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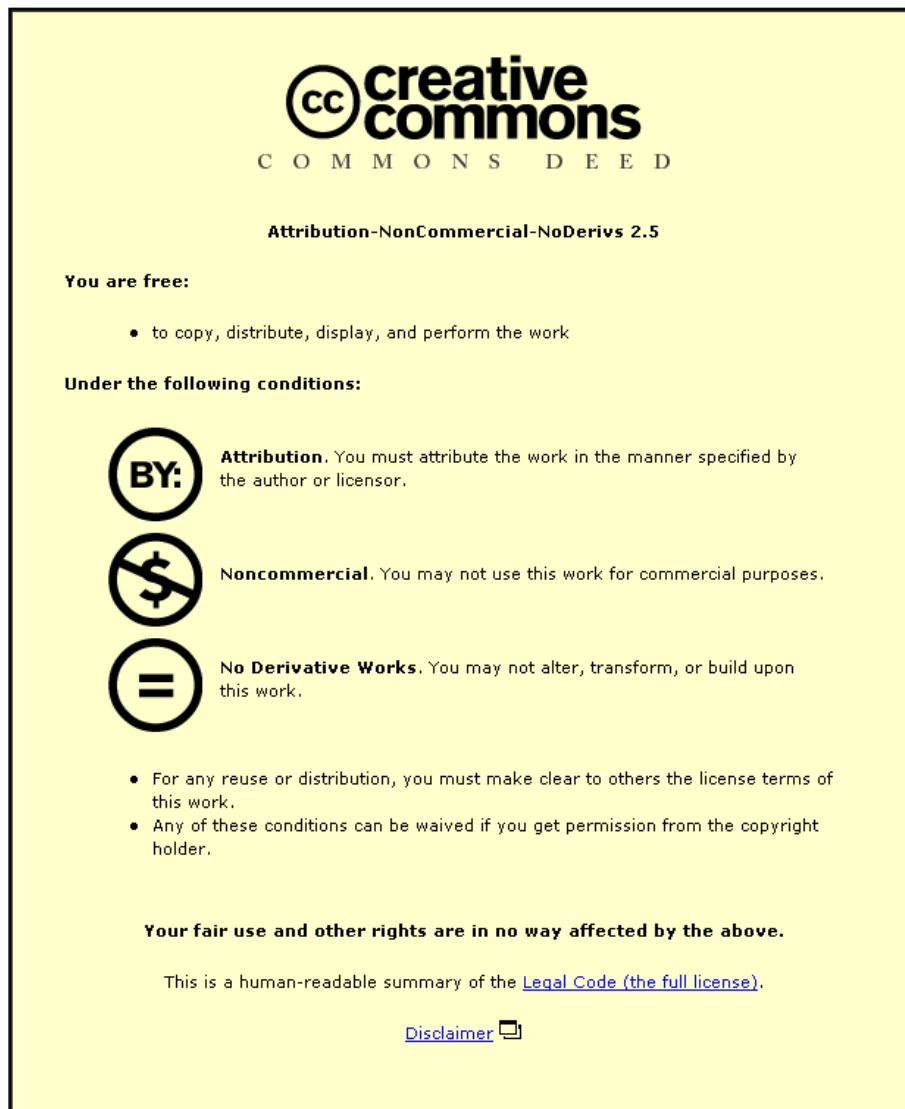
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NANOFILTRATION: A METHOD FOR IMPROVING THE PURITY OF FUELS AND NON-AQUEOUS SOLVENTS

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ABSTRACT

This paper describes some of the principal features of solvent resistant nanofiltration and its potential in fuel processing. Experimental data for both fuel simulants and a petrol fuel are presented. The solute rejection mechanism for low polarity mixtures was size exclusion with a membrane cut-off in the region of 1-2 nm. The extent of solute rejection was dependent on the degree of membrane crosslinking, the membrane swelling induced by the feed and the filtration pressure. Nanofiltration experiments with the petrol fuel showed a good correlation with the data obtained for the fuel simulants, both in terms of permeate flux and solute rejection. Provided that higher polarity oxygenates were not present in the fuel, it was possible to remove undesirable poly-nuclear aromatic and organometallic solutes to an extent that was sufficient to significantly reduce valve deposits and emissions gases in engine tests.

