell side of the spacer-knitted module, the relationship between the NMR signal detection and operating flow conditions were investigated. Fig. 7 presents a series of cross-sectional images for the spacer-knitted configuration by applying a gradual increase on the shell-side volumetric flow rates from 10 to 2500 $mL\cdot min^{-1}$ (*i.e.,* 0.017 to 41.7 $mL\cdot s^{-1}$), with a selected slice thickness of 5 cm and an echo time of 29.5 ms, which is similar to that employed in the velocity images. Similar to what was observed in Fig. 5 (b), a region of signal loss appears in the center of the module when the flow rate increases to 40 $mL\cdot min^{-1}$, and drastically enlarges with further increasing flow velocity till an almost complete loss of signal at 2500 $mL\cdot min^{-1}$. This phenomenon is consistent with comparatively rapid, channeled flow in this central region, which increases with externally-applied flow rates.

Signal loss occurs due to ‘dispersion’ effects [70] in these fast flow channels coupled with the comparatively poor, inherent signal-to-noise (~10:1) for these images along with the relatively long echo time over which signal loss can occur. Fig. 8 presents a plot of NMR signal magnitude (slice averaged) as a function of volumetric flow rate in the shell side of the spacer-knitted module, as extracted from Fig. 7. The initial sharp decrease corresponds to loss of signal (*e.g.,* occurrence of signal “black-out” from 40 mL/min onwards) from the fast-flowing central channel. The subsequent more gradual decrease corresponds to loss of signal from within the surrounding spacer-knitted bundle itself. This almost complete loss of MRI signal from the bundle at much higher flowrate (*i.e.,* > 1 L/min, matching the operating conditions in MD performance tests in [36]) indicates that virtually no static dead-zone regions are present, as these would continue to present NMR signal, consistent with the enhanced performance of this module shown in Fig. 4. Moreover, combined with the DCMD performance investigations in previous work [36], the effect of recirculated feed velocity over a range of 1-5.6 L/min (corresponding to feed-side Reynolds number of $Re_f$~500-2700) showed that the permeation flux of the spacer-knitted module was insensitive to the variation of flow conditions from extremely low $Re_f$ (laminar condition, e.g., $Re_f < 500$) to turbulent conditions ($Re_f > 2000$). This was mainly due to much higher mixing intensity induced by the vibration of spacer-knitted fibre arrangement, compared to a randomly-packed configuration.

A rich depth of hydrodynamic information is available via propagator measurements and analysis. For example, Figs. 9 (a) and (b) present the displacement propagators for spacer-knitted module as a function of an increasing volumetric flow rate from 20 to 400 $mL \cdot min^{-1}$ in the shell side of the module. Higher flowrates resulted in erroneous signal loss (> 10%) in the acquired propagators due to the 'dispersion' effects, as noted in Fig. 5 (b). As the flowrate increases, there is an obvious velocity tail extension in Fig 9 (a) in the superficial flow (Y) direction and a reduction in apparently immobile fluid centered on zero velocity. This is an indication of more intensive flow interaction taking place induced by the combination of faster externally-applied flow condition and internally-altered flow channel. In the transverse (Z) direction (Fig. 9 b), the probability distribution curve lowers and widens as the applied volumetric flow rate increases, but retains its general shape. This is very encouraging signal for expecting a strong transversal mixing and a subsequent improvement on the overall flow distribution.

## 5. Conclusions

With the aid of nuclear magnetic resonance imaging (MRI) technique, further insight was acquired into the internal flow hydrodynamics of various fibre configurations in novel hollow-fibre modules for membrane distillation (MD) applications. The pulse field gradient (PFG) experimental technique was used to acquire the spatial information of molecular displacement in the various flow channels. Specifically the internal structure of the shell-side fluid was imaged, cross-sectional 2D velocity images and probability distributions of displacement (propagators) were investigated.

