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THE ASSESSMENT OF MATERIALS FOR CROSSFLOW NANOFILTRATION OF ORGANIC/ORGANIC LIQUIDS AND THE DEVELOPMENT OF SCALE-UP OPTIONS

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ABSTRACT

With the aqueous applications of crossflow filtration being well established, comparable developments in the field of organic/organic liquid systems remain in their infancy. Progress within the field has been hindered by the fact that there are few systems which are both robust to hydrocarbon solvents and provide good fluxes/separations under realistic operating conditions. The authors of the current paper have explored a number of materials for crossflow filtration of organic media and found that the dense organic polymer PDMS (polydimethyl siloxane) affords the best results (see Figure 1).

Building on initial results, a full assessment of the membrane performance has been undertaken. Using a laboratory set-up, a range of pure and mixed hydrocarbon streams have been passed across the PDMS to assess performance with time and under variable operating conditions. Recent papers and presentations by the afore mentioned authors have considered transport mechanisms across a 2 µm PDMS membrane supported on PAN.

Results from flat sheet experiments have been used to design a larger scale unit. The operation of this system has shown excellent read across in terms of flux and selectivity. It is hoped that the work detailed within this presentation will prompt other workers in the field to consider the development of novel organic polymers to build on the applicability of filtration for organic/organic separations.

KEYWORDS

Nanofiltration; Membrane; PDMS; Non-aqueous; Crossflow; Scale-up.

INTRODUCTION

Whilst nanofiltration (NF) applications for aqueous systems are commonplace, for example in drinking water purification, those for organic/organic liquid systems remain relatively unexplored. The primary reasons for this include:

- a lack of suitable materials - most membranes are not stable in organic solvents
- a preference to avoid processes which involve high temperatures and pressures.

The current paper considers the use of NF membranes under crossflow filtration (Figure 2). The principle of crossflow filtration is relatively simple. A feed is pumped in a direction parallel to a semi-permeable membrane and pressure applied perpendicular to the direction of flow (transient pressure). The result of this is the generation of two product streams, that which passes across the membrane (referred to as the permeate) and that which does not (referred to as the retentate). The relative factions of the two product streams is dependent on an array of factors including: membrane chemistry, operating parameters and feed composition.

Although many membranes are unstable in the presence of organic solvents, one material which is robust is poly dimethyl siloxane (PDMS). The stability and characteristics of this membrane for organic applications have resulted in uses including: gas chromatography, vapour recovery systems,[1] vapour permeation and pervaporation.

If the wider use of crossflow filtration for organic/organic separations could be realised, then many applications spanning a variety of processes may be feasible. As trace amounts of impurities can have a severe impact on the performance of some hydrocarbon products, it would be commercially advantageous in many petrochemical related processes if membrane filtration could be used to separate/concentrate these species (referred to throughout the rest of this document as solutes)[2].

The key objectives of the current study were to:

- investigate the effectiveness of a variety of commercially available membranes for use in organic/organic liquid systems
- to assess each membrane on its ability to separate polar species and those with high molecular weights from a common hydrocarbon stream
- to use results from the scouting study to build a larger scale, pilot plant
- to assess read across of the pilot plant in terms of flux and separation characteristics.

Additionally, the results of this scouting study have fed into a more detailed model systems analysis conducted by the same authors. By detailing a series of results the authors hope to engage with the filtration industry such that the unique opportunities which can be exploited via membrane techniques can be considered in greater detail. This work was conducted jointly between Shell Global Solutions (UK), Shell Global Solutions International, BV and Loughborough University. In addition the authors would like to thank Dr Klaus Ohlrigge and his team at GKSS for their invaluable insights and inputs.

EXPERIMENTAL

The bulk of scouting study was performed on a dedicated, small scale, crossflow filtration rig, referred to as the SEPA (separation) rig. A variety of commercially available membranes were assessed under a common set of operating conditions and using a well characterised hydrocarbon stream. The efficacy of the membranes were assessed by the flux and through the purity of the permeated hydrocarbon stream (using a suite of routine laboratory analyses).

Test Matrix

A literature search identified a list of possible NF membranes. A number of the most promising were targeted. A full list is given in Appendix A with those used in the test series highlighted. The experimental method outlined below was performed on the following membranes (Table 1). Full details and relevant properties of these membranes can be found in the results section.

