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Separation of *p*-Xylene from Multicomponent Vapor Mixtures Using Tubular MFI Zeolite Membranes

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Zeolite Membranes for Xylene Separations

Objectives:

Development of stable and selective membranes to effectively separate pX from other isomers

Energy Savings Potential: ≈ 8.3 trillion BTUs by 2030

Combined membrane synthesis, process modeling, and evaluating the economics of the membrane assisted processes

Attract an end-user chemical / petrochemical company to participate in development of process

Project Scope

On-going DOE program to develop stable and selective membranes for p-X
Cooperation of Sandia National Laboratories
University of Cincinnati
TEMEC

Zeolite Membrane: development needs precise control of pore structure and adsorption properties of defect-free modified zeolite thin film membranes.

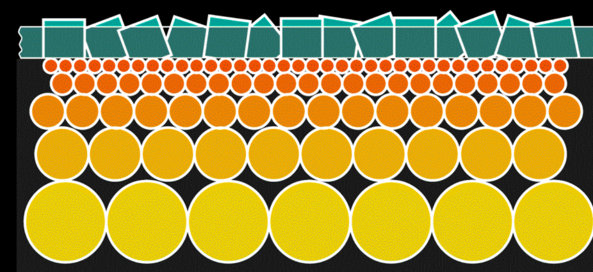
Project includes:

- synthesize zeolite membranes (disks/tubes) & test
- synthesize modified zeolite membranes
- model process scenarios, membrane feeds
- test selectivity of modified zeolite membranes
  - 25/50/25 p/m/o-xylene
  - diluted industrial simulant stream (C8 without Nonane)
  - concentrated industrial simulant stream (without nonane)

Zeolite Membranes

Hydrothermal synthesis for the growth of defect-free zeolite phases for preferential adsorption and size selectivity.

Schematic:
Nonselective porous membrane support w/ selective molecular sieve top layer in green. →



Actual Membrane Supports →

- *Ceramic*
- *Stainless steel*
- *Hybrid materials*

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MFI Thin Film Membranes

Support:

α-Al_2O_3, 8cm long, 7 ID, 10 mm OD
Ends coated w/glass sealing layers
Bore side top layer: 0.2μm, porosity of 35-40%

Membrane Synthesis:

Hydrothermal synthesis of zeolite: NaOH + SiO_2 + TPAOH
resulting in a visually clear solution
Solution was filtered, and transferred to cylindrical autoclave
Support suspended horizontally in the solutions in an autoclave
Autoclave rotated 3rpm, 180°C, 20 hours