Compared to the conventional randomly-packed module, the curly-fibre module designs were shown to promote transverse flow and correlated with improved MD performance. However, as a well-performed configuration testified via MD water flux experiments, an enhanced reduction in stagnant zones in a spacer-knitted module construction was speculated to be responsible for its superior measured MD performance (permeation flux). This was a surprising result given the very obvious flow channel established in the centre of this module, which would be expected to degrade performance. Clearly, the transverse flow between the channel and the surrounding ‘knitted’ zones (which featured comparatively less stagnant fluid) was sufficient to overcome this limitation.

Of significant importance, this study has demonstrated the capability of a low-field (0.3 T permanent magnet) bench-top NMR instrument to analyze the fluid dynamics non-invasively. Compared to typical super-conducting NMR systems (> 4.7 T), this obviously presents significantly poorer signal-to-noise ratios (SNR) and imaging quality. However, the system is cheaper, more mobile and hence more accessible. Our data indicated that the best insight into the interplay of hydrodynamics and module performance is obtained from propagators, which were significantly less influenced by SNR. In particular, more rapid NMR methods could be employed to measure targeting moments [71] and acquire full propagators [72] of the flow. Future work will focus on implementing these more rapid methods on the low field NMR instruments for faster and non-invasive screening of module designs via propagator acquisitions, especially for scale-up modules, which would be prohibitively expensive to access at high fields.

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## Nomenclature

| | |
|---|---|
| $A$ | Effective membrane area, $m^2$ |
| $B_0$ | External magnetic field, Tesla |
| $d_o$ | Outer diameter of the hollow fibre, mm |
| $d_s$ | Inner diameter of the hollow fibre, mm |
| $g_{\max}$ | Maximum magnetic field gradient, $mT \cdot m^{-1}$ |
| $G$ | Constant magnetic field gradient applied across the sample, $mT \cdot m^{-1}$ |
| $N$ | Vapor flux,$kg \cdot m^{-2} \cdot h^{-1}$ |
| $p_0(r)$ | Initial signal probability distribution as a function of initial position $r$ |
| $\bar{P}$ | Averaged propagator |
| $r$ | Nuclei spin location/position, mm |
| $T_f$ | Bulk temperature of the feed, K |
| $T_p$ | Bulk temperature of the permeate, K |
| $t$ | Time, s |
| $v_f$ | Recirculated feed velocity, $m \cdot s^{-1}$ |
| $v_p$ | Recirculated permeate velocity, $m \cdot s^{-1}$ |

*Greek letters*

| | |
|---|---|
| $\varepsilon$ | Membrane porosity, % |
| $\phi$ | Phase change of NMR signal |

| | |
|---|---|
| $\sigma^2$ | Variance, $mm^2$ |
| $\omega_0$ | Larmor frequency, Hz |
| $\delta$ | Gradient pulse interval, ms |
| $\Delta$ | Observation time for propagator acquisition, ms |
| $\gamma$ | Gyromagnetic ratio of the nuclei (*e.g.* $^1$H) |
| $\mu$ | Central moment of probability distributions of displacement in NMR signal analysis |

*Subscripts*

| | |
|---|---|
| $f$ | Feed |
| $p$ | Permeate |

## References


[1] K. W. Lawson and D. R. Lloyd, Membrane distillation, J. Membr. Sci., 124 (1) (1997) 1-25

[2] M. S. El-Bourawi, Z. Ding, R. Ma and M. Khayet, A framework for better understanding membrane distillation separation process, J. Membr. Sci., 285 (1-2) (2006) 4-29

[3] P. Wang, M. M. Teoh and T.-S. Chung, Morphological architecture of dual-layer hollow fiber for membrane distillation with higher desalination performance, Water Research, 45 (17) (2011) 5489-5500

[4] M. Khayet, T. Matsuura, J. I. Mengual and M. Qtaishat, Design of novel direct contact membrane distillation membranes, Desalination, 192 (1-3) (2006) 105-111