SEPA Rig

The rig, Figure 3, is located in a self-contained test cell which incorporates fire, smoke and hydrocarbon detectors. When assessing flat sheet, organic membranes the heart of the operation was a flat sheet stainless steel membrane housing (a DESAL high-pressure cell) - purchased from

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[1] Vapour recovery is a technique in which volatile vapours are forced through a membrane with the effect of condensing the vapour. This effectively recycles volatile components that would otherwise have been lost to the atmosphere.

[2] Undesirable solutes in hydrocarbon streams can come in many forms, for example organometallics, poly nuclear aromatics, heteroatomic molecules, polymerics and organic acids.

Osmonics (US). The housing can be operated at pressures of up to 69 bar with flow rates of up to 12 L/min. Flow around the rig is provided by a Cat®Pump 431, powered by a flameproof motor fitted with a pulsation damper. A pre-filter has been fitted to the rig to prevent particulate matter clogging/damaging the surface of the membranes. The pressure and flow can be altered manually via control valves. The system is designed for relatively small scale operation and is equipped with a reservoir that can hold up to 30 L of feed.

In terms of data monitoring, the rig is connected to a 'Schenk' computer system located outside the test cell. This logs temperature, pressure, sample flow rate and sample mass continuously at one-minute intervals. This data can be downloaded to CD for further analysis.

Due to the risks associated with handling volatile organic liquids, the system has been equipped with a variety of safety trips. The key features include: two temperature sensors; one in the reservoir (Bulk Tank Temp) and one in the feed line to the membrane housing (Membrane Inlet Temp). The reservoir is fitted with an electronic level indicator which prevents the pump running dry and ensures shut-off of the system should a leak occur during unmanned operation. Additionally, the membrane pressure out is limited to 1.5 bar and a minimum flow rate set at 0.5 L/min.

Test Fluid

The test fluid used throughout the programme was a well characterised hydrocarbon stream with known organometallic and polymeric content.

Operating Parameters

Membranes were initially tested at a feed flow of 4 L/min and with pressure of 4 bar. In the absence of any flux or a very low rate of permeate collection, the pressure was raised (to a maximum value of 20 bar).

Test Procedure

Part 1: Assessing the Membrane Stability

- Immerse a membrane sample in the feed mixture for one week at ambient temperature and pressure. This serves as a check of the stability of the membrane[3]. The sample was agitated on a daily basis to avoid layering of the hydrocarbon mixture. The membrane was assessed visually for possible degradation.

Part 2: Experimental Set-Up

- The reservoir was filled with 10 L of fresh feed.
- The membrane preparation consists of soaking the flat sheet membrane for 24 hours in the feed and then mounting it in the membrane housing. This is followed by flushing of the membrane for 1 hour with a feed flow of 4 L/min. The permeate collecting during this period is separated and retained for further analysis. (Step run to remove possible contaminants from the polymerisation reaction.)
- A short conditioning step is then run involving a flow rate of 4 L/min and a pressure of 4 bar. Permeate collected during this time was returned to the reservoir.

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[3] The membrane structure can be unstable in solvent for a variety of reasons. For example, the solvent could swell the support layer and the membrane at different rates, causing tearing or buckling of either one or both of these layers. Also the powerful nature of hydrocarbons as solvents can mean that a membrane may undergo dissolution under test conditions.

Part 3: Testing

- Testing can end when both a 5% stage cut has been obtained and the rig has been run for a minimum of 4 hours. Thus enough permeate is produced to be able to perform all necessary analysis.
- Test time can be extended to a maximum of 20 hours if permeate collection is very slow (until the morning of the next day when a new test will be started).
- Draining of the rig, removing all excess hydrocarbon mixture, followed by thorough cleaning. All components of the hydrocarbon stream should be drained into pre-weighed jugs enabling an overall mass balance calculation. The membrane cell should be cleaned to remove possible contaminants and the sintered filter in the pump inlet checked and cleaned after testing to avoid particulate contamination.
- Storing of membrane in an air tight environment.

Scale-up – The LPTU Rig

The LTPU rig is essentially similar to the SEPA rig, with the principal differences being an increased volume in the feed, permeate and retentate streams; and in addition a recirculation option with respect to the retentate stream (see Figures 4 and 5). This facilitates higher percentage yields of permeate.

