

Solvent recovery from lube oil filtrates with a polyimide membrane

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Abstract

A polyimide membrane manufactured from a co-polymer of diaminophenylindane with benzophenone tetracarboxylic dianhydride has been shown to have excellent chemical resistance and economically viable flux and rejection characteristics for the separation of light hydrocarbon solvents from lube oil filtrates. This asymmetric membrane was subjected to a series of bench scale hyperfiltration studies. After 2 months of continuous high pressure tests, the membrane demonstrated recovery of chilled solvent (a mixture of methyl ethyl ketone and toluene at -10°C) from the lube filtrates at a purity of better than 99% with a steady permeate rate. When a membrane system is combined with a conventional solvent lube dewaxing process, significant increases in energy efficiency and solvent recovery capacity are realized. Subsequently, this work led to the installation of a commercial membrane plant designed for a maximum feed rate of 11 500 cubic meters per day (72 000 barrels per day) at Mobil's Beaumont, Texas refinery. This process, trademarked MAX-DEWAX[®], provides a low capital method for expansion of solvent dewaxing units and is available for licensing. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

An asymmetric polyimide membrane has been developed for recovering cold solvents from lube oil in the solvent dewaxing process. Solvent lube oil dewaxing processes are practiced world-wide in refineries. In this process, waxy lube raffinate feedstocks are processed in block operations to produce lube base stocks having distinct viscosity characteristics. The raffinates are first dissolved in a light hydrocarbon solvent mixture, for example a blend of methyl ethyl ketone (MEK) and toluene. This mixture is cooled to precipitate the wax component, then is filtered to remove the wax. The solvent mixture is then recov-

ered from the lube oil and the solvents recycled to the process. For most feeds, overall production and dewaxed oil yield is limited by solvent circulation and/or refrigeration capacity.

A membrane process (Fig. 1) can be used to substantially debottleneck the refrigeration and recovery sections of a solvent lube plant. Significant equipment and energy savings can be realized by recovering cold solvent directly from the filtrate and by reducing the amount of solvent subjected to the heating and cooling in the solvent recovery section. Initial developmental targets were to produce a membrane with a sufficiently high flux and oil rejection that a 160 cubic meters feed/day (1000 barrels feed/day) membrane unit could recover 25% of the solvent in the filtrate with less than 300 m² of membrane. Potential savings can be found in energy and operating costs, reduced capital expenditure versus conventional debottleneck, better

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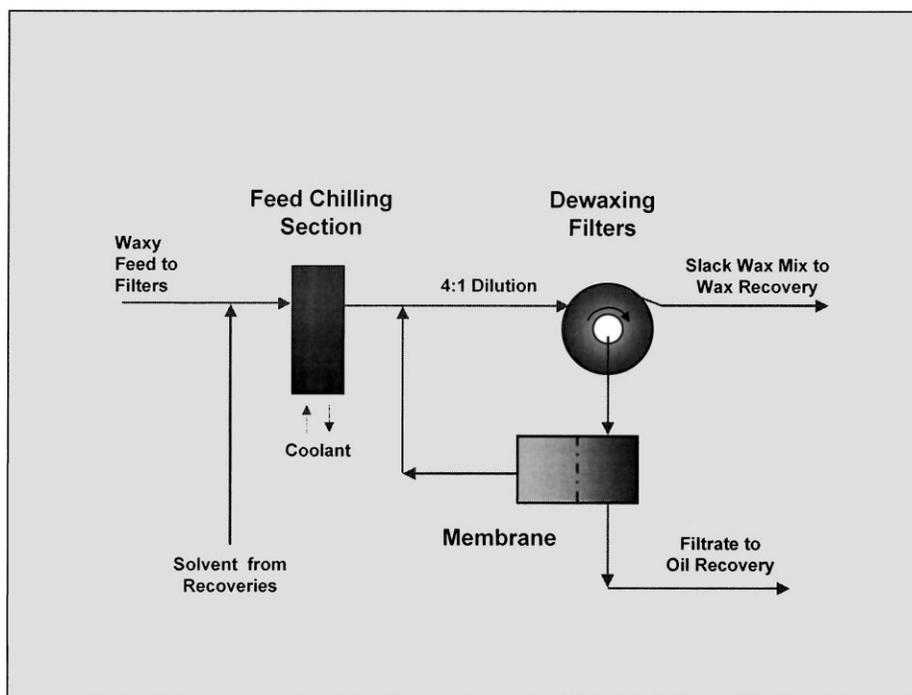