[5] Y. Liao, R. Wang, M. Tian, C. Qiu and A. G. Fane, Fabrication of polyvinylidene fluoride (PVDF) nanofiber membranes by electro-spinning for direct contact membrane distillation, Journal of Membrane Science, 425–426 (2013) 30-39

[6] Y. Liao, R. Wang and A. G. Fane, Engineering superhydrophobic surface on poly(vinylidene fluoride) nanofiber membranes for direct contact membrane distillation, Journal of Membrane Science, 440 (2013) 77-87

[7] L. Song, B. Li, K.K. Sirkar and J. L. Gilron, Direct contact membrane distillation-based desalination: novel membranes, devices, larger-scale studies, and a model, Industrial & Engineering Chemistry Research, 46 (2007) 2307-2323

[8] R. W. Schofield, A. G. Fane and C. J. D. Fell, The efficient use of energy in membrane distillation, Desalination, 64 (1987) 231-243

[9] G. Zuo, R. Wang, R. Field and A. G. Fane, Energy efficiency evaluation and economic analyses of direct contact membrane distillation system using Aspen Plus, Desalination, 283 (2011) 237-244

[10] G. Guan, R. Wang, F. Wicaksana, X. Yang and A. G. Fane, Analysis of membrane distillation crystallization system for high salinity brine treatment with zero discharge using Aspen flowsheet simulation, Ind. Chem. Eng. Res., 51 (2012) 13405-13413

[11] M. Gander, B. Jefferson and S. Judd, Aerobic MBRs for domestic wastewater treatment: a review with cost considerations, Sep. Purif. Technol., 18 (2) (2000) 119

[12] M. Khayet, M.P. Godino and J.I. Mengual, Possibility of nuclear desalination through various membrane distillation configurations: a comparative study, International Journal of Nuclear Desalination, 1 (1) (2003) 30-46

[13]A. Zhu, P. D. Christofides and Y. Cohen, Minimization of energy consumption for a two-pass membrane desalination: effect of energy recovery, membrane rejection and retentate recycling, J. Membr. Sci., 339 (1-2) (2009) 126-137

[14]C. Cabassud and D. Wirth, Membrane distillation for water desalination: how to chose an appropriate membrane?, Desalination, 157 (1-3) (2003) 307-314

[15]H. Susanto, Towards practical implementations of membrane distillation, Chem. Eng. Process., 50 (2011) 139-150

[16]H. Lee, F. He, L. Song, J. Gilron and K. K. Sirkar, Desalination with a Cascade of Cross-Flow Hollow Fiber Membrane Distillation Devices Integrated with a Heat Exchanger, AIChE Journal, 57 (7) (2011) 1780-1795

[17]R. W. Schofield, A. G. Fane and C. J. Fell, Heat and mass transfer in membrane distillation, J. Membr. Sci., (33) (1987) 299-313

[18]X. Yang, R. Wang and A. G. Fane, Novel designs for improving the performance of hollow fiber membrane distillation modules, Journal of Membrane Science, 384 (1-2) (2011) 52-62

[19]I. Noda, D. G. Brown-West and C. C. Gryte, Effect of flow maldistribution on hollow fibre dialysis-experimental studies, J. Membr. Sci., 5 (1979) 209

[20]R. Prasad and K. K. Sirkar, Dispersion-free solvent extraction with microporous hollow-fiber modules, AIChE J., 34 (2) (1988) 177

[21]M. J. Costello, A. G. Fane, P. A. Hogan and R. W. Schofield, The effect of shell side hydrodynamics on the performance of axial flowhollowfibre modules, J. Membr. Sci., 80 (1993) 1-11

[22]J. Lemanski and G. G. Lipscomb, Effect of shell-side flows on hollow fiber membrane device performance, AIChE J., 41 (1995) 2322-2326

[23]J. Wu and V. Chen, Shell-side mass transfer performance of randomly packed hollow fiber modules, J. Membr. Sci., 172 (2000) 59

