Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Concentration of Synfuel Process Condensates by Reverse Osmosis

S. B. Mccray[a]; Roderick J. Ray[a]
[a] Bend Research Inc., Bend, Oregon

To cite this Article Mccray, S. B. and Ray, Roderick J.(1987) 'Concentration of Synfuel Process Condensates by Reverse Osmosis', Separation Science and Technology, 22: 2, 745 — 762
To link to this Article: DOI: 10.1080/01496398708068979
URL: http://dx.doi.org/10.1080/01496398708068979

SEPARATION SCIENCE AND TECHNOLOGY, 22(2&3), 745-762, 1987

Concentration of Synfuel Process Condensates by Reverse Osmosis

S. B. McCRAY and RODERICK J. RAY

BEND RESEARCH, INC.
64550 RESEARCH ROAD
BEND, OREGON 97701

ABSTRACT

In this paper we will discuss the use of a novel, fouling-resistant, inside-skinned hollow-fiber membrane configuration as an energy-efficient and cost-effective alternative to conventional treatment of synfuel process condensate waters. Reverse osmosis has been used in the past only to "polish" condensate waters that were first treated by conventional means. In the work described in this paper, a reverse-osmosis system actually replaces traditional biotreatment of condensate waters or replaces the solvent-extraction process in the treatment train. The membranes used in this reverse-osmosis system are capable of rejecting at least 90% of the phenols as well as high percentages of other organics contained in actual process condensate waters. Furthermore, these membranes have operated for several months on synfuel condensate waters and showed no significant decrease in performance. Energy and cost estimates of a reverse-osmosis system based on such membranes will be discussed in detail, including a comparison of operating costs of this system with the operating costs of conventional treatment systems.

INTRODUCTION

Liquid and gaseous fuels produced from coal or shale oil (i.e., synthetic fuels) are expected to be a major source of fuel in the future as supplies of petroleum-based fuels diminish. However, a significant problem associated with the production of synthetic fuels is the large volume of waste water that is generated. This waste water, broadly classified as "process condensate," is the result of a stripping process by which vaporized coal or shale oil is contacted with water or steam to remove contaminants. A plant that processes 250 million cubic feet of coal per day is estimated to produce anywhere from 200,000 to 3,700,000 gallons of process condensate per day (1). These process condensates normally contain high concentrations of 1) organics, such as phenols, oils and greases, carboxylic acids, and heterocyclic hydrocarbons; and 2) inorganics, such as ammonia, sulfides, carbonates, cyanides, and traces of heavy metals. Many of these compounds are suspected carcinogens or are otherwise toxic, and they must be removed before the waste water can be discharged into the environment.

A number of conventional unit processes are being considered for the treatment of process condensates. For example, solvent extraction and biotreatment are being studied for removal of the carboxylic acids and phenols (1), which make up most of the soluble organics in the condensates. Reverse osmosis (RO) is being investigated as a final polishing step that would remove heavy-metal ions and salts from condensates after the soluble and suspended organics have been removed (2-4).

Bend Research, Inc., is investigating a novel application of RO to the treatment of process condensates. Rather than using RO as a final polishing step in the treatment train, we are studying the use of this membrane process to concentrate raw condensate, replacing conventional treatment processes and thereby reducing the volume of waste water that must be treated in subsequent steps. With a minimum of posttreatment, RO can produce reusable water—an important advantage in arid regions.

Figure 1 shows a proposed "conventional" condensate-treatment scheme. The raw condensate water is first fed to a gravity-separation pond, where most of the oil, grease, tar, and some of the suspended solids are removed. Next, a series of steam-stripping processes removes most of the NH_3, CO_2, and H_2S. Table I gives a typical composition of the condensate at this point in the treatment train. Note that the majority of the remaining components are phenolic compounds (5). Next, as shown in Figure 1, most of the phenols and other organic compounds are removed by either a biotreatment unit, a solvent-extraction process, or both. Finally, in order to produce reusable water, the stream is polished by processes such as carbon adsorption, ion exchange, or conventional RO.

Biotreatment units, which are based on the action of microorganisms that break down organic compounds into nontoxic forms, are capable of removing organics from waste water efficiently. As waste water is fed into a biotreatment unit, microorganisms consume the organics while cell matter is removed as sludge for disposal or possible resale as fuel. However, the microorganisms in biotreatment units are extremely sensitive to feed concentration and are easily poisoned. Thus, process condensates intended for biotreatment must be diluted, for example, by mixing with other waste-water streams from the plant. This is especially true when high concentrations of phenols are present, since some of these compounds are resistant to