Fig. 1. Membrane separation of cold solvents from lube oil filtrate.

quality of wax recovered, and increased oil yield. For a membrane unit receiving a filtrate stream, it is estimated [1] that this can allow a 20% reduction in the size and capacity requirements for the oil/solvent recovery section. There is a 25% reduction in the heat energy required to recover solvent and at least 10% reduction in the total refrigeration requirements.

Two membrane materials, widely used in the reverse osmosis market, are cellulose acetate and polysulfone. These polymers, in the common grades, dissolve on contact with MEK. However, one can select examples from a number of reports in the literature for varied

applications [2–8] that suggest the hyperfiltration of organic solvents and compounds can be accomplished. We chose to work with the polyimide formed by the condensation of diaminophenylindane with benzophenone tetracarboxylic dianhydride. This structure is shown in Fig. 2. This polyimide is also under investigation for other membrane applications [9–14].

The membrane must be robust and able to withstand a sufficient period of continuous service in order to keep membrane replacement costs at a reasonable level. This program aimed to demonstrate that a membrane has the potential for meeting these various

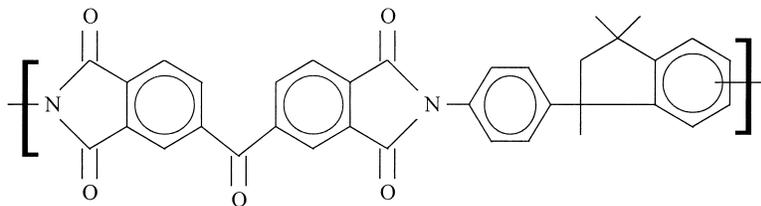


Fig. 2. Polyimide structure.

goals and can be manufactured on continuous process equipment suitable for large-scale production.

2. Experimental

2.1. Polymer

The polymer from 1(or 3)-(4-aminophenyl)-2,3-dihydro-1,3,3(or 1,1,3)-trimethyl-1H-inden-5-amine and 5,5'-carbonylbis-1,3-isobenzofurandione (CAS number 62929-02-6) was used to fashion an asymmetric membrane. The polymer was purchased as Matrimid[®] 5218 from Ciba-Geigy Corporation.

2.2. Pilot casting

In order to demonstrate a continuous manufacturing process, the membrane was prepared upon a pilot coater. The process steps involve polymer dope preparation, casting of membrane upon the support fabric, with quenching in a water bath to form the asymmetric membrane structure. The wet membrane is then taken through a solvent exchange process. The membrane is finally air dried to give the finished product. Finished membrane is shiny and smooth, yellow in color, without visible defects, and appears dry.

This process is detailed in an earlier publication [15]. Membrane produced by this process is used in all of the laboratory performance studies in this report. Fig. 3 shows cross-sectional views of the asymmetric membrane. Note that we chose to prepare a structure free of macrovoids in order to avoid potential weak spots in the membrane during high pressure operations. The skin layer on the membrane surface appears to be less than 0.2 μm in thickness.

2.3. Collection of membrane performance data

The membrane performance tests were done with coupons on a bench scale test system with four high pressure cells. The cells are connected in series with the retentate from each cell serving as feed for the next cell. A distributor plate over the surface of the membrane spreads the feed across the membrane from the center. The cells are mounted in an insulated box which is kept cold with chilled air produced by vortex tubes (Exair Corporation, Cincinnati, OH). The small pump (Pulsa 680 from Pulsafeeder, Rochester, NY) used to circulate the feed was run at full flow (46 ml/min). A jacketed cooling coil was used to chill the feed before entering the test cells.