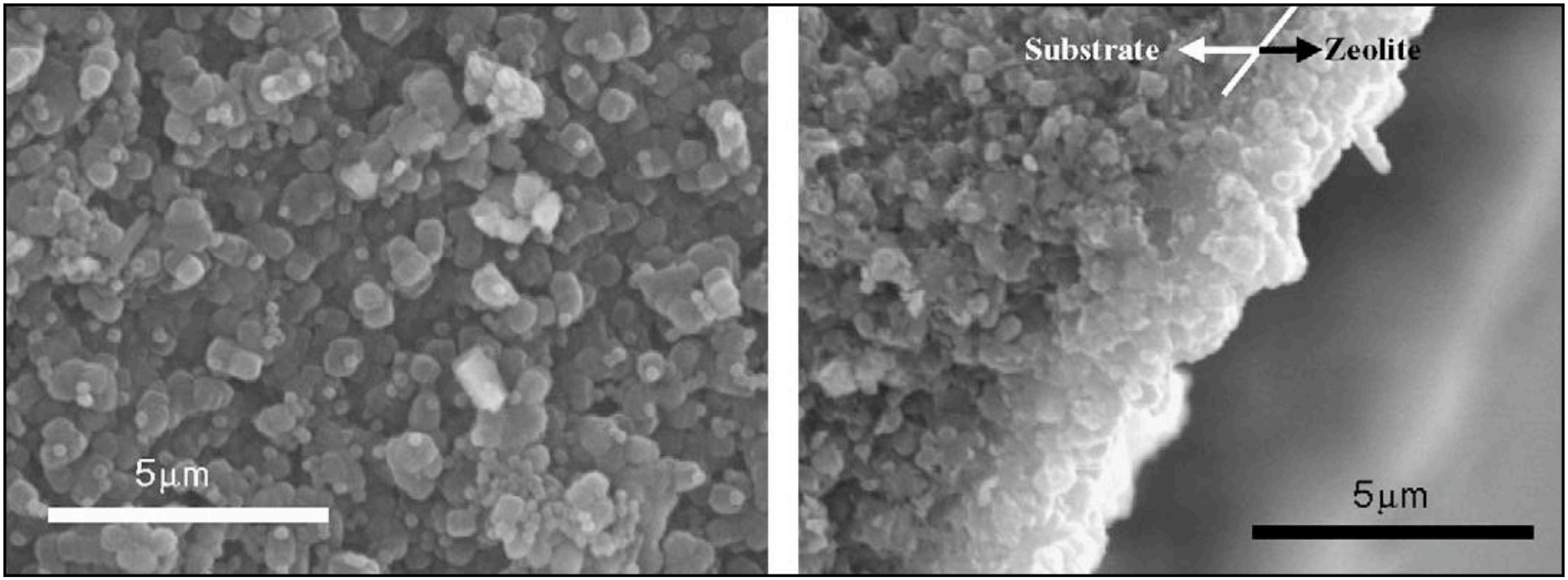
Removed, washed, dried, heated 450°C for 8 hrs
Thermal treatment repeated 2x

Recovered, washed, dried in air

Zeolite membrane on inner tube surface only ≈ 2 micron thick film

Synthesized MFI Zeolite Characterization

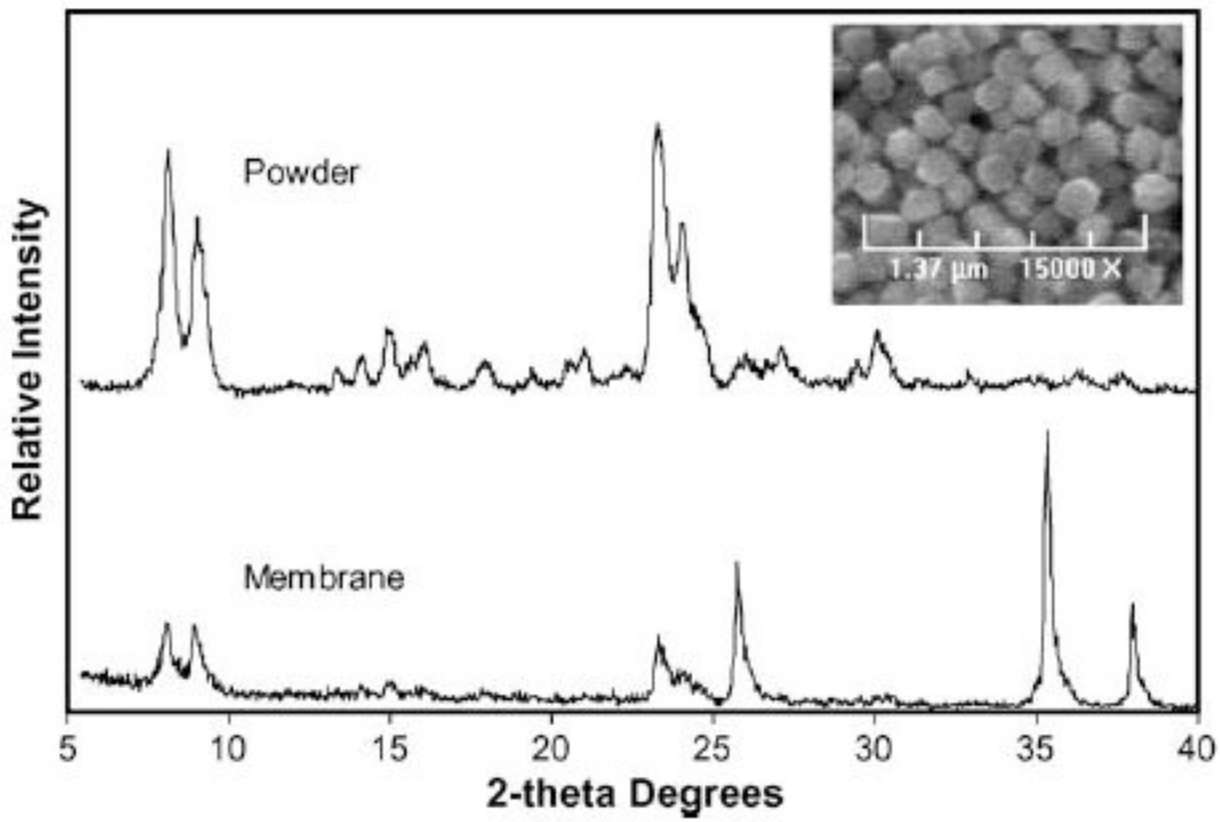
Micropore : Mesopore volume ≈ 7:1
Micropore size = 5.8Å