KEYWORDS

Nanofiltration; Organic solvents; PDMS; Solvent resistant membranes.

INTRODUCTION

The application of solvent resistant nanofiltration (SRNF) in petroleum processing has the potential to deliver products without the addition of thermal energy, which is appealing given current energy costs and ongoing environmental concerns. Fuel quality improvements can be achieved by the selective removal of intrinsic components which contribute to the fouling of engine inlet valves and fuel injectors. Typical concentrations of impurities are of the order 10 ppb – 100 ppm and examples include copper and iron organometallic (OM) species, sulphur bearing compounds such as mercaptans and thiophenes, and poly-nuclear aromatics (PNAs).

EXPERIMENTAL

The apparatus used for nanofiltration experiments is shown in Figure 1. An air-driven pump caused the process mixture to move through a standard Osmonics DESAL membrane module (75 cm² wetted area) at crossflow rates up to 0.7 l/min and filtration pressures up to 800 kPa. The retentate passed through a heat exchanger and back into the feed reservoir. The permeate was either also returned to this reservoir or sampled for subsequent solute rejection analysis by UV-vis spectroscopy or refractive index; rejection is defined as $1 - C_p/C_f$ where C_p is solute concentration in the permeate and C_f is solute concentration in the feed. Experiments were performed using 1 L of a solvent/solute mixture with a 10% stage cut.

Alkane, aromatic and alcohol solvents were used, either solely or as binary mixtures. These span a range of polarity as evidenced by their solubility parameter $\delta = 14.3\text{--}29.2 \text{ MPa}^{0.5}$ and were representative of the classes of solvents found in a typical petrol fuel (e.g. xylene - aromatics, n-heptane - paraffins). Ten solutes, classed as either PNAs or OMs with molecular weight's in the range 154-612, were available and chosen to be representative of those typically present in a petrol fuel (see Robinson *et al.* (2005) for a listing).

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A number of composite, two or three layer, flat sheet membranes were utilised. Most experiments were performed using polydimethylsiloxane (PDMS)/polyacrylonitrile (PAN) membranes (see Figure 2). The PDMS ($\delta \approx 15.3 \text{ MPa}^{0.5}$) acted as the selective layer whilst the inert PAN acted as a support. In a nanofiltration experiment the dense PDMS layer, which exhibited no manufactured/visible pores, faced toward the feed mixture and membranes were available with unswollen PDMS thicknesses between 1 μm and 10 μm . During manufacture the membranes were thermally and/or radiation crosslinked to provide structural integrity and chemical stability. A few experiments were performed with Starmem™ 122 polyimide (PI) membranes to extend the range of data; selective layer thickness here was estimated at 75 μm .

A novel laboratory apparatus was developed to determine the swelling of an 'as manufactured' membrane in a given solvent (Tarleton *et al.* 2005). In brief, a sample of membrane is placed in a dish, a spacer is rested on top of the sample and a linear measurement probe (resolution 0.1 μm) is then positioned over the spacer. Subsequent introduction of *circa* 5 ml of solvent initiates any swelling and allows a quantitative measurement to be taken. With the addition of a cantilever loading bar it was possible to impose a pressure up to 2000 kPa upon a membrane sample prior to, and throughout, solvent induced swelling.

Nanofiltration experiments were also performed with a petrol fuel containing *circa* 60% aromatics, 30% paraffins and 10% olefins as well as contaminating solutes at ppm level concentrations; this is denoted as the base fuel. Whilst the exact nature of the solutes was unknown, they were a blend of OMs, PNAs and sulphur compounds. A standard test bed was used to evaluate the performance of a road car engine with the base fuel, permeated fuel, retentate fuel (i.e. that remaining on the feed side of the membrane) and the base fuel plus a detergent additive that is typically added to a commercial fuel to reduce engine deposits (i.e. denoted as additivated fuel).