Samples are mounted in the cells, air coolers are turned on to prechill the test cells, the pump turned on to circulate the feed, and the system brought up to the

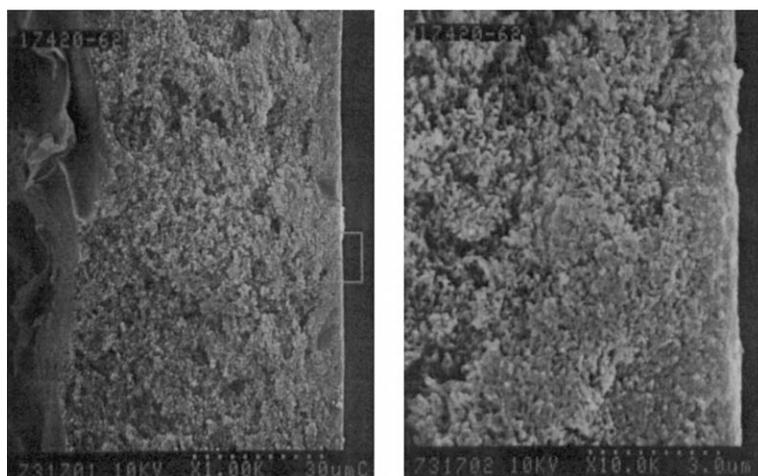


Fig. 3. Cross-section scanning electron microscopy views of asymmetric polyimide membrane at 1000 \times and 10000 \times magnification of the active separation layer. The membrane was first washed with hexane to remove conditioning agents and the backing removed. The active surface layer is on the right.

desired operating pressure, generally 41 atm (600 psi). The first samples are collected after about 2 h in order to allow the permeate lines to flush. Oil content of samples were determined by gravimetric analysis. The solvent ratio (MEK/toluene) as a weight ratio was determined from gas chromatography (GC) analysis. An OV-101 column (6 ft, 1/8 in.) (Alltech Associates, Deerfield, IL) was used to split the samples into MEK and toluene peaks.

Rejection refers to the ability of the membrane to keep lube oil out of the permeate in a single stage process. It was calculated by

$$\% \text{rejection} = \left[1 - \left(\frac{\% \text{ oil in permeate}}{\% \text{ oil in retentate}} \right) \right] \times 100$$

2.4. Correction factors

Nominal feed composition was 20 wt.% lube oil, 80 wt.% solvent with a 1:1 MEK/toluene ratio, and an operating temperature of -10°C (14°F). Due to sample collection and solvent loss during loading and unloading of coupons the oil content was rarely 20% exactly, but usually in the range of 18–22%. Temperature of the cells was also found to vary from day to day but were generally in the range of 0 to -10°C . The MEK/toluene ratio also changed as permeate was removed and this value was constantly monitored.

Since the membrane optimization process requires looking for relatively small changes in membrane performance, it is useful to reference the data to a standard set of conditions. These reference conditions were chosen at -10°C and 20% lube oil. The variation in the solvent (MEK/toluene) over the range of ratios that were tested did not appear to be a major factor and no corrections were applied. The variations in the actual test conditions were recorded with each set of readings. Earlier work had determined that both temperature and oil content influence the permeate flow

rate though the coupon, but that rejection was unaffected. Therefore, we used scaling factors to correct flux values to reference conditions.

3. Results

3.1. Permeation properties

Typical performance data is shown in Table 1. We have good rejection of lube oil and substantial solvent flux through the membrane. From this data one can calculate permeation coefficients for this membrane. Using a membrane transport equation [16]

$$J_i = D_i K_i (c_{i0} - c_{ip} \exp(-v_i(P_o - P_p)/RT))/L$$

where J_i is the membrane flux for component i , D_i the diffusion coefficient for component i , K_i the membrane sorption coefficient for component i , c_{i0} the concentration of component i in the liquid at the feed interface (mole fraction), and c_{ip} the concentration of component i in the liquid at the permeate interface (mole fraction). Molar volume for component i is v_i , P_o the applied pressure, P_p the permeate pressure, R the gas constant, T the temperature, and L the membrane thickness.