[24]J. Zheng, Y. Xu and Z. K. Xu, Flow distribution in a randomly packed hollow fiber membrane module, J. Membr. Sci., 211 (2003) 263-269

[25]X. Yang, R. Wang, A. G. Fane, Chuyang Y.Tang and I. G. Wenten, Membrane module design and dynamic shear-induced techniques to enhance liquid separation by hollow fiber modules: a review, Desalination and Water Treatment, 51 (16-18) (2013) 3604-3627

[26]R. Prasad and K. K. Sirkar, Hollow fiber solvent extraction: performances and design, Journal of Membrane Science, 50 (1990) 153-175

[27]W. S. W. Ho and K. K. Sirkar, Membrane Handbook, Van Nostrand Reinhold, 1992

[28]Z. Ding, L. Liu and R. Ma, Study on the effect of flow maldistribution on the performance of the hollow fiber modules used in membrane distillation, J. Membr. Sci., 215 (2003) 11-23

[29]L. Cheng, P. Wu and J. Chen, Modeling and optimization of hollow fiber DCMD module for desalination, J. Membr. Sci., (318) (2008) 154–166

[30]M. M. Teoh, S. Bonyadi and T.-S. Chung, Investigation of different hollow fiber module designs for flux enhancement in the membrane distillation process, J. Membr. Sci., 311 (1-2) (2008) 371-379

[31]R. Schneider, W. Hölz, R. Wollbeck and S. Ripperger, Membranes and modules for transmembrane distillation, J. Membr. Sci., 39 (1) (1988) 25-42

[32]H. Yu, X. Yang, R. Wang and A. G. Fane, Analysis of heat and mass transfer by CFD for performance enhancement in direct contact membrane distillation, Journal of Membrane Science, 405- 406 (2012) 38- 47

[33]X. Yang, H. Yu, R. Wang and A. G. Fane, Analysis on the effect of turbulence promoters in hollow fiber membrane distillation module via computational fluid dynamic (CFD) simulations, Journal of Membrane Science, submitted (2012)

[34]X. Yang, H. Yu, R. Wang and A. G. Fane, Optimization of microstructured hollow fiber design for membrane distillation applications using CFD modeling, Journal of Membrane Science, 421-422 (2012) 258-270

[35]H. Yu, X. Yang, R. Wang and A. G. Fane, Numerical simulation of heat and mass transfer in direct membrane distillation in a hollow fiber module with laminar flow, Journal of Membrane Science, 384 (1-2) (2011) 107-116

[36]X. Yang, R. Wang, L. Shi, A. G. Fane and M. Debowski, Performance improvement of PVDF hollow fiber-based membrane distillation process, J. Membr. Sci., 369 (1-2) (2011) 437-447

[37]G. Chen, X. Yang, R. Wang and A. G. Fane, Performance enhancement and scaling control with gas bubbling in direct contact membrane distillation, Desalination, 308 (2013) 47-55

[38]R. W. Baker, , Membrane Technology and Applications John Wiley and Sons, 2004

[39]S. Bhattacharjee, S. Ghosh, S. Datta and C. Bhattacharjee, Studies on ultrafiltration of casein whey using a rotating disk module: effects of pH and membrane disk rotation, Desalination, 195 (1-3) (2006) 95-108

[40]B. Li and K. K. Sirkar, Novel membrane and device for vacuum membrane distillation-based desalination process, Journal of Membrane Science, 257 (1-2) (2005) 60-75

[41]V. Chen, H. Li and A. G. Fane, Non-invasive observation of synthetic membrane processes – a review of methods, Journal of Membrane Science, 241 (1) (2004) 23-44

[42]M. C. Porter, Handbook of Industrial Membrane Technology, William Andrew Inc, 1990

[43]J. Bear, Dynamics of Fluids in Porous Media, Dover Publications, New York, 1972