RESULTS AND DISCUSSION

In no instances during nanofiltration did fouling due to solute accumulation at the membrane occur, presumably because of the low concentration of solute in a feed, and solvent flux was independent of solute concentration up to the 75 ppm maximum tested. Moreover, mixtures of low polarity solvents, including those constituting the base petrol fuel, did not undergo separation upon nanofiltration.

Fuel Simulants

The simplest behaviour in SRNF is demonstrated by low polarity solvent systems. For example, Figure 3 shows that for a fixed crossflow, xylene solvent and 9,10-diphenylanthracene (PNA) solute at 20 ppm concentration, the flux-pressure relationship is linear in accordance with Darcy's Law. The flux for a given pressure is dependent on the membrane used and influenced by the thickness of the selective PDMS layer. Whilst a doubling in flux could intuitively be expected for a membrane with a 1 μm PDMS layer compared to an otherwise identical membrane with a 2 μm layer, the situation is complicated by solvent induced swelling. The extent of membrane swelling is influenced by the solubility parameter (δ) of the solvent relative to the δ value for the polymer(s) comprising the membrane; greatest swelling was observed when $\delta_{\text{membrane}} = \delta_{\text{solvent}}$. For a xylene solvent with $\delta = 18.2 \text{ MPa}^{0.5}$, a PDMS layer was observed to swell by 123%, 115% and 50% for the membranes designated 'radiation, 2 μm ', 'radiation, 1 μm ' and 'thermal, 1.5 μm ', respectively. It is clear that the purely thermal treated membrane is more crosslinked which leads to the lower flux levels seen in Figure 3. An increased filtration pressure also led to a progressive, but non-linear, improvement in solute rejection toward a limiting value which was often accompanied by a significant reduction in swollen PDMS thickness.

Figure 4 shows examples of PNA and OM rejection vs. solute size for two different membranes at a fixed filtration pressure with xylene solvent. Correlations with maximum solute size were good and showed a typically sharp transition in rejection level around 1.5 nm which is indicative of the PDMS layer rejecting low-polarity, minimally interacting solutes on the basis of size-exclusion and viscous solvent transport to an extent dependent upon the degree of swelling induced change in size of the membrane transport regions. When the membrane was more crosslinked, for example the membrane labelled 'thermal 1.5 μm ' in Figure 4, then rejection was generally higher for a given solute.

Petrol Fuel – Filtration Performance

As the exact nature and concentration of the contaminating solutes in the base petrol fuel, or the permeate and retentate obtained by nanofiltration, could not be routinely determined the term 'fuel clean-up' was used to quantify solute removal. Higher values are indicative of a better rejection of solutes and the term is defined as $1 - A_p/A_f$ where A_p and A_f are the UV-vis absorbance of the feed and permeate respectively at any given wavelength; these values correspond to the total concentration of impurities in the permeate and feed. A wavelength of 420 nm was used for measurements. Preliminary filtration studies using a PDMS/PAN membrane and a petrol fuel rich in organic copper and iron compounds showed that separation does not involve adsorption to the membrane material, a result that is consistent with nanofiltration of the fuel simulants.

The following behaviour was observed for nanofiltration of the base petrol fuel:

- *Effects of pressure:* Fuel clean-up improved with increasing pressure, however, a limiting rejection was not generally achieved. A plot of permeate flux vs. filtration pressure exhibited a linear relationship. Membrane swelling and solvent viscosity were identified as the predominant factors governing permeate flux and the base petrol fuel behaved similar to a mixture of low polarity solvents.
- *Effects of fuel composition:* By diluting fuel samples with either xylene to give a 50/50 by volume solution with an estimated $\delta = 17.6 \text{ MPa}^{0.5}$, or with heptane to give $\delta = 16.4 \text{ MPa}^{0.5}$, it was determined that fuels with a high aromatic content are likely to yield good clean-up when treated by PDMS/PAN membranes, whereas fuels that are rich in alkanes are more likely to exhibit a lower clean-up at a higher flux.
- *Effects of crosslinking and membrane type:* A more crosslinked PDMS/PAN membrane showed greater fuel clean-up, but lower permeance. A PI membrane yielded low permeate flux which appeared to be a consequence of the small degree of membrane swelling.
- *Effects of oxygenate addition:* Adding methanol or ethanol to the base fuel at 20% by volume prior to nanofiltration with a PDMS/PAN membrane reduced fuel clean-up by up to 45%, primarily because of alcohol rejection by the membrane. Adding ethers did not affect either permeate flux or fuel clean-up.