We do not have available in this laboratory a method to independently measure the thickness (L) of the active layer of the asymmetric membrane. The conditioning agent present in the membrane also interferes with this measurement. It is possible to experimentally determine sorption (K_i) and diffusion (D_i) coefficients for dense film samples but these values do not necessarily correspond to values for an asymmetric membrane. Since we do not have these three values the factor of $D_i K_i / L$ was lumped into one value. Multiplying by molar volume leads to a transport rate in mm/h for each component in the feedstock.

Table 1
Permeation experiment with polyimide membrane^a

Component	Feed (wt.%)	Permeate (wt.%)	Relative $D_i K_i / L$	Relative transport rate
MEK	46.5	61.0	1057	214
Toluene	34.7	38.6	227	54.3
Lube oil	18.8	0.40	1	1

^a Conditions: temperature of -5°C (23°F), 41 atm (600 psi) applied pressure, permeate flux of 16.1 ml/h, and lube oil rejection of 98%.

Each of the other factors in the equation can be estimated. Therefore, if one knows the permeate flux of a component and the concentrations and pressures at which this value was measured then one can calculate the transport rate of the component. Table 1 lists a three component solution of MEK, toluene, and lube oil. Although, lube oil is a complex hydrocarbon mixture, this calculation was based on an oil containing one representative component, $C_{25}H_{52}$. For this discussion, oil is assigned a relative rate of 1. One estimates that rates are in the order of $MEK > \text{toluene} \gg \text{lube oil}$. This also indicates that if the MEK/toluene ratio increases there are gains in flux without a corresponding increase in oil content in the permeate.

3.2. Feedstock variation

Most of the laboratory tests were run with a feedstock prepared from Mobil light neutral base oil and pure solvents purchased from Aldrich Chemical Company (Milwaukee, WI). In order to confirm that our results were not dependent upon this single feedstock, tests were made with two additional feedstocks. These feedstocks were collected by sampling from a commercial refinery filtrate stream directly after rotary filters used to remove wax. Drums of these materials were sent to the laboratory and used without further treatment in our test unit. These samples were labeled as low viscosity and high viscosity filtrates.

Table 2
Coupon tests of various filtrate streams^a

Feed solution	Flow (ml/h)	Rejection (%)
Low viscosity filtrate	15.9	95
High viscosity filtrate	7.5	99
Laboratory filtrate	12.5	96

^a Conditions: 41 atm (600 psi), normalized to -10°C and 20% lube oil content.

Table 3
Analysis of filtrate solutions used for membrane tests

Parameter	Low viscosity	High viscosity	Laboratory
Oil (wt.%)	19.0	21.1	18.4
Water content	0.5%	0.4%	0.4%
MEK/toluene ratio	1.82	0.96	1.30
Temperature: $^{\circ}\text{C}$ ($^{\circ}\text{F}$)	-8 (18)	-7 (19)	-7 (19)

Results are listed in Table 2 for testing of coupons with different feedstocks. The actual test conditions for each feedstock are listed in Table 3. In this test the low viscosity filtrate behaved in the same manner as the laboratory feedstock. This was as expected, since both solutions were of similar viscosity. In addition, the high viscosity feedstock was also successfully treated with this membrane process at cold temperatures. The high viscosity filtrate has lower flux with slightly higher rejection of lube oil. This indicates that a commercial plant can process feedstocks at economically viable rates over a range of viscosities.

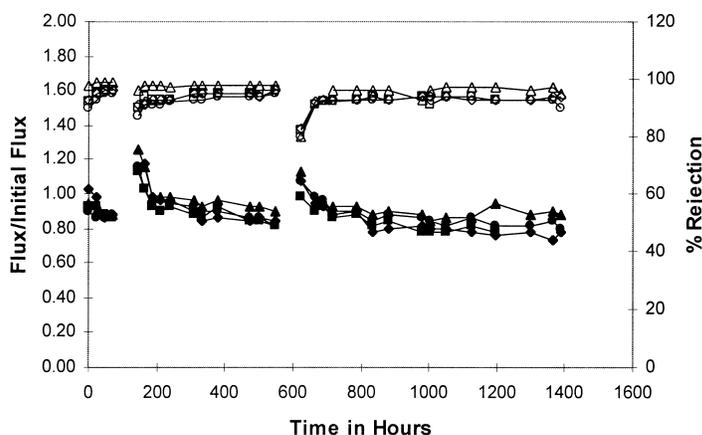


Fig. 4. Two month test of polyimide membrane at -10°C , 41 atm (600 psi), and 20% lube oil. Flux (solid symbols) and rejection (open symbols) for four coupons.