[44]P. T. Callaghan, A. Coy, D. MacGowan, K. J. Packer and F. O. Zelaya, Diffraction-like effects in NMR diffusion studies of fluids in porous solids, Nature 351 (1991) 467 - 469

[45]E. O. Fridjonsson, Colloidal suspension hydrodynamics and transport processes in microcapillary and porous media flows studied using dynamic nuclear magnetic resonance, (2005)

[46]A. P. S. Yeo, A. W. K. Law and A. G. Fane, The relationship between performance of submerged hollow fibers and bubble-induced phenomena examined by particle image velocimetry, Journal of Membrane Science, 304 (1-2) (2007) 125-137

[47]H. Li, A.G. Fane, H.G.L. Coster and S. Vigneswaran, Direct observation of particle deposition on the membrane surface during crossflow microfiltration, J. Membr. Sci., 149 (1998) 83-97

[48]E. Fukushima, Nuclear magnetic resonance as a tool to study flow, Annu. Rev. Fluid Mech, 31 (1999) 95-123

[49]L. F. Gladden, Nuclear magnetic resonance in chemical engineering: principles and applications, Chem. Eng. Sci., 49 (1994) 3339-3408

[50]J. M. Pope and S. Yao, Quantitative NMR imaging of flow, Concepts Magn. Reson., 5 (1993) 281-302

[51]S. Yao, A. G. Fane and J. M. Pope, An investigation of the fluidity of concentration polarization layers in crossflow membrane filtration of an oil-water emulsion using chemical shift selective flow imaging, Magn. Reson. Imaging, 15 (1997) 235-42

[52]A. Caprihan and E. Fukushima, Flow measurements by NMR, Physics Reports, 198 (1990) 195-235

[53]M. Nakagawa, S. A. Altobelli, A. Caprihan, E. Fukushima and E. K. Jeong, Non-invasive measurements of granular flows by magnetic resonance imaging, Exp. Fluids, 16 (1993) 54-60

[54]K. Kose, Spatial mapping of velocity power spectra in Taylor-Couette flow using ultrafast NMR imaging, Phys. Rev. Lett., 72 (1994) 1467-1470

[55]J.R. Brown, E.O. Fridjonsson, J.D. Seymour and S. L. Codd, NMR measurement of shear-induced particle migration in Brownian suspensions, Physics of Fluids, 21 (2009) 093301

[56]J. D. Seymour and P. T. Callaghan, Generalized approach to NMR analysis of flow and dispersion in porous medium, AIChE Journal, 43 (1997) 2096-2111

[57]P. T. Callaghan, Principles of NMR microscopy, Clarendon Press, Oxford, 1991

[58]J. J. Tessier and K. J. Packer, The characterization of multiphase fluid transport in a porous solid by pulsed gradient stimulated echo nuclear magnetic resonance, Phys. Fluids, 10 (1998) 75-85

[59]B. J. Pangrle, E. G. Walsh, S. C. Moore and D. DiBiasio, Investigation of fluid flow patterns in a hollow fibre module using magnetic resonance velocity imaging, Biotechnol. Tech., 3 (1989)

[60]B. J. Pangrle, E. G. Walsh, S. C. Moore and D. DiBiasio, Magnetic resonance imaging of laminar flow in porous tube and shell systems, Chem. Eng. Sci., 47 (1992) 517-526

[61]B. E. Hammer, C. A. Heath, S. D. Mirer and G. Belfort, Quantitative flow measurements in bioreactors by nuclear magnetic resonance imaging, Biotechniques, 8 (1990) 327-330

[62]C. A. Heath, G. Belfort, B. E. Hammer, S. D. Mirer and J. M. Primbley, Magnetic resonance imaging and modelling of flow in hollow-fibre bioreactors, AIChE J, 36 (1990) 547-557

[63]S. Yao, M. Costello, A. G. Fane and J. M. Pope, Non-invasive observation of flow profiles and polarisation layers in hollow fibre membrane filtration modules using NMR micro-imaging, J. Mem. Sci., 99 (1995) 207-216