Petrol Fuel – Engine Tests

A sufficient quantity of the base petrol fuel was nanofiltered using a radiation crosslinked PDMS/PAN membrane to allow engine tests to be performed. The inlet valve deposit (IVD) and combustion chamber deposit (CCD) weights (Figure 5) and carbon monoxide (CO) / nitrous-oxide (NO_x) emissions (Figure 6) were determined. The average IVD weight with the permeate fuel was less than half that of the base fuel, and is significantly lower than the IVD weight obtained using the additivated fuel. Interestingly, the retentate also gives lower IVDs than the base fuel. One possible explanation is that IVDs are caused by combinations of impurities when they combust, and that splitting the base fuel into two streams separates these combinations. CO levels obtained with the permeate fuel are lower than both the base fuel and the additivated fuel. The NO_x levels

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of the permeate fuel are lower than the feed, however, the exhaust-contaminant levels of the retentate fuel are marginally higher than that of the feed. The results suggest that nanofiltered fuel could bring about a 10-15% reduction in NO_x/CO emissions.

CONCLUSIONS

The work presented highlights the key features of SRNF and, by way of example, how the technology could potentially be used to upgrade fuel quality. The principal factors influencing a separation are membrane swelling, as dictated by the difference in solubility parameter between the solvent(s) and the selective membrane material and the extent of membrane crosslinking, solvent properties such as viscosity, the maximum dimensions of the solute(s) present and solvent polarity which can strongly influence individual flux levels. SRNF is a trade-off between product flux and product quality and a correlation appears to exist between the two for different membranes made from the same material. Improved solvent fluxes are favoured by higher filtration pressure, greater membrane swelling, thinner selective layers etc. Greater swelling, however, allows more solutes to pass into the permeate and thus more crosslinking tends to favour better product (permeate) quality, albeit with the need to provide more membrane area in order to achieve a given throughput. When more polar solvents are present in the feed then separation performance is often compromised.

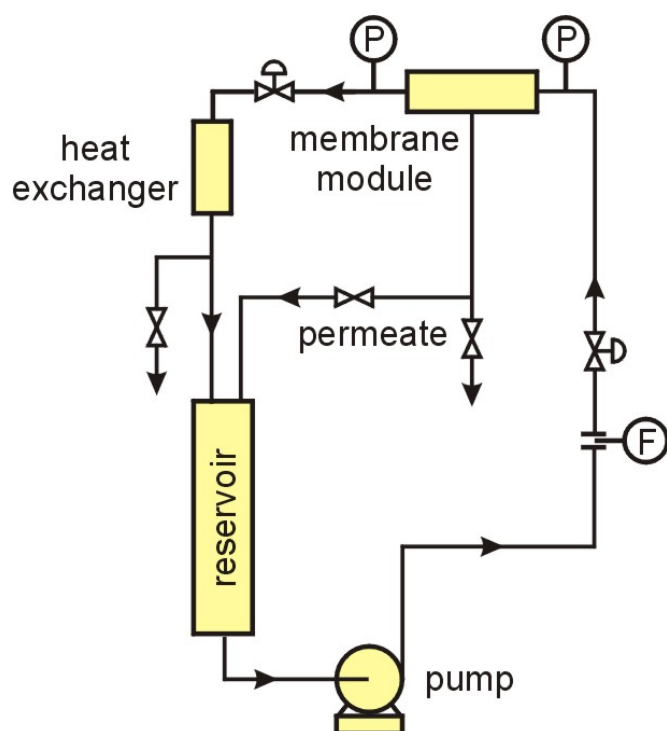
ACKNOWLEDGEMENTS

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Figures and tables



Figures 1: Schematic of the crossflow membrane filtration apparatus.