SEM of tubular MFI membrane (left - surface; right - cross section)

Synthesized MFI Zeolite Characterization

XRD pattern of MFI zeolite powders collected from residual liquid Phase and the MFI tubular membrane (insert: SEM picture of the Particles from the residual solution).



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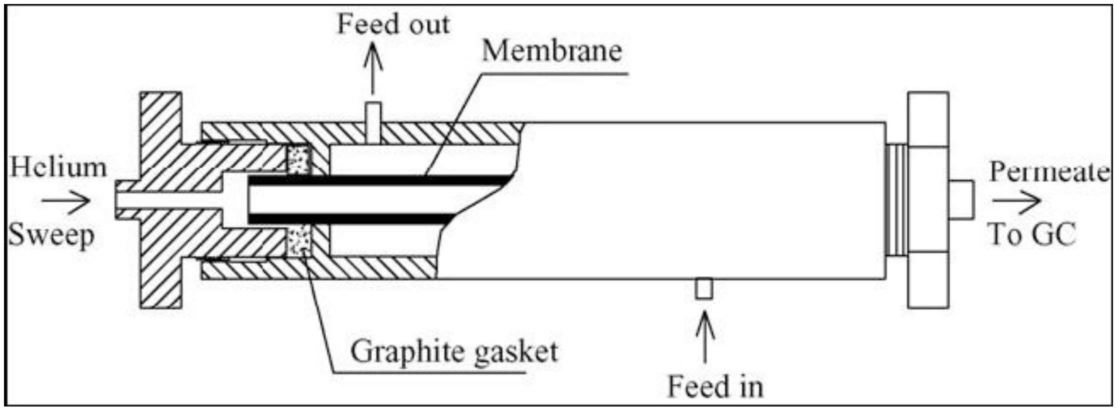
Membrane Separation

Permeation Testing:



Separation factor of component i for a multicomponent stream S_i

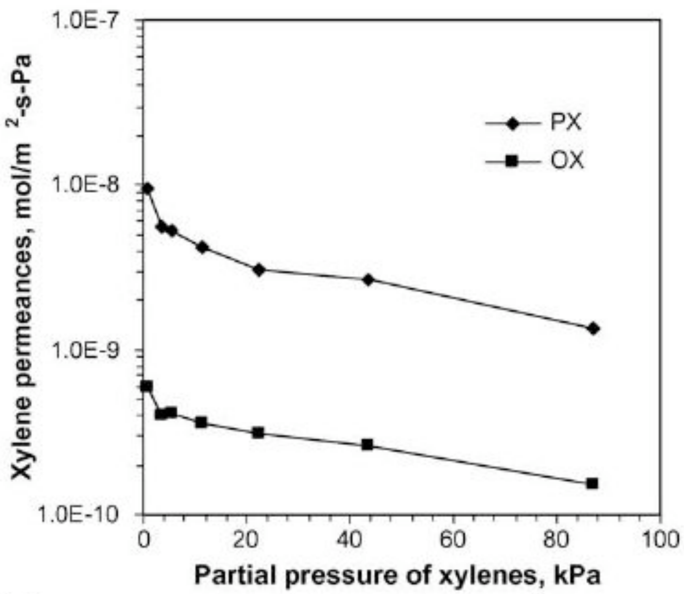
$$S_i = \frac{y_i/(1-y_i)}{x_i/(1-x_i)}$$