3.3. Longer term membrane testing

A critical question in the performance of a commercial membrane unit is the expected useful lifetime of the membrane. Experiments were run to demonstrate membrane stability and estimate long term performance of the membrane.

Fig. 4 shows data for coupons tested over a 2-month period. As expected, initial flux declined to a steady state performance level due to membrane compaction at 41 atm (600 psi). After the first 100 h the coupons reached lined out performance. Compaction is a slow process where the structure just below the dense working layer of the membrane densifies under pressure to reduce flux through the membrane.

There are two breaks in the test, at 100 and 600 h, when we were forced to shutdown the system over two different weekends. In each case there was a temporary jump in flux and loss in rejection upon restart.

Experience in other membrane systems suggests that the best method to predict long term membrane performance from extrapolated data is to use a plot of flux versus log hours. This is shown in Fig. 5, where flux versus log hours are fit to straight lines. Due to the two interruptions from weekend shutdowns, only the data from the last readings before shutdowns are used to estimate the long term performance. At these points the coupons all had high rejection (95%) and it is assumed that lined out performance had been achieved. When the lines are extrapolated to 12 500 h the estimate of flux at -10°C remains 84% of the

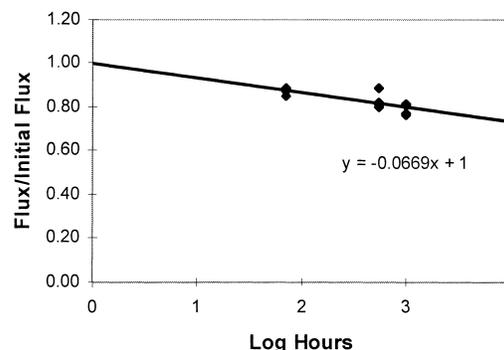


Fig. 5. Extrapolation of long term membrane performance at -10°C and 41 atm (600 psi) with 20% lube oil in MEK/toluene. The line represents the least squares fit of the data.

flux observed at 100 h. It also appears that solvent with less than 1% oil impurity can be maintained. This time of 12 500 h corresponds to 1.5 years, and is representative of desired performance life for a membrane system in solvent dewaxing.

With high values for membrane rejection, less membrane area is required in order to produce the same quality permeate compared to a low rejection membrane. If the membrane has lower flux at higher rejection, one can compensate in the membrane system design in order to keep the cost the same. System design is dependent on membrane performance. Subsequent to the laboratory work a membrane system using a commercial version of polyimide membrane has been installed and integrated with a solvent

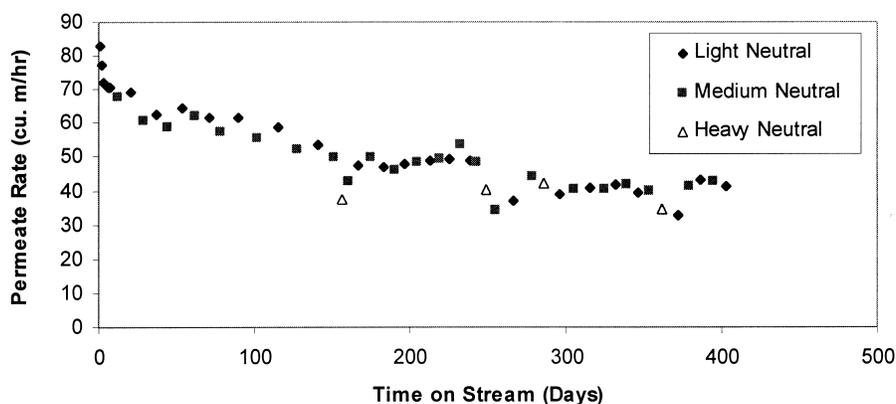


Fig. 6. Permeate production rate on commercial membrane unit for solvent recovery. Plant operating conditions vary as different neutral base stocks are processed.