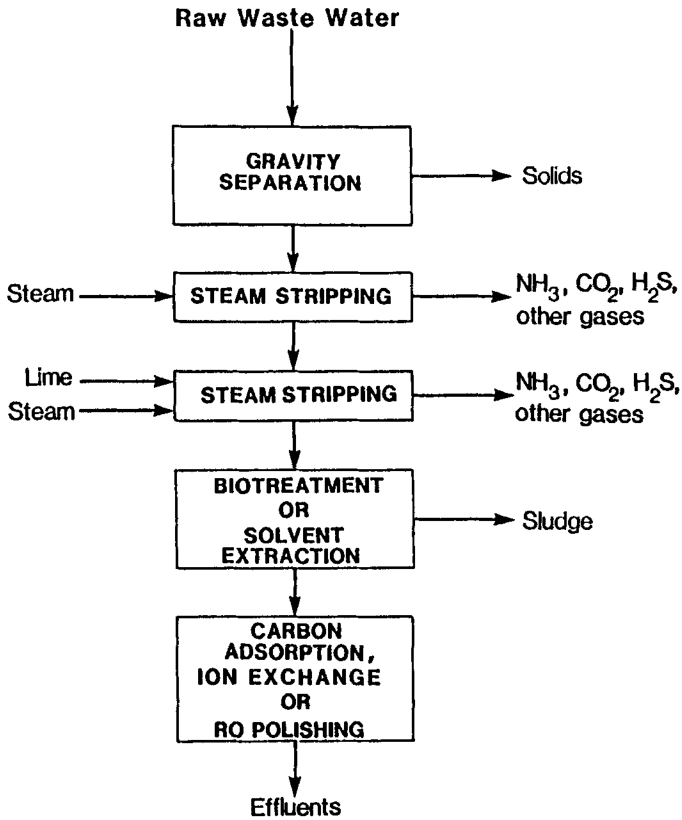

Fig. 1. Typical "Conventional" Treatment Scheme Proposed for Synfuel Condensate Treatment

biological degradation (1). Another disadvantage of biotreatment units is that the action of the microorganisms is slow. For example, a condensate stream of the composition shown in Table I would need to be held in a conventional biotreatment unit for at least 15 days for efficient removal of contaminants (6). Therefore, the reactor vessels or biotreatment ponds must be large enough to hold large volumes of waste water for a long period of time. And such large vessels or treatment ponds would require a correspondingly large capital investment.

Solvent extraction can effectively remove most organic compounds in the condensate stream in addition to allowing for the recovery of potentially valuable by-products, such as phenols (1). However, the solvent used in a solvent-extraction unit must be recovered if the

TABLE I
Concentrations of Major Constituents of Synfuel Condensate After Steam Stripper

Contaminant	Nominal Concentration (ppm)
Phenol	2000
Resorcinol	1000
Catechol	1000
O-Cresol	400
P-Cresol	250
Acetic Acid	400
Benzoic Acid	100
Pyridine	120
Aniline	20
Quinoline	10
$MgSO_4$	23
NH_4Cl	150

operation is to be economical; thus, the choice of solvents is limited. Furthermore, solvent extraction is not effective in removing inorganic salts (1). The remaining contaminants, then, as well as any residual solvents in the water, must be removed by a subsequent treatment step. Of note here is that solvent extraction, being a partitioning, unit operation, is more efficient at high contaminant concentrations than at low concentrations.

The RO technology being considered here would replace the biotreatment or solvent-extraction step shown in Figure 1, resulting in the condensate-treatment train shown in Figure 2. RO would be used to split the steam-stripped condensate into two streams: 1) a reject stream concentrated in about 20% of the total feed volume that would contain most of the organic contaminants and virtually all of the inorganic contaminants, and 2) a relatively clean permeate stream in the remaining 80% of the feed volume. Depending on the composition of the condensate, the concentrated reject stream will either be combusted as-is to generate usable heat (e.g., by wet-air oxidation (7)) or further concentrated by solvent extraction, which operates more efficiently on concentrated waste streams. The permeate stream from this RO unit may require some polishing, such as by carbon adsorption, to remove any remaining organics.

THE REVERSE-OSMOSIS PROCESS

RO is a pressure-driven membrane separation process, in which a feed solution is pressurized to between 400 and 800 psi against a