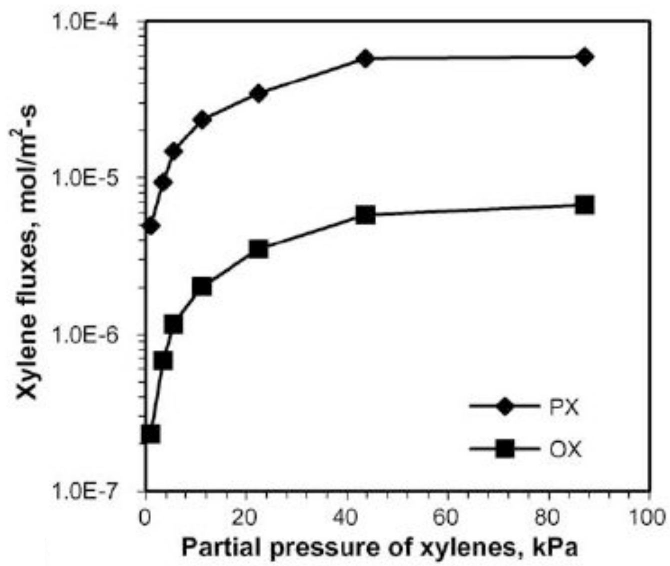
Membrane selectivity for component i over component j

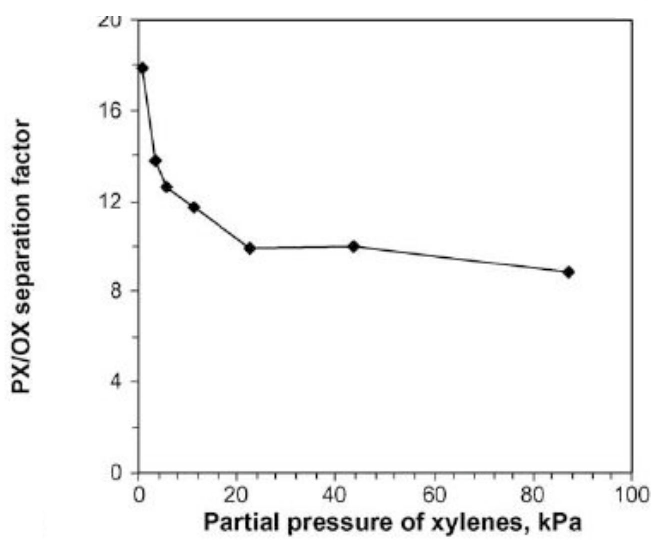
$$\alpha_{i/j} = \frac{y_i/y_j}{x_i/x_j}$$

Membranes tested for permeation using the Wicke-Kallenbach method
Sweep flow = 15 ml/min, Atmospheric Pressure (87kPa)
Temperature = RT ≈ 400°C

Separation Results vs. Feed Pressure







PX/PO separation =17.8 for binary mixture
At 250°C, PX permeance = 9.5×10^{-9} mol/(m^2sPa)

Max PX/PO permselectivity 72.9 at 150°C

Multicomponent Stream

8 component (C8) Industrial Stream Simulant

Components	Feed flow rate (mol/s)	Composition (mol%)
Hydrogen	7.44E-6	48.8
Methane	1.27E-6	8.3
Benzene	1.52E-7	1.0
Toluene	1.52E-7	1.0
Ethylbenzene	9.6E-7	6.3
P-xylene	1.28E-6	8.4
M-xylene	2.71E-6	17.8
O-xylene	1.28E-6	8.4

