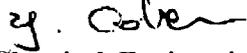


MEMORANDUM

October 28, 1997

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HE: Annual Progress Report for the Period 9/15/1996-9/14/1997
"Novel Ceramic-Polymer Composite Membranes for the Separation of Liquid Waste"
Award: DE-FG07-96ER14715;A000

Attached is the annual progress report in connection with the above referenced project. Significant progress was made last year and we are now in a position to apply for a patent on a novel pervaporation membrane, optimize our ultrafiltration membrane for oil-in-water treatment and develop a pervaporation membrane for the separation of organic-organic mixtures. A series of fundamental studies are also underway to explore the structure of the surface polymer and the mode of solute diffusion through the brush layer.

Confidential Report
For Review by
Dr. William Millman
and Dr. Ramoncita Massey

**Novel Ceramic-Polymer Composite Membranes
for the Separation of Liquid Waste**

Annual Progress Report

Period: 9/15/1996-9/14/1997

Submitted to:

U.S. Department of Energy

By

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For Review by
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**Novel Ceramic-Polymer Composite Membranes
for the Separation of Liquid Waste**

Annual Progress Report
Period: 9/15/1996-9/14/1997

by
Yoram Cohen
Department of Chemical Engineering
University of California, Los Angeles

Synopsis

The project on ceramic-supported polymer membranes focuses on the development of a novel class of membranes for the separation of organics from both organic-aqueous and organic-organic mixtures. These membranes are fabricated by a graft polymerization process where polymer chains are grown onto the surface of a ceramic support membrane. The surface graft polymerization process, developed at UCLA, results **in the** formation of a thin polymer layer covalently bonded to the membrane pore surface as **a** layer of terminally anchored polymeric chains. Through the selection of the polymer most appropriate for **the** desired separation task, the graft polymerized surface layer can be synthesized to impart specific separation properties to the membrane. It is expected that this project will lead to the demonstration of a new technology for the “tailor design” of a new class of selective **and** robust ceramic-supported polymer membranes. This new approach will allow the rapid deployment of task-specific membranes for **the** separation of waste constituents for subsequent recovery, treatment or disposal.

Progress to date includes the preparation of successful silica-polyvinylpyrrolidone (PVP) membrane for the treatment of oil-in-water emulsions and a silica-polyvinylacetate (PVAc) pervaporation membrane for the separation of organics from water. Current work is **ongoing** to study the performance of the pervaporation membrane for the removal of chlorinated organics from water **and** to develop a pervaporation membrane for organic-organic separation. In another aspect of the study, we are studying the hydrophilic PVP CSP membrane for oil-in-water emulsion treatment with the goal of determining the optimal membrane **polymer** surface structure as a function of various operating conditions (e.g., tube-side Reynolds number and transmembrane pressure). Work is **also** in progress to characterize the polymer layer by AFM and internal reflection FTIR, and to model the conformation of the polymer surface layer,

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CSP Membranes for Separation of Oil-in-Water Emulsions

Successful tubular silica-polyvinylpyrrolidone (silica-PVP) membranes was prepared for the separation of oil-in-water emulsions. This membrane was prepared after initial studies with silica disk supports (Castro et al., 1996). Initial performance studies with the new tubular Silica-PVP membrane revealed that the separation properties of the membrane can be controlled by the density and size of the grafted surface chains. For example, a surface of short and dense PVP chains was shown to reduce the adsorption of oil droplets onto the surface of the membrane and thereby significantly reducing membrane fouling (Figure 1). A grafted layer of longer chains with surface density that permits the penetration of liquid through the brush layer resulted in membrane performance that significantly surpassed that of the unmodified membrane at high Reynolds numbers (Figure 2). The behavior of this latter membrane is linked to the flow-induced deformation of the polymer chains. As the shear rate at the wall (on the membrane tube-side) is increased the surface chains arc stretched and begin to align in the flow direction. At a sufficiently high shear rate the polymer chains align with the flow to the point where the chains screen the membrane pores from the oil droplets while allowing water, **which solvates the polymer, to permeate through the membrane.**

I am pleased to report that the AIChE Separation Divisions has selected our most recent work on the PVP CSP membrane for the best Faculty/Student Research Paper Award which to be presented, to my student Robert Castro and I, at the Annual AIChE Meeting which will be held in Los Angeles, November 16-21, 1997. Also, my student Ron Faibish, who is also working in on ultrafiltration with CSP membranes, was awarded a fellowship to attend the Gordon Research Conference last August.