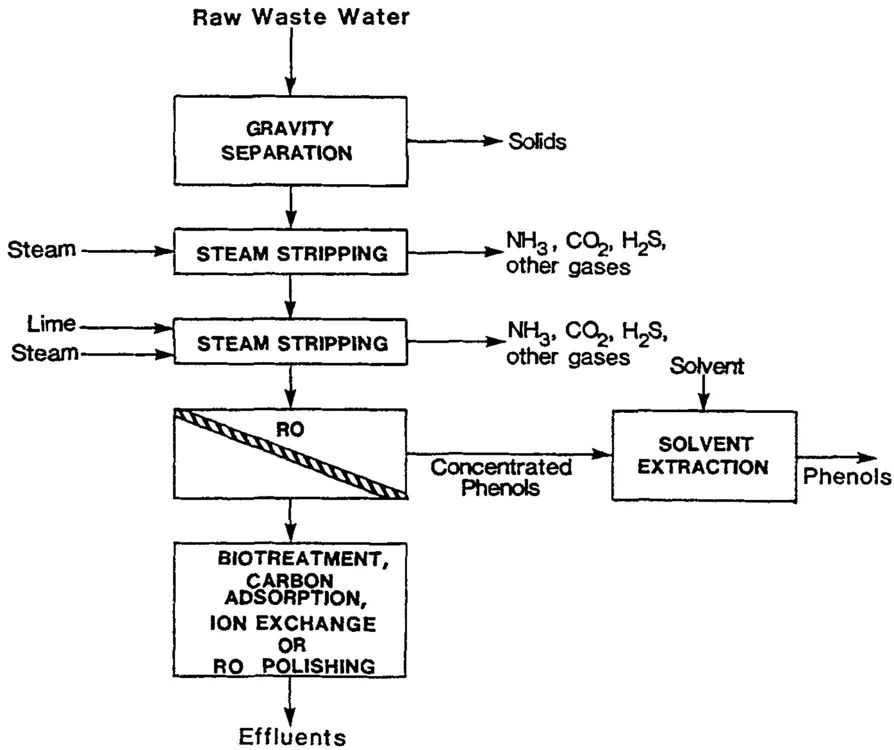

Fig. 2. Proposed Membrane-Based Treatment Scheme

semipermeable membrane. Water selectively permeates the membrane, while ions and most organic compounds in the solution are rejected.

The major application of RO today is in the desalting of brackish water and seawater. The most widely used membrane-module configurations in this application are the spiral-wound flat sheet and the shell-side-feed hollow fiber. A major problem with these types of modules is that they are easily fouled. This problem has been well-documented in water-desalting plants. Even with relatively clean well waters and offshore seawater, from 25% to 50% of the investment cost of RO desalting plants is for the pretreatment processing that is required to minimize fouling (8-10). Raw synfuel condensates, which contain very high levels of suspended oils, greases, and particulates, simply could not be treated using conventional module configurations.

Fouling resistance can be attained in hollow-fiber modules by using a tube-side-feed design. This design is shown in Figure 3. Positive feed flow across the entire active surface of the membrane

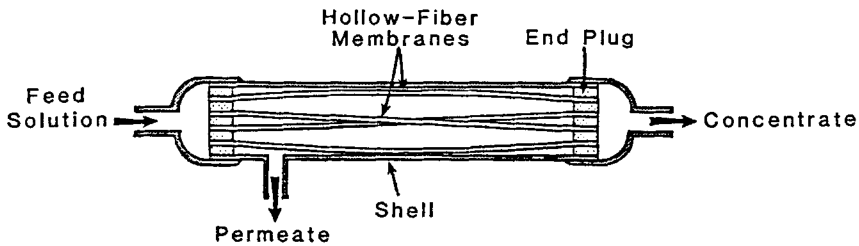

Fig. 3. Tube-Side-Feed Hollow-Fiber Module

eliminates the "dead spots" that cause fouling in spiral-wound modules and hollow-fiber modules with shell-side feed. Tube-side-feed modules do not seriously foul, even when used on feeds that have very high concentrations of suspended matter, such as cheese whey, latex paints, and oil-in-water emulsions (11). Another potential advantage of this design is that the fibers act as their own pressure vessels, thereby eliminating the need for an external vessel, resulting in lower capital equipment cost.

RESULTS

Experiments were conducted in our laboratory to investigate the capability of RO technology to treat condensate waste waters. Tube-side-feed hollow-fiber membrane modules, some with 2 ft^2 and some with 10 ft^2 of membrane area, were operated on feed solutions of actual synfuel condensate provided by the Pittsburgh Energy and Technology Center (PETC). A typical composition of synfuel condensate after steam stripping is given in Table I. All experiments were conducted at constant pressure (400 psi), temperature (24°C), pH (11), and velocity down the fiber lumen (20 cm/sec).

Contaminant concentrations of phenols were determined using a Varian Model 5000 high-performance liquid chromatograph (HPLC) equipped with an ultraviolet detector, which was set at 270 nm for detection of phenols. Typical HPLC traces of a PETC synfuel condensate feed solution and permeate from a hollow-fiber membrane module are shown in Figure 4. Contaminant rejections[a] were determined from differences in HPLC area.[b]

[a]Percent Rejection $= \left(1 - \dfrac{\text{Concentration of contaminant in permeate}}{\text{Concentration of contaminant in feed}}\right) \times 100$

[b]The hollow-fiber membrane modules used in this study gave inorganic salt rejections of more than 95% in all experiments.

CONCENTRATION OF SYNFUEL PROCESS CONDENSATES BY RO