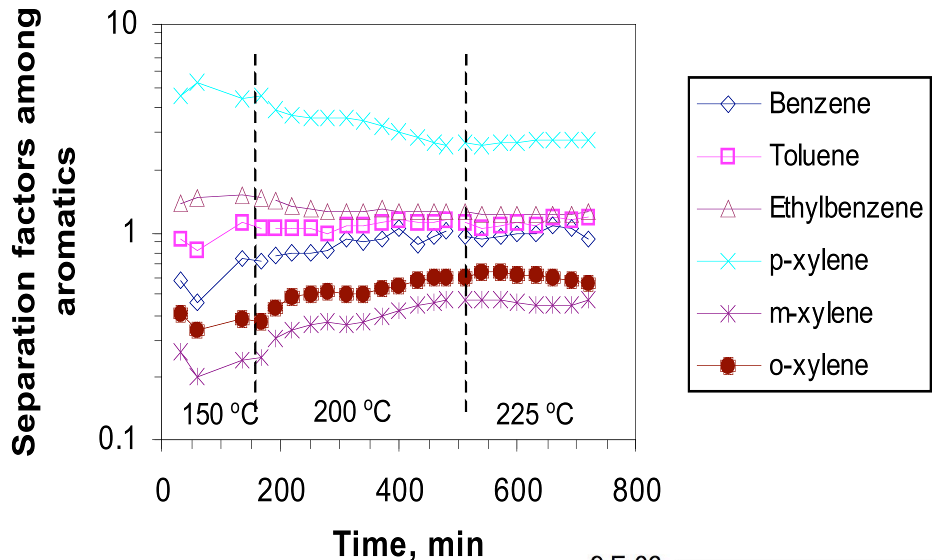
Relative ratios approximate concentrated industrial stream

The highest separation of p-X over other aromatic components were obtained 250-275°C.

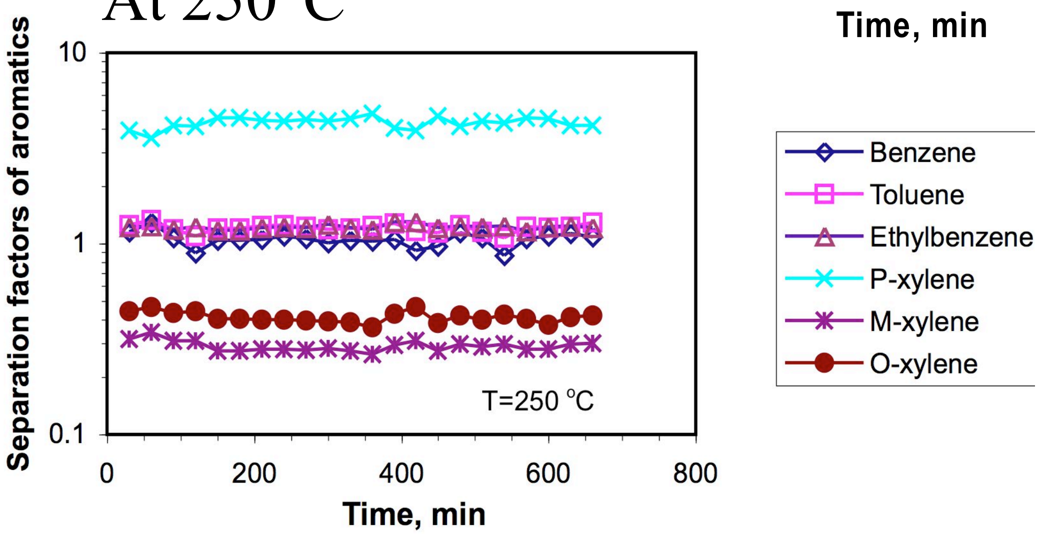
Over 300°C, decline in performance; reversed by regeneration at 400°C.