References

(Castro, K., H. Monbouquette and Y. Cohen, "Polyvinylpyrrolidone-Silica Membranes for the Treatment of Oil-in-Water Emulsions", *J. Membrane Science*, 115, 179-187 (1996)

Pervaporation with CSP Membranes

In order to expand the potential use of CSP membranes for pervaporation we developed a protocol for the pervaporation of silica and zirconia-based pervaporation membranes with polyvinylacetate as the active membrane layer. A number of membranes were synthesized and their properties are provided in the attached table.

In order to evaluate the pervaporation performance of the membranes a pervaporation apparatus was built (as shown in Figure 3. In this system, a charge of a solution containing the solute to be separated is circulated through the pervaporation membrane module. The permeate is collected in a cryogenic trap for monitoring and the concentration in the reservoir is also monitored as a function of time. In the initial experiments trichloroethylene (TCE) was **selected** as a model solute to be removed from aqueous TCE solutions. The concentration reduction in the reservoir as a function of time, for three **different** tube-side Reynolds numbers, is shown in Figure 4 along with the **values** of the tube-side mass transfer coefficient as calculated from the appropriate literature correlations. The plot of the dimensionless concentration (where C_0 is **the** initial concentration of TCE in the reservoir) is shown in Figure 6 **along** with the enrichment factors (enrichment **factor** = TCE concentration in permeate/TCE concentration in reservoir feed solution). Clearly, the membrane resistance is negligible since the concentration decline is predicted essentially by the boundary layer mass transfer coefficient. Moreover, the enrichment factors are high such that the collected permeate consists of two **phases**, pure TCE and a TCE saturated aqueous phase. Experiments have shown **that** the performance of the PVAc membrane remains unchanged even at low concentrations of TCE, down to the low ppm level.

The PVAc CSP pervaporation membranes are the first successful ceramic-based pervaporation membranes for chlorinated solvents, These new membranes represent a major development and I expect that UCLA will submit a patent application for the PVAc CSP membrane.

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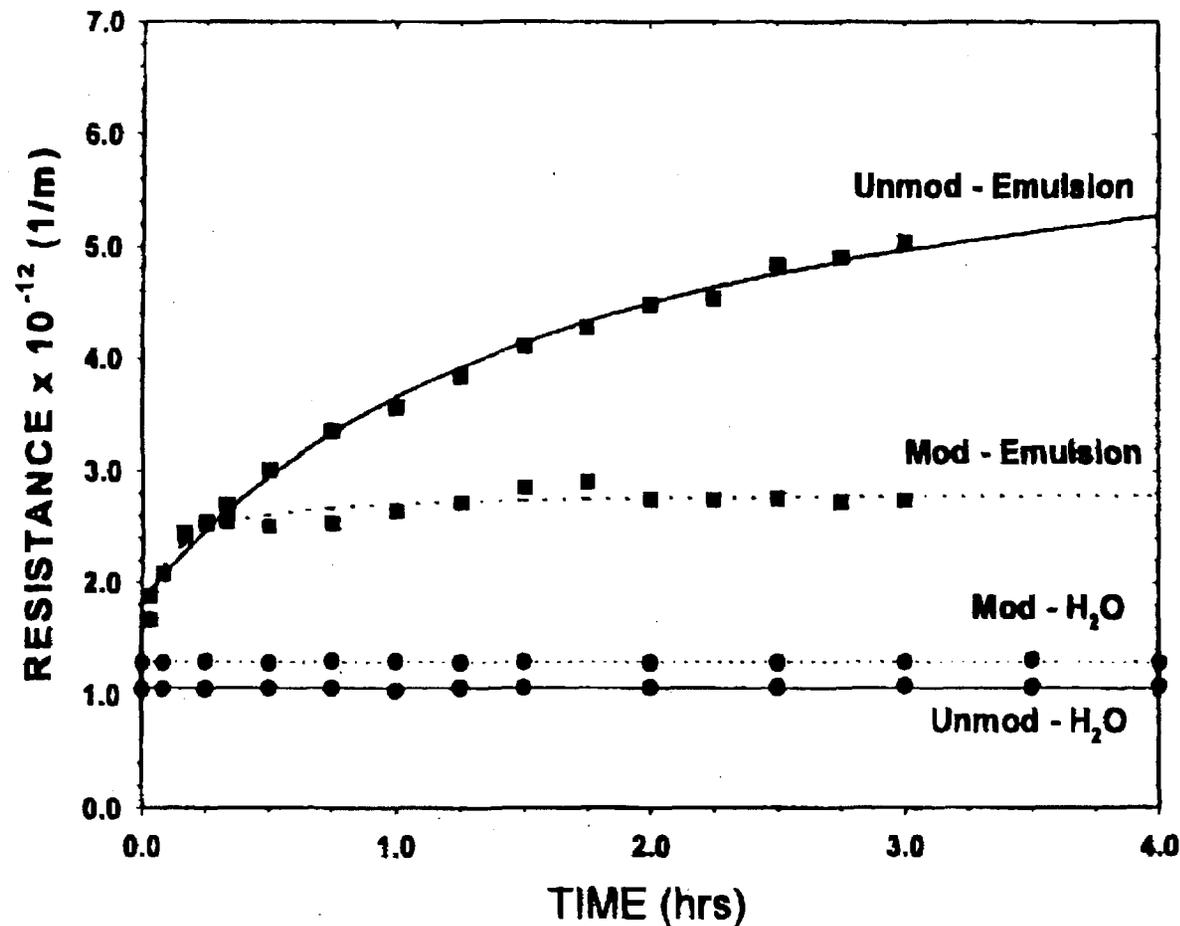
Plans for the Period 9/15/1997-9/14/1998