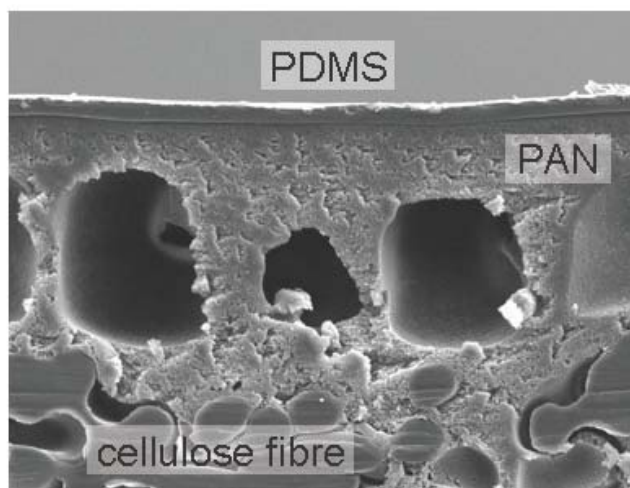


Figure 2: SEM of a PDMS/PAN membrane cross-section.

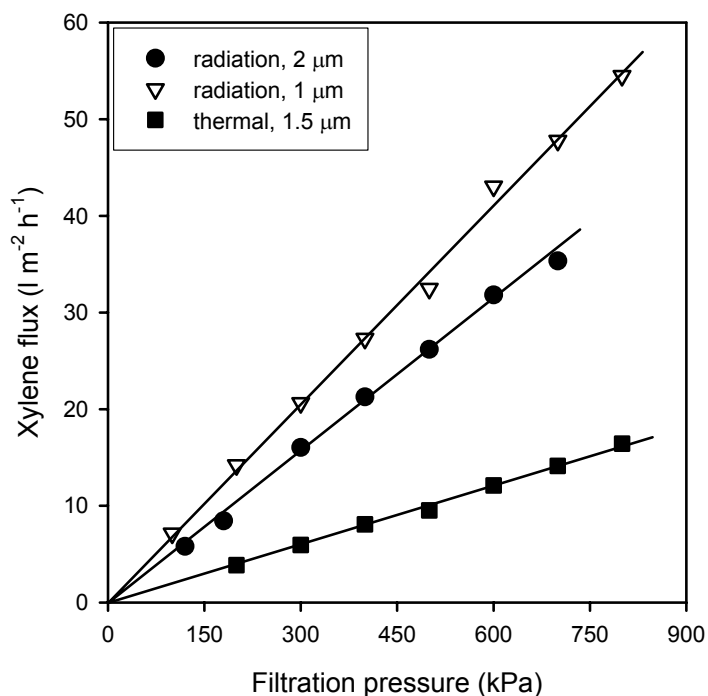


Figure 3: Permeate flux-pressure relationships for PDMS/PAN membranes; the length dimension on a legend is PDMS thickness before swelling whilst 'thermal' and 'radiation' indicate the primary crosslinking method.