The operation of the LPTU rig is much the same as that of the SEPA rig, only on a much larger scale. The feed (~2000 L) enters the system through the feed reservoir and a flow rate of ~150 L/min is maintained along with an applied pressure of ~16 bar. After the membrane has filtered the feed, the permeate stream is collected and the retentate can either be collected or returned directly to the feed reservoir for recirculation.

The AMA Filter

The AMA filter illustrated in Figure 6 is the system of membranes used in the LTPU rig. This filter is manufactured by GKSS incorporating 5 flat sheet PDMS membranes and provides highly effective crossflow filtration at high flow rate.

RESULTS AND DISCUSSION

Scouting Study

Following a comprehensive literature survey (see Appendix 1), a large list of possible membranes were identified from suppliers based in both Western Europe and the USA. A selection of those shown to be stable to the organic, 14 in total, were tested using the SEPA rig.

Results from Initial Screening Exercise

The 14 membranes identified within the scouting study and shown to be stable to organic solvents were tested using the SEPA rig. For each membrane there was an initial washing process followed by a brief conditioning step. A summary of the key observations are provided in Table 2. The following observations we also made:

PDMS 10 μm Active Layer

- During conditioning with the hydrocarbon feed, the entire upper membrane layer separated from the support layer. To overcome this the membrane was mounted dry.

- Analysis showed a reduction in organometallics between feed and permeate, a reduction in high molecular mass species and a reduction in PNA's.
- It was noted that the permeate was visibly paler in colour when compared to feed and retentate samples.

MPF60

- The membrane exhibited stability to the hydrocarbon mixture during conditioning. However, under standard conditions a tear developed in upper membrane layer. As a result the required mass of permeate was collected in 14 s.
- As the other Koch membranes did not show any improvements to the fuel properties the membrane was not subjected to further testing.

POMS 150

- Due to a low flux the run was run over two days. On the first 400 g of permeate (3% stage cut) were collected in a time of 199 minutes and on the second 371 g (a further 3% stage cut) were collected in 360 minutes.
- When analysed, both permeate samples showed significant reductions in organometallics and heavier molecular weight species.
- A concern noted during the test was some metal pick-up. This issue is well documented in other hydrocarbon stream processes and care is needed to ensure the test fluid does not contact copper or copper based alloys.

PDMS 2 µm Active Layer

- Some pitting of the membrane surface was noted to the upper layer of the membrane. The nature of the marking indicated this was due to metal swarf contamination rather than chemical instability.

- Analysis showed a significant reduction in organometallics between feed and permeate.

MPF44

- This membrane failed to produce any sample, as it was non-permeable at the operating pressures being considered within the current study.

On the basis of this data, it is apparent that PDMS offers the optimal performance in terms of maximising both flux and selectivity.

Research Findings for PDMS

As a result of field experience, Shell Group expertise and data generated during recent test programmes, PDMS has been subjected to further analysis. This work can be broadly characterised under two headings:

- **Fundamental research:** The mode of operation for this membrane at a molecular level has been explored using a series of model systems
- **Application based research:** Taking the idea of crossflow filtration the impact of various operating parameters has been explored.

In the following section we provide a general overview of some of the key observations made to date. (Note: all work reported within this section was conducted using the flat sheet, DESAL membrane unit within the SEPA rig.)

The Impact of Membrane Thickness (2 µm vs.10 µm)

The PDMS membranes (10 µm and 2 µm thickness) were unstable when soaked overnight in the mixed hydrocarbon feedstock. This observation was attributed to different rates of swelling between the support and active layers. However, when loaded dry into the membrane housing in such a way that the layers where physically bound together (rather than via a purely chemical attraction) and run under standard conditions both thicknesses of membrane performed well. There were no signs of instability and benefits to the permeate stream included significant reductions in organometallic and higher molecular weight species.

In terms of performance the results appeared to show:

- increased selectivity with increased polymer thickness
- reduced flux with increased polymer thickness. The 10 µm PDMS had a flux of 2.7 g/min compared to 8.3 g/min for the 2 µm material.

This result indicates that for a given application the selectivity can be altered via changes to the membrane thickness, albeit that there will be a trade off with flux. For applications considered by the reporting authors, the 2 µm material was progressed.