Our plans for this year include the systematic evaluation of the CSP pervaporation PVAc CSP pervaporation membrane over a range of conditions (including temperature) and over an extended period of usage in order to ascertain the long-term stability of the membrane. If the potential for long-term stability is shown to be positive, then I will work to obtain additional funds in order to construct a larger pilot-system for continuous operation. An additional task for the period 9/15/1997-9/14/1998 is to synthesize a pervaporation membrane for organic-organic separation. We are currently searching for an appropriate model system to demonstrate the technology and are also considering the use of a hydrophilic PVP CSP membrane for dehydration of a reaction mixture in a membrane/reactor configuration.

In addition to the membrane evaluation studies, a number of other projects were initiated this year in support of the membrane development work. Work was initiated on the study of the grafted polymer layer using Atomic Force Microscopy and internal reflection FTIR. The purpose of this part of the work is to better understand the degree of uniformity of surface coverage by the terminally anchored polymer chains and in relation to the reaction conditions. Another part of the program also involves the development of a theoretical model to study the conformation of the polymer surface chains when subjected to shear flow. Such information will help us understand the performance of the PVP CSP membrane for ultrafiltration operations.



EFFECT OF GRAFTED LAYER ON MEMBRANE RESISTANCE



EMULSION: Nonane/1-Butanol/Dodecylbenzenesulfonate/Water

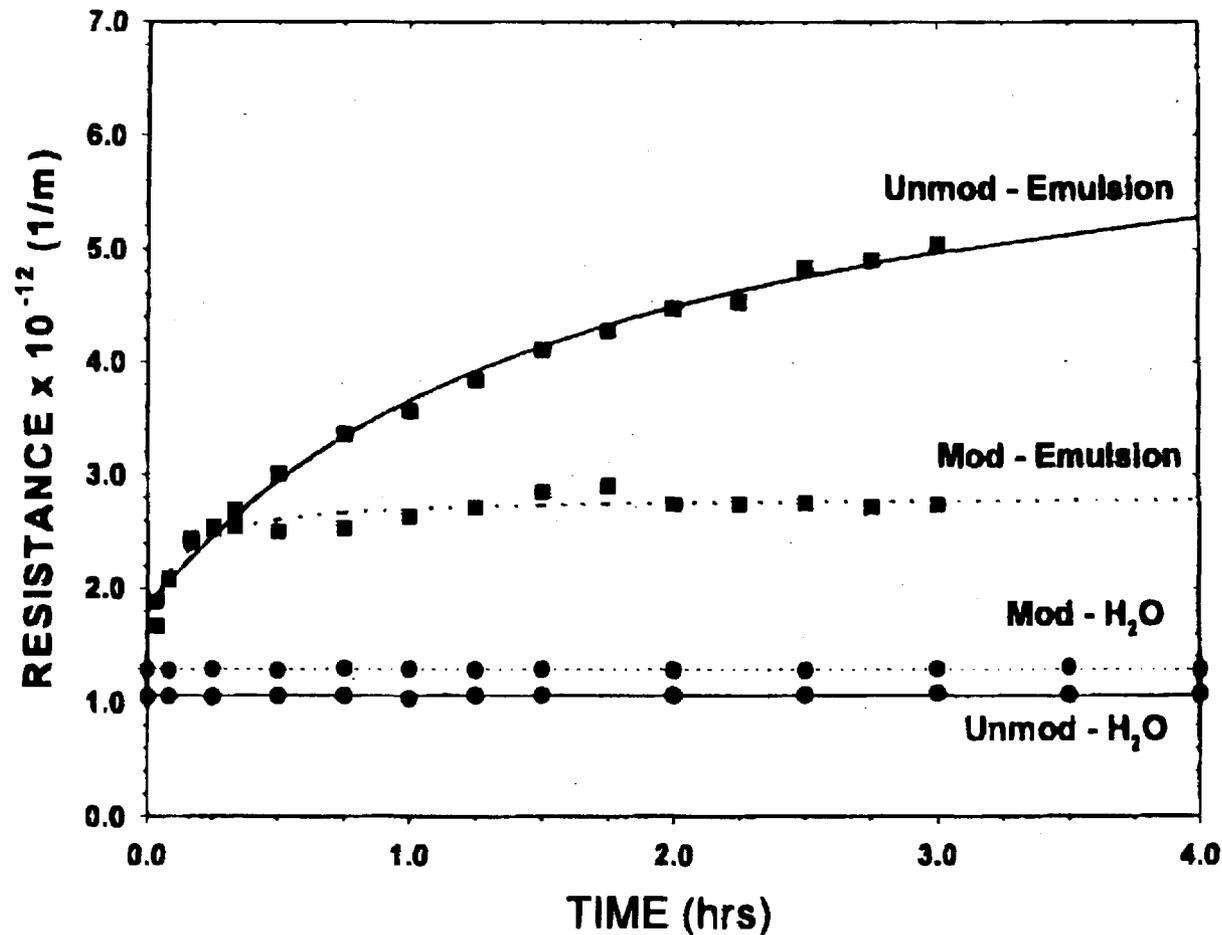
SUPPORT: Silica Tube (2000 Å)

$\Delta P = 8$ psig; $N_{Re} = 5320$

Figure 1



EFFECT OF GRAFTED LAYER ON MEMBRANE RESISTANCE



EMULSION: Nonane/1-Butanol/Dodecylbenzenesulfonate/Water

SUPPORT: Silica Tube (2000 Å)