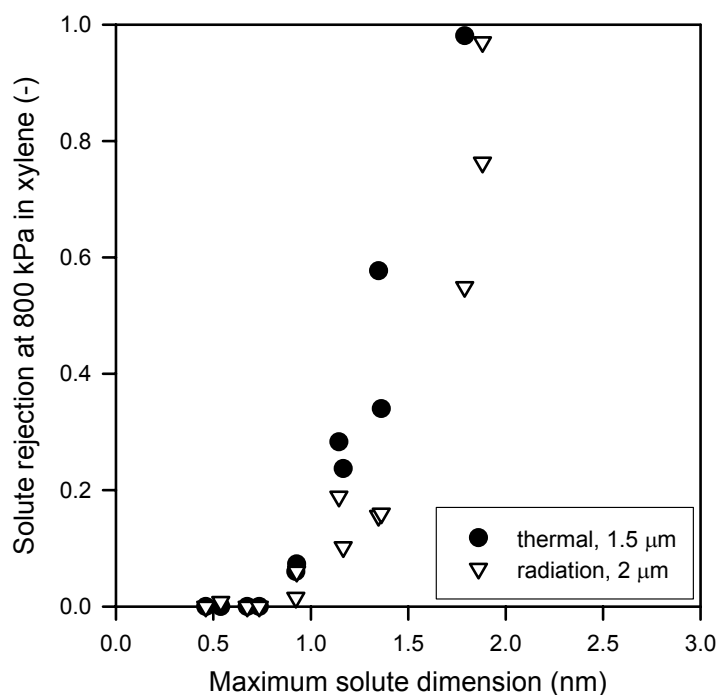


Figure 4: Effect of OM and PNA solute dimension (as determined by ChemDraw 3D) on rejection for two membranes.

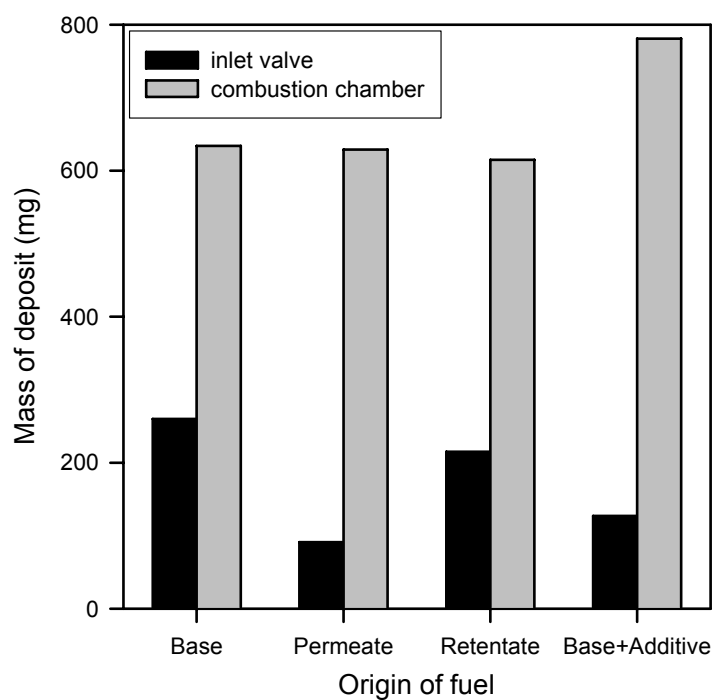


Figure 5: Amounts of inlet valve and combustion chamber deposits from engine tests.

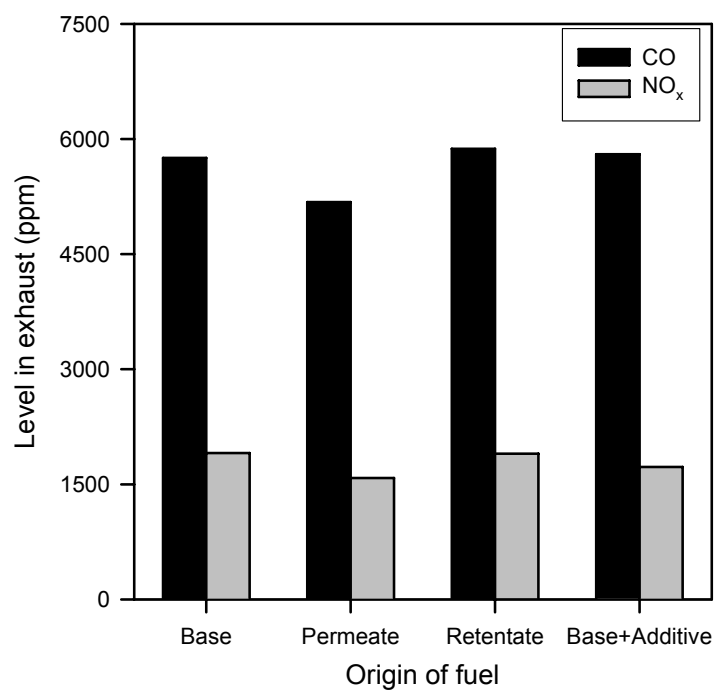


Figure 6: Emission levels from engine tests.