Assessment of the Full Membrane Structure

The membrane layer responsible for selectivity is the PDMS, this has been shown by testing just the substrate material. The result was a very high flux and zero selectivity for organometallics and higher molecular weight species. The PDMS needs however to be bonded to a substrate material (linked via chemical interactions referred to as van der Waal's forces) to prevent possible disintegration and stress under normal crossflow operating conditions. Various polymeric layers with highly porous structures have been considered with polyethylene (PE) and polyacrylonitrile (PAN) currently being the most favoured. The majority of work within the current report has focused on PDMS supported by a 40 µm layer of PAN (see Figure 1).

The PDMS/PAN composite membrane is bonded to a cellulose support layer, this provides a rigid structure to the membrane and facilitates ease of handling.

Impact of Physical and Chemical Parameters on Flux

A wide range of parameters, both physical and chemical, have an impact on the flux. To summarise, the following observations have been made:

- **Pressure:** As the pressure is increased so the flux increases (this is as predicted by both the Hagen Poiseuille equation and Solution-Diffusion models).
- **Rate of crossflow:** The rate of flow does not have an impact on flux or selectivity – within the ranges considered, i.e. above a relatively low threshold value.
- **Temperature:** Although not explored explicitly, the temperature at which the system operates will have an impact on the flux. From the feed side, a higher temperature will equate to lower density/higher viscosity and this should result in a higher flux. From the membrane side, higher temperatures will encourage a more fluid structure and hence the flux should again be increased. The disadvantage of higher operating at higher temperatures may be lower selectivities. (Note: high temperature operation may result in additional safety concerns and the possibility of damage to the PDMS structure.)
- **Nature of the feed:** The bulk characteristics of the feed have an impact on performance. Materials which are highly viscous have been shown to permeate more slowly across the membrane. Model studies at Loughborough using simple solvent systems have also

demonstrated the impact of a solvents ability to swell the membrane. Those with higher swelling abilities lead to higher fluxes but poorer selectivities.

- **Level of crosslinking:** Higher levels of crosslinking within the PDMS structure will reduce the flux but increase the selectivity (more accurately may reduce the molecular weight cut off point).

These parameters can be tailored for a particular system so as to maximise on the basis of throughput and selectivity.

Filtration vs. Absorption

A question frequently asked is whether the process is a genuine separation or more simply a case of absorbing onto the membrane surface or even forming a surface layer (cake formation). The results from model studies and complete system analyses are unambiguous, through mass balance equations[4], it has been possible to demonstrate that this is a genuine separation and not absorption.

Findings from the LPTU

Having demonstrated the suitability of PDMS for improving the value of a hydrocarbon stream and having built a better understanding of the mechanisms behind the process, a larger scale system has recently been purchased. The unit which incorporates 5 flat sheet PDMS membranes with a total surface area of 0.525 m^2 and was designed by GKSS.

The rig's performance has been assessed using the same feedstock as used with the smaller scale unit. The key findings include:

- **Selectivity:** the selectivity of the membranes overlaps perfectly with smaller scale experiments. This confirms good batch-to-batch repeatability in the preparation of the membrane.
- **Flux:** the operating pressure (typically ~16 bar) and flow rates (150-300 litres/hour) were comparable to some of the testing with the smaller scale unit. As such the flux across the membrane was as predicted from the small scale experiments. This is a valuable result which confirms the ability to design a unit to deliver a given product volume based on a known operating pressure and membrane surface area.

The operation of the LPTU in both single pass and recirculation mode has provided unique insights into the possible extension of applications to larger scale systems.

CONCLUSIONS

As highlighted in the abstract, one of the goals of presenting this paper was to highlight to the industry that opportunities which currently exist for a more widespread review of the application of crossflow filtration to organic/organic separations. Work with both small and mid-scale units has demonstrated an ability to control the flux for a given feed based on pressure and the level of membrane crosslinking.

Exciting research by various institutions has revealed that a membrane's selectivity can be controlled through the level of swelling and this may indicate a potential for tailoring systems to optimise removal of precious catalysts from waste chemical process streams.

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[4] The initial mass of a certain species (e.g. PNA's) in the feed was determined prior to cross flow filtration. After a cut of e.g. 10% had been made the mass of PNA's in the retentate stream was determined. A comparison of the two values determined the destination of PNA molecules.

Opportunities are abundant to tailor membranes and improve fluxes. Surface coatings and membrane chemistries are two areas worthy of further analysis.