$\Delta P = 8 \text{ psig}$; $N_{Re} = 5320$

Figure 1



Oil-in-Water Emulsion Treatment with a Tubular Silica-PVP Membrane

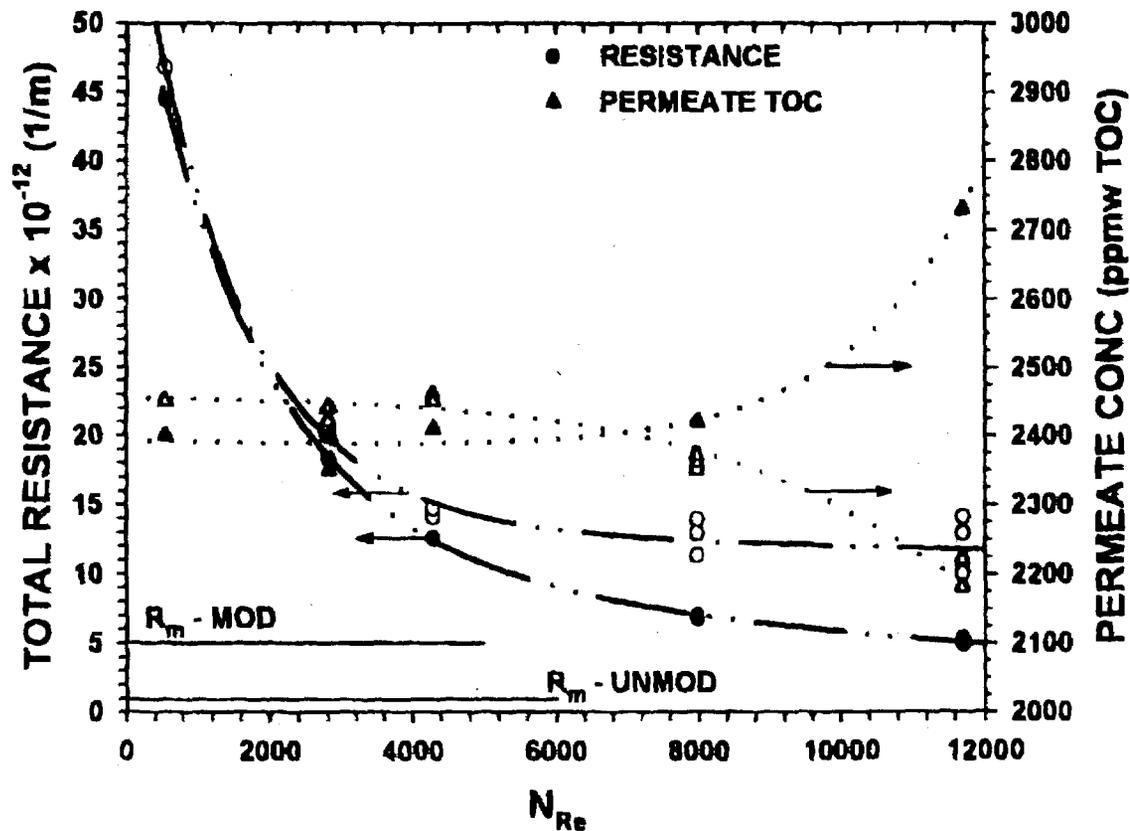


Figure 2

Experiment Apparatus for Pervaporation

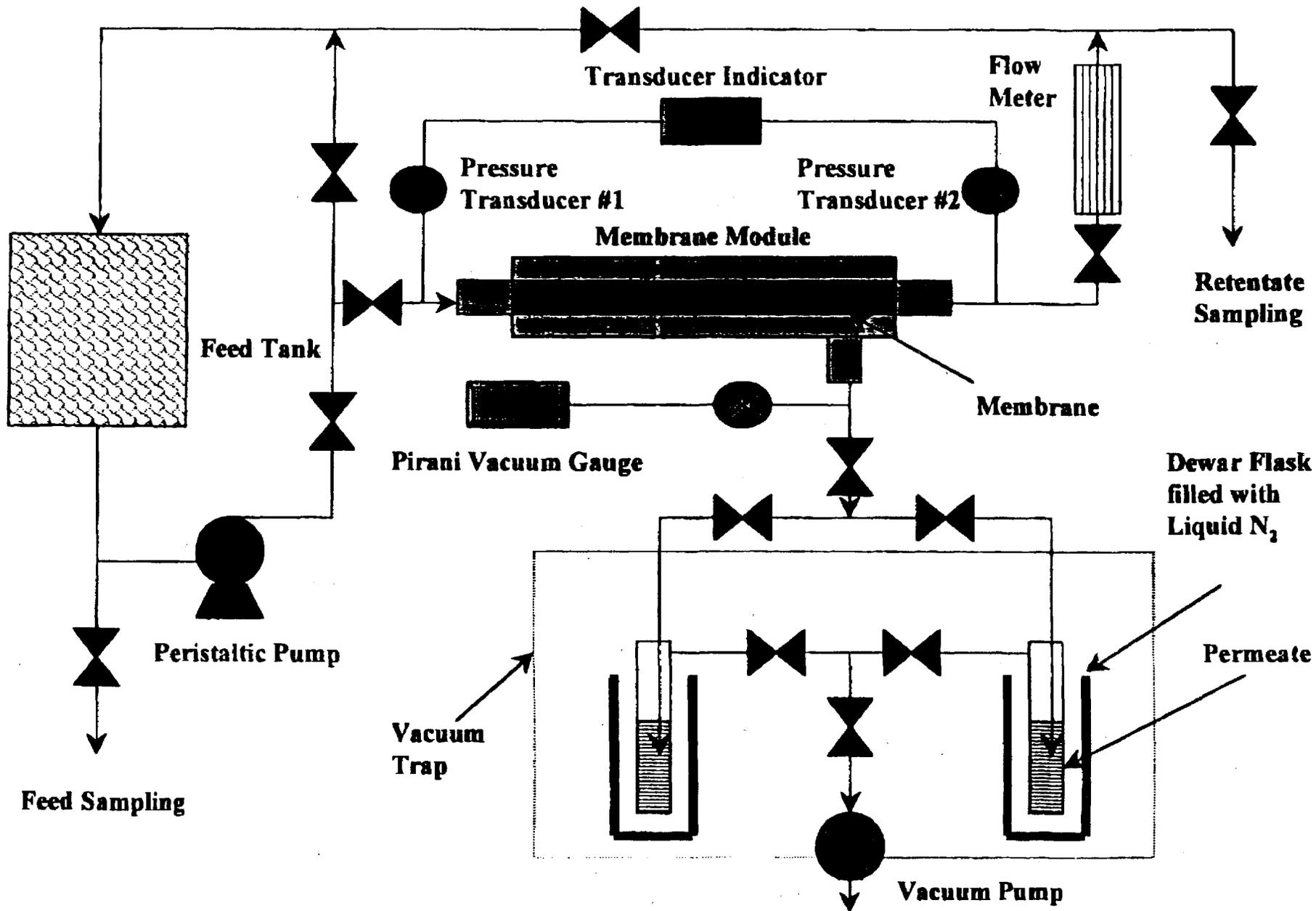


Figure 3

TCE Concentration in the Retentate

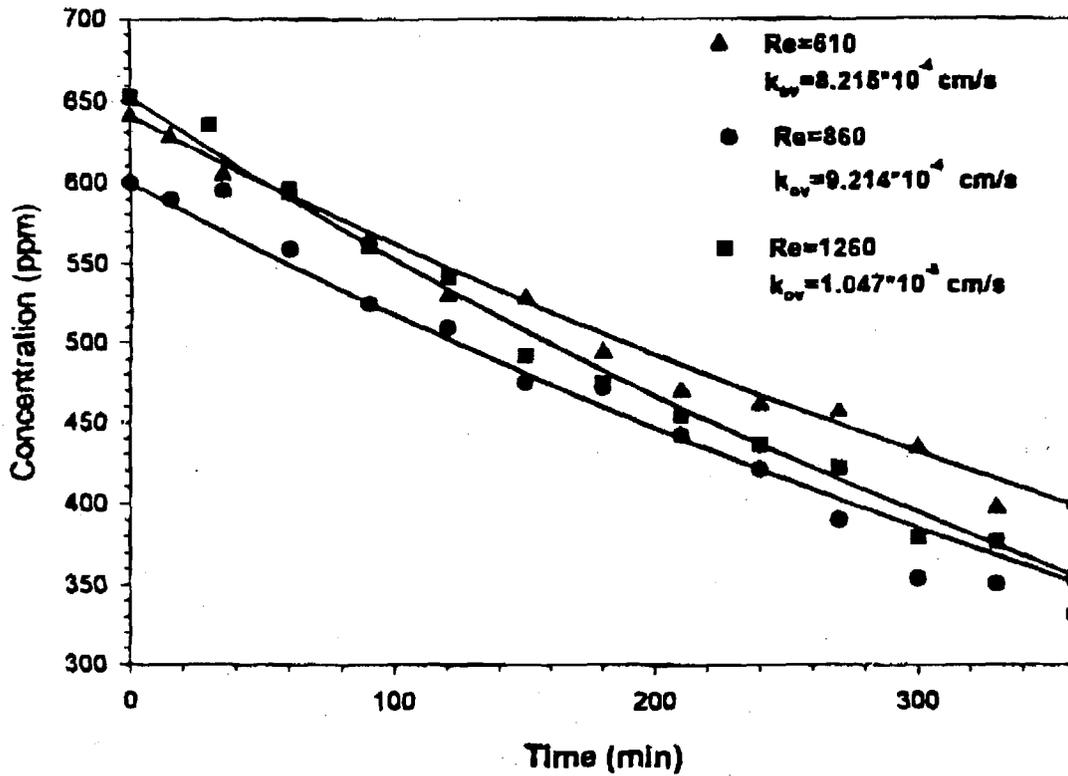


Figure 4

Enrichment Factors with Different Renolds Numbers for Pervaporation

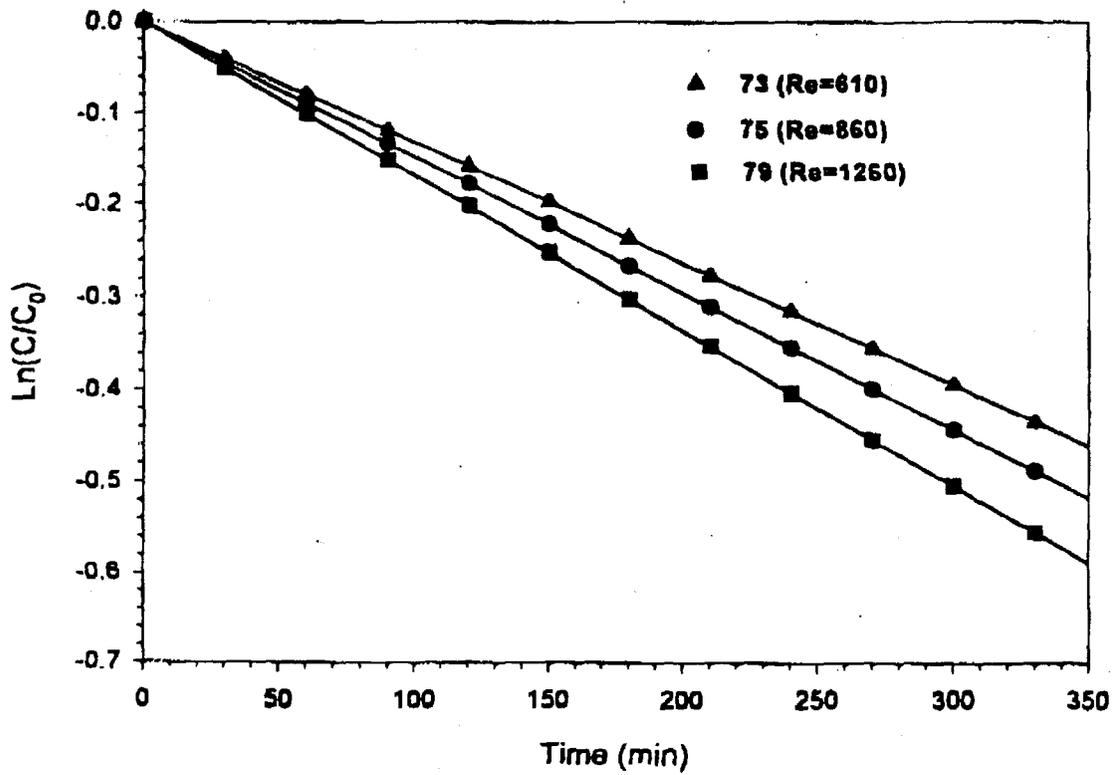