dewaxing unit [17]. Developing a membrane module that has mechanical, thermal, and solvent stability required a multi-year program to identify and control the key features of the process. This included working out the process for commercial scale membrane production, identifying solvent resistant materials and a design for the module, finding non-destructive quality control tests for these modules, and gaining critical process experience through operation of a large scale demonstration unit at the refinery with actual feedstock for 16 months. The resulting commercial unit, designed for a maximum feed rate of 11 500 cubic meters per day (72 000 barrels per day), is at Mobil's Beaumont, Texas refinery. It is thought that this is the largest membrane separator of liquid organics in the world. The process was designated as a 1999 Kirkpatrick Honor Award recipient [18].

Permeate flow data from the commercial Beaumont unit is shown in Fig. 6 over the initial 400 days of operation. Although, these values are from membrane packaged as spiral-wound modules and operated under plant parameters, the shape of this curve mirrors that developed with coupon tests. In at least this system, it is possible to project potential membrane performance over a period of months using coupon data. In addition, the oil content in the solvent from the permeate stream of the commercial unit has been consistently under 1%, exceeding expectations from the original laboratory work.

4. Conclusions

The polyimide membrane for lube oil separation shows flux and rejection that exceed the targets for a conceptual commercial membrane system to have favorable economics. Better than 95% rejection of lube oil at -10°C (14°F) with 20 wt.% lube oil yields cold solvent at better than 99% purity. With the high rejection levels obtained it is possible to use the membrane system as a one stage design and still maintain low levels of oil in the permeate stream. This permeate stream of cold solvent can then be directly recycled back into the feedstock in a lube dewaxing unit.

Transport rates are estimated using a solution-diffusion model for this asymmetric membrane. This solvent recovery process is driven by a pressure gradient, and the low transport rate for lube oil compared

to solvents reflects the high rejections observed in the experiments. In addition, the observation that high viscosity filtrate, containing lube oil molecules of higher molecular weight, has better rejection than low viscosity filtrate is consistent with a diffusion controlled mechanism. The membrane also has solvent selectivity, since MEK molecules permeate at a greater rate than toluene, changing the ratio of solvents in the permeate compared to the feed. This dependence upon molecular parameters indicates that the membrane operates in a hyperfiltration mode.

Laboratory tests of the membrane show stable performance with 2 months of continuous testing. The projected performance at 12 500 h (1.5 years) from this data at -10°C is for a membrane that maintains 84% of the flux observed after the first 100 h. Therefore, these experiments demonstrate that this polyimide membrane can meet the demands of a hybrid process for solvent recovery from the chilled dewaxing process.

A commercial version of a polyimide membrane packaged as spiral-wound modules by Grace Davison Membranes was installed in 1998 as the separation membrane in a process called MAX-DEWAX. The objective of the MAX-DEWAX unit at Mobil's Beaumont refinery was to maximize base oil production up to the capacity of the existing refrigeration compressors. An engineering study had indicated that expansion beyond that point would be cost prohibitive. Prior to installation of the membranes, the solvent dewaxing unit was simultaneously limited by refrigeration and solvent handling capacity in the dewaxed oil recovery section when running light neutral stock. It was limited by both chilling train hydraulic capacity and filter surface area availability when running heavier stocks. The MAX-DEWAX process, combined with selected ancillary equipment upgrades, increased base oil production by over 25 vol.% and improved dewaxed oil yields by 3–5 vol.%. Total energy consumption at the higher throughput was essentially the same as before the expansion. Consequently, energy use per unit volume of product was reduced by nearly 20%. The installed cost of the membrane unit was about one-third of that which would have been required for equivalent process improvements using conventional technology. The capital expenditure was paid back in less than 1 year by the increase in the net profitability of the lube dewaxing plant.

MAX-DEWAX is a trademark of Mobil Oil Corporation.

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