ACKNOWLEDGEMENTS
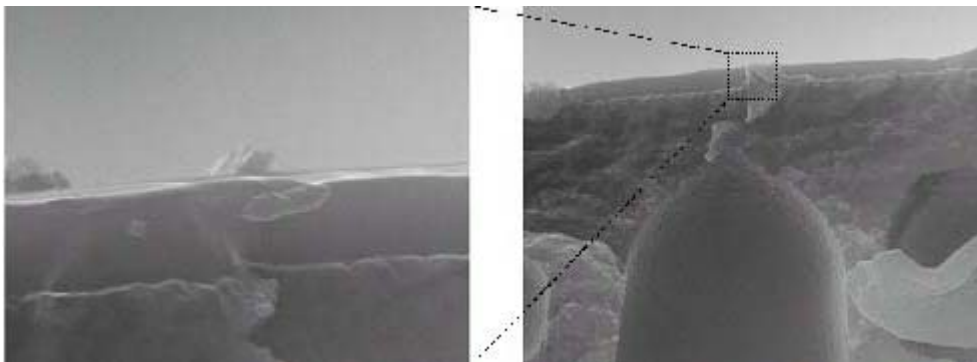
FIGURES AND TABLES

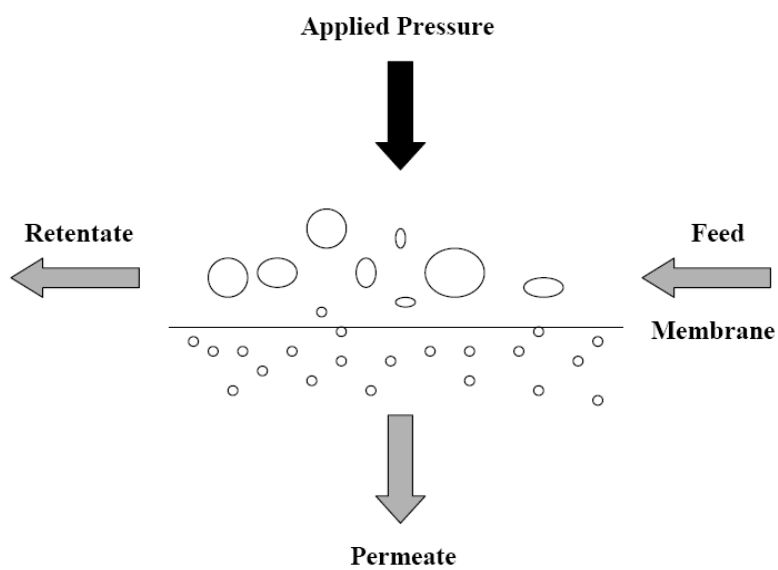Figure 1: PDMS composite membrane; cellulose-fibre support, 40 µm porous PAN substrate and 2 µm crosslinked PDMS.

Figure 2: Diagram illustrating the process of crossflow filtration.

1) Feed pipe
2) Feed pipe
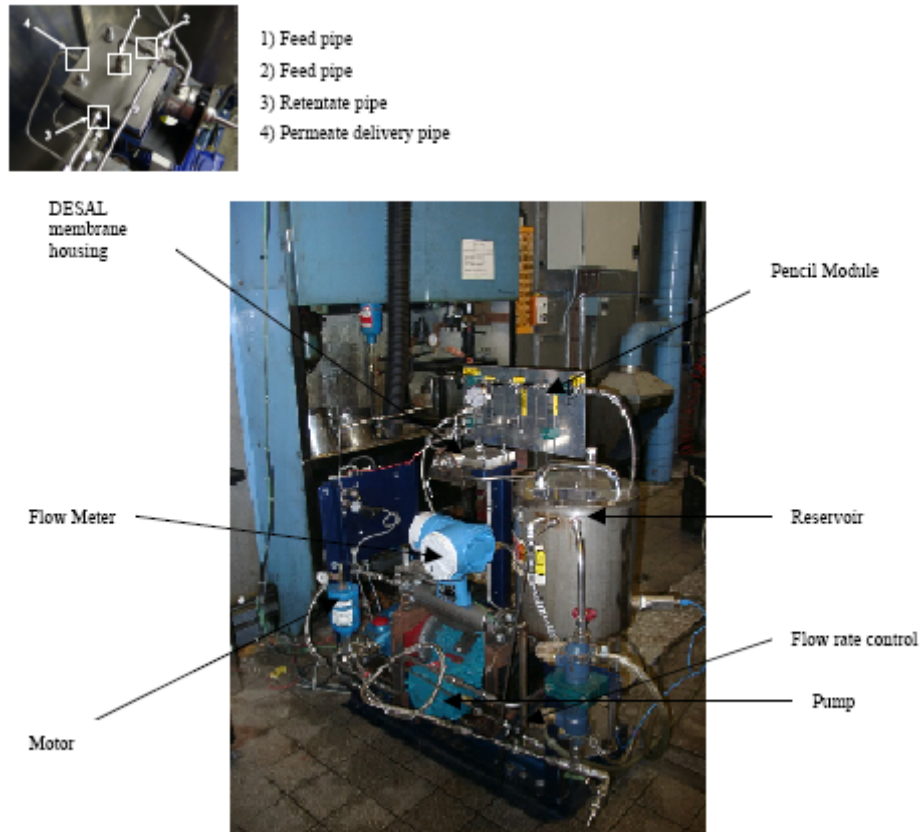3) Retentate pipe
4) Permeate delivery pipe

Figure 3: SEPA rig, standard set-up with Pencil Module. See Appendix 2 for Pencil Module operation and Appendix 3 for schematic.

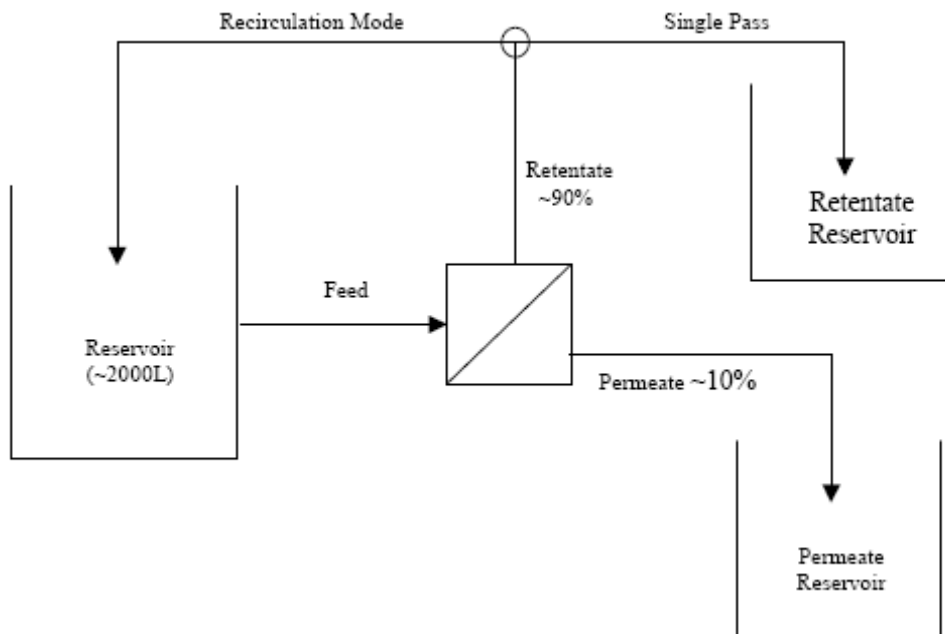Figure 4: A simple schematic of the larger scale LPTU rig.

Figure 5: The LPTU rig.
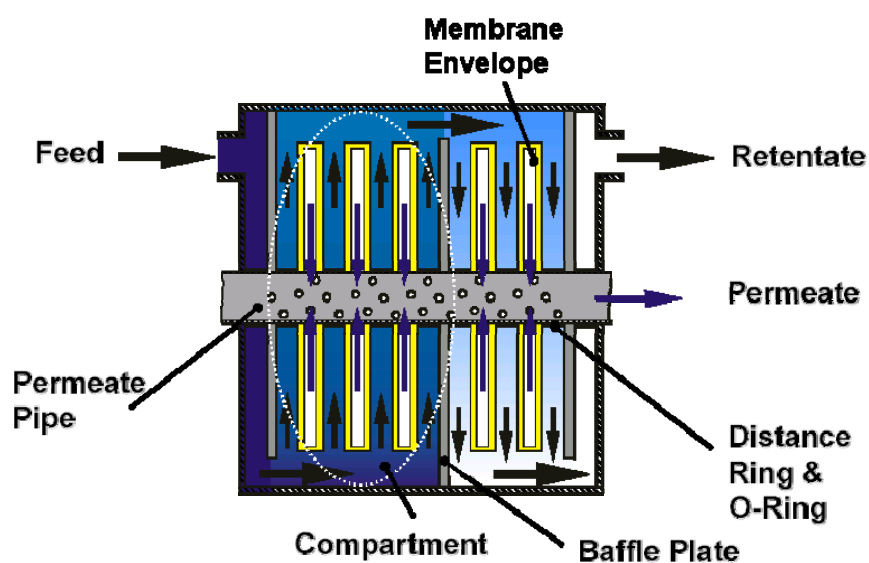
Figure 6: The AMA filter.

Membrane	Manufacturer	Material	Treatment
HL	Osmonics	Polyether sulphone	Soaked in gasoline 24 h
HG19	Osmonics	Polyether sulphone	Soaked in gasoline 24 h
AN09	Osmonics	Fluoropolymer	Loaded dry
PDMS (10 µm)	GKSS	Polydimethyl siloxane	Loaded dry
MPF50	Koch	-	Soaked o/n in IPA. Gasoline for 5 minutes
MPF60	Koch	-	
POMS 150	GKSS	-	Loaded dry
POMS 150 repeat	GKSS	-	Loaded dry
DL	Osmonics	-	Loaded dry
HL	Osmonics	Polyether sulphone	Soaked in methanol 5 days. Allowed to dry
HG09	Osmonics	Polyether sulphone	Loaded dry
BQ01	Osmonics	Polypropylene	Loaded dry
PDMS (2 µm)	GKSS	Polydimethyl siloxane	Loaded dry
SX01	Osmonics	Cellulosic RO	Loaded dry
MPF44	Koch		

Table 1: The membrane test matrix.

Membrane	Manufacturer	Stability in hydrocarbon mixture?	Mass of Permeate (g)	Improvement to Purity of Hydrocarbon Stream?	Run duration (mins)
HL	Osmonics	Y	669	N	15
HG19	Osmonics	Y	687	N	47
AN09	Osmonics	Y	542	N	24
PDMS (10 µm)	GKSS	N	700	Y	262
MPF50	Koch	Y	608	N	103
MPF60	Koch	N	609	N	14 s
POMS 150	GKSS	N	684	N	115
POMS 150 repeat	GKSS	Y	400 + 371	Y	199 + 360
DL	Osmonics	Y	686	N	249
HL	Osmonics	Y	700	N	12
HG09	Osmonics	Y	700	N	82
BQ01	Osmonics	Y	747	N	-
PDMS (2 µm)	GKSS	N	753	Y	91
SX01	Osmonics	Y	717	N	279
MPF44	Koch	Y	0	N	274

Table 2: Table summarising the results from the 14 tested membranes. Tests showing an improvement in fuel quality have been highlighted.

APPENDIX 1: RESULTS OF LITERATURE SEARCH

Membrane code	Supplier	Material	MWCO	Comments
Pebax 1074	GKSS	poly-ether-block-polyamide	-	rape oil purification
Pebax 3000	GKSS	poly-ether-block-polyamide	-	rape oil purification
PDMS	GKSS	polydimethyl siloxane	-	10 micron film
PDMS	GKSS	polydimethyl siloxane	-	2 micron film
PAN/POMS 150	GKSS	-	-	-
Persep	Rhodia	polyamide TFC	not given	RO membrane
Research	poly-glycidyl-methacrylate	not given	pervaporation	-
Research	polyimide	170-400	oil upgrading	-
Desal-5	Osmonics	-	nanofiltration	-
Desal-3	Osmonics	-	RO	-
HL	Osmonics	Polyethersulphone	-	
HL	Osmonics	Polyethersulphone	-	Treated with methanol
HG 09	Osmonics	Polyethersulphone	-	-
HG 19	Osmonics	Polyethersulphone	-	-
AN09	Osmonics	Fluoropolymer	-	-
BQ 01	Osmonics	Polypropylene	-	-
DL	Osmonics	Polyethersulphone	-	-
SP 28	Osmonics	Cellulosic	-	-
SX 01	Osmonics	Cellulosic	-	-
ESNA	Hydranautics	Composite polyamide	nanofiltration	-
ESPA	Hydranautics	Composite polyamide	RO	-
NTR-729HF	NittoDenko (Hydranautics)	Poly(vinylalcohol)/poly-amide	200-400	very high rejection for pesticides with sulphur groups
NTR 7250	Nitto Denko (Hydranautics)	poly(vinylalcohol)/poly-amide	not given	-
NTR 7450	Nitto Denko (Hydranautics)	sulphonated polyether sulphone	600-800	hydrophilic
NTR 7410	Nitto Denko (Hydranautics)	sulphonated polyether sulphone	-	-
NF-70	Filmtec (Dow)	crosslinked aromatic polyamide	250	-
MPT-10	Koch	-	200	pH 2-11
MPT-20	Koch	-	600	partial solvent stability
MPS-21	Koch	-	400	partial solvent stability
MPT-30	Koch	-	400	pH 0-12, max temp 70ºC acid purification
MPT-34	Koch	-	200	pH 0-14, max temp 80ºC acid purification
MPT-36	Koch	-	1000	pH 0-13, max temp 70ºC acid purification
MPS-34	Koch	-	300	pH 0-14, max temp 70ºC acid purification
MPS-36	Koch	-	1000	pH 0-13
MPS-44	Koch	-	250	excellent solvent

				stability
MPS-50	Koch	-	700	excellent solvent stability
MPS-60	Koch	-	400	excellent solvent stability
MPF-44	Koch	-	-	-
MPF-50	Koch	-	-	-
MPF-60	Koch	-	-	-
UTC-20	Ropur (Toray)	polyamide	180	-
ANM	Trisep	polyamide	nanofiltration	-
ACM	Trisep	polyamide	RO	-
CA	Trisep	cellulose acetate	RO	-
X-20	Trisep	polyamide	RO	-
Permasep	DuPont	polyamide	RO	-
Nafion	DuPont	perfluorinated sulphonic acid polymer	-	stable
Kerasep	Rhodia	Al_2O_3-TiO_2	1000	nanofiltration
Silica-zirconia	Research	Silica-zirconia (3 nm)	300	PEG/methanol

Table 2: List of possible membranes and suppliers from literature search. (Highlighted rows represent those membranes purchased for further testing).

APPENDIX 2: PENCIL MODULE SET UP OF SEPA RIG

Figure 7: Pencil module set-up.
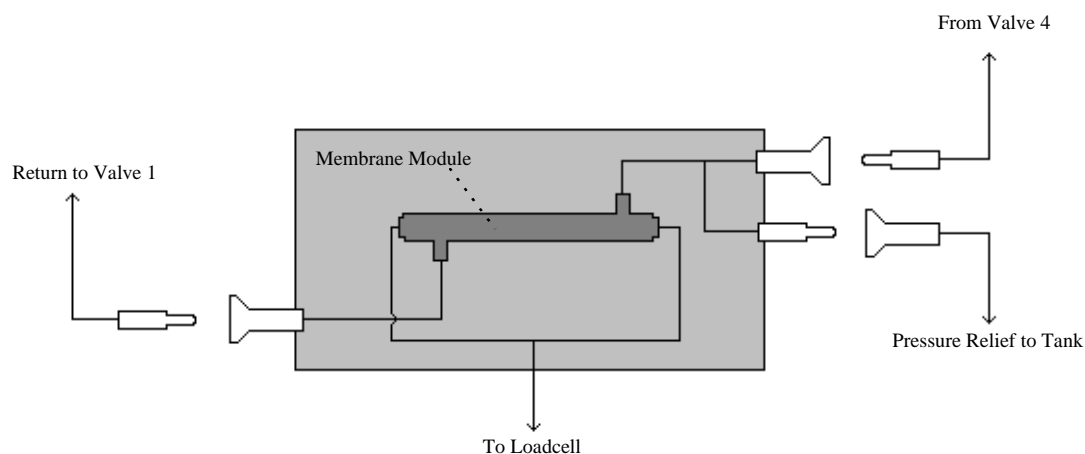

Figure 8: Pencil module.

Figure 9: Schematic of pencil module. When using the pencil module, then the valves mentioned earlier need to be changed. Valves 1 and 4 should be open, valves 2 and 3 closed.

APPENDIX 3: SCHEMATIC OF SEPA RIG