Figure 5

Hydraulic Permeability and Graft Polymerization Results

500Å Silica Membrane
Diameter=5 mm
Thickness=3.937×10⁻⁴ m
Surface Area: 45.5217 m²/g

	Surface Water (mg/m ²)	Hydraulic Permeability (cm ²)	Graft Yield (mg/m ²)	Pore Size (Å)
Unmodified Membrane #1	-	1.070×10 ⁻¹⁵	-	500
Unmodified Membrane #2	-	9.602×10 ⁻¹⁶	-	500
Unmodified Membrane #3	-	1.279×10 ⁻¹⁵	-	500
Unmodified Membrane #4	-	9.760×10 ⁻¹⁶	-	500
Silylated Membrane #1	12.84	negligible	0.71	-
Silylated Membrane #2	13.07	negligible	0.70	-
Silylated Membrane #3	12.91	negligible	0.69	-
Silylated Membrane #4	12.93	negligible	0.69	-
1 st Grafted Membrane* #2	-	negligible	0.20	-
1 st Grafted Membrane* #3	-	negligible	0.17	-

* 25% Vinyl Acetate in Ethyl Acetate with 45 min reaction time and 70°C reaction temperature.

* 10% Vinyl Acetate in Ethyl Acetate with 5 hrs reaction time and 60°C reaction temperature.