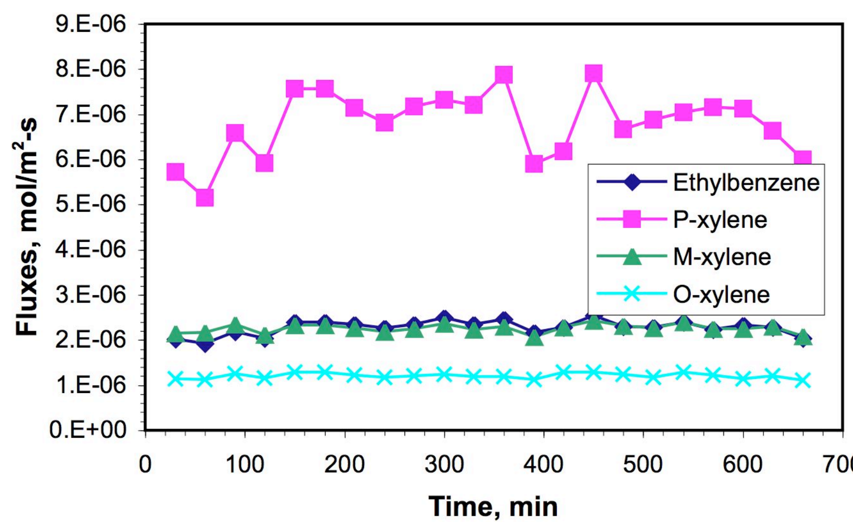
Multicomponent C8 Stream Separations

Best permeation factors based on separation, flux and stability with time

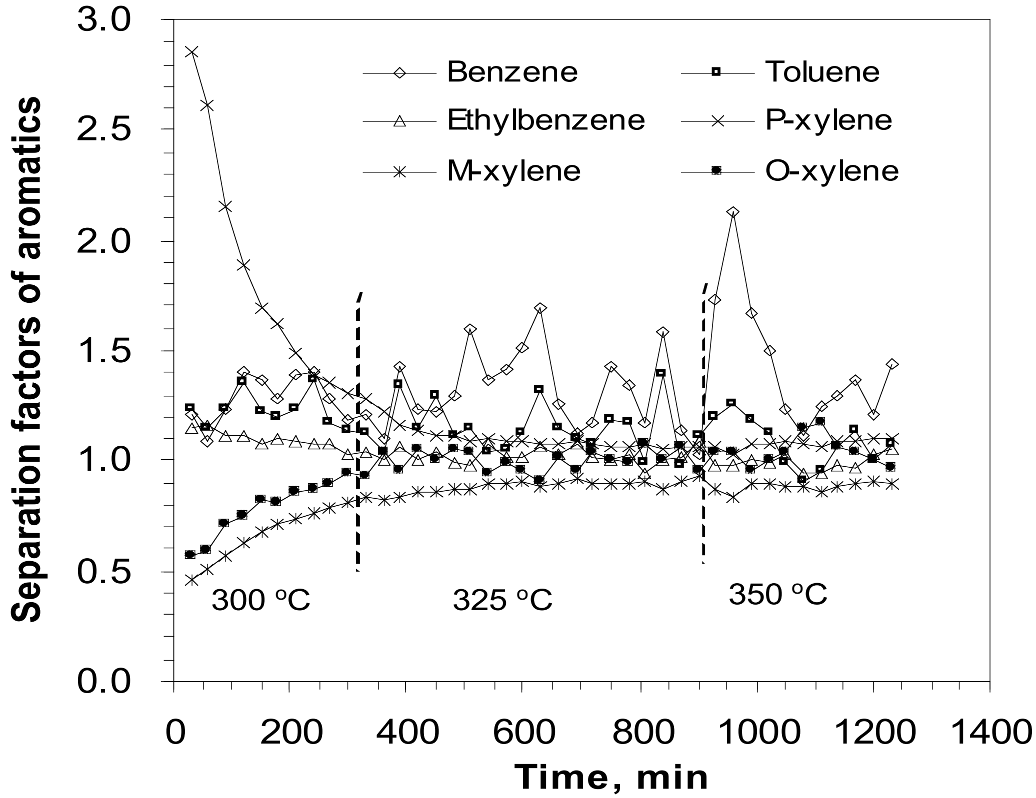


At 250°C





Separations vs. Operation Temperature

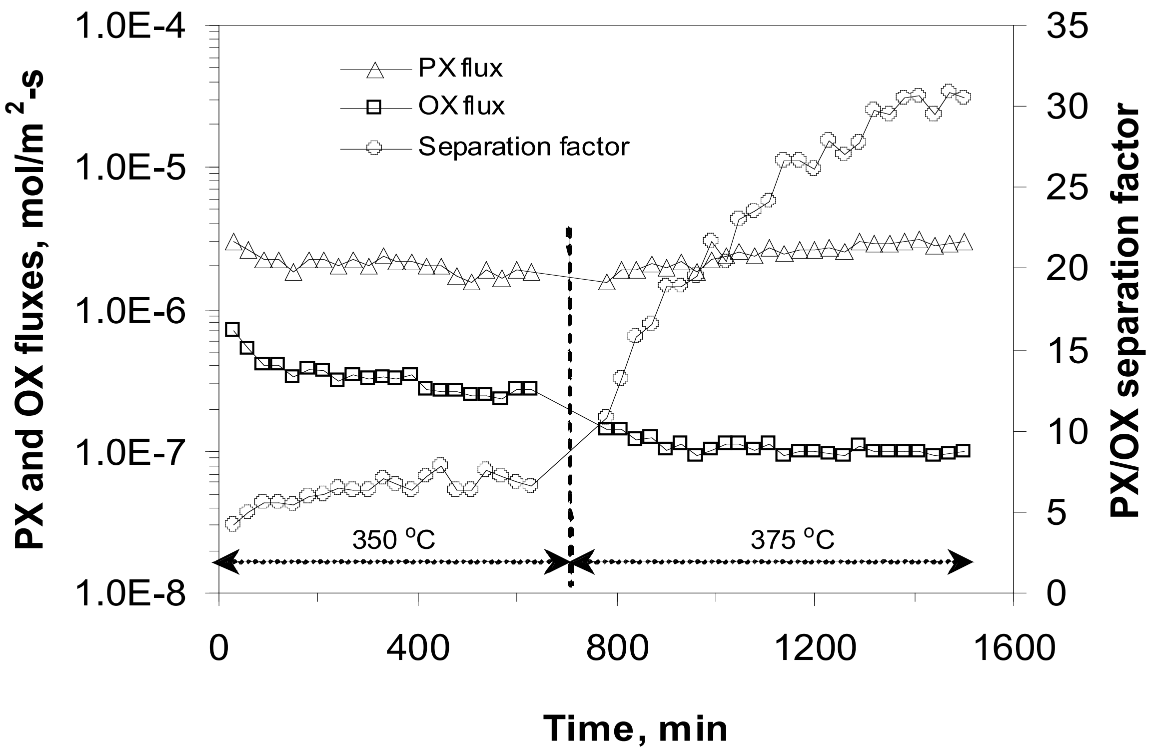


Over 300°C, PX flux and PX/(MX + OX) selectivity decline drastically in 5hrs of operation

On-line Membrane Modification/Repairing

Modification: on-line vapor addition of 1,3,5-triisopropylbenzene (TIPB, molecular size 8.4Å).

Added by bubbling 5ml/min He through a TIPB column at 70°C (permeate side was swept by H_2 at 8ml (STP)/min



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Conclusion

• Tubular MFI zeolite Membranes for separation of PX from simulated multicomponent mixtures under practical conditions.

• PX separation from MX and OX based on size selectivity is achieved by minimizing xylene adsorption level.

• high separation values are enhanced in multicomponent streams by On-line membrane repairing method with TIPB

• Economic Viability of these membranes, PX flux may be the key factor to Implementation of the membrane in commercial processes.