[64]M. C. M. V. Loosdrecht, L. Bereschenko, A. Radu, J. C. Kruithof, C. Picioreanu, M. L. Johns and H. S. Vrouwenvelder, New approaches to characterizing and understanding biofouling of spiral wound membrane systems, Water Science and Technology, 66 (1) (2012) 88-94

[65]S. A. Creber, J. S. Vrouwenvelder, M. C. M. v. Loosdrecht and M. L. Johns, Chemical cleaning of biofouling in reverse osmosis membranes evaluated using magnetic resonance imaging, J. Mem. Sci., 362 (1-2) (2010) 202-210

[66]S. Laukemper-Ostendorf, H. D. Lemke, P. Blümler and B. Blümich, NMR imaging of flow in hollow fiber hemodialyzers, J. Membr. Sci., 138 (1998) 287-295

[67]P. A. Hardy, C. K. Poh, Z. Liao, W. R. Clark and D. Gao, The use of magnetic resonance imaging to measure the local ultrafiltration rate in hemodialyzers, J. Membr. Sci., 204 (2002) 195-205

[68]C. K. Poh, P. A. Hardy, Z. J. Liao, Z. Huang, W. R. Clark and D. Gao, Effect of spacer yarns on the dialysate flow distribution of hemodialyzers: a magnetic resonance imaging study, ASAIO J, 49 (2003) 440-448

[69]R. C. Reid, J. M. Prausnitz and T. K. Sherwood, The Properties of Gases and Liquids, 3rd edn., McGraw-Hill, New York, 1977

[70]D. O. Kuethe and J. H. Gao, NMR signal loss from turbulence - model of time dependence comparedwith data, Phys. Rev. E, 51 (4) (1995) 3252-3262

[71]U. M. Scheven, D. Verganelakis, R. J. Harris, M. L. Johns and L. F. Gladden, Quantitative NMR measurements of pre-asymptotic dispersion in flow through porous media, Physics of Fluids, 17 (2005)

[72]J. Mitchell, A. J. Sederman, E. J. Fordham, M. L. Johns and L. F. Gladden, A rapid measurement of flow propagators in porous rocks, J. Magn. Reson, 191 (2) (2008) 267-272

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Fig. 2. Schematic of NMR experiments for flow inspection in membrane modules

Fig. 3. Top-bottom and side-view NMR images of multi-fibre membrane modules (a) Randomly-packed module; (b) Spacer-knitted module; (c) Semicurly-fibre module; (d) Curly-fibre module(the membrane matrix appears as dark rings, the imaging slice thickness is 5 cm, 256×256 pixels)

Fig. 4. Effect of feed temperature on the permeation flux for various hollow fibre module configurations [3.5% NaCl solution as feed $Q_f$ =3 $L \cdot min^{-1}$($v_f$ =0.33$m \cdot s^{-1}$), $Q_p$ =0.4 $L \cdot min^{-1}$ ($v_p$ =0.08$m \cdot s^{-1}$), $T_p$ = 298 K, $T_f$ =313 – 343 K]

Fig. 5. Cross-sectional velocity maps of multi-fibre membrane modules (a) Randomly-packed module; (b) Spacer-knitted module; (c) Semicurly-fibre module; (d) Curly-fibre module (The brightness of the signal represents the magnitude of the flow velocity. NMR experimental parameters: 128×128 pixels, 32 average, 5 cm slice. Gradients applied G: gradient pulse interval $\delta$ = 4ms, observation time $\Delta$ = 100 ms, $Q_f$ =100 $mL \cdot min^{-1}$)

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Fig. 7. Cross-sectional velocity maps of spacer-knitted module at varied flowrates (The brightness of the signal represents the magnitude of the flow velocity. NMR experimental parameters: 128×128 pixels, 32 average, 5 cm slice. Gradients applied G: gradient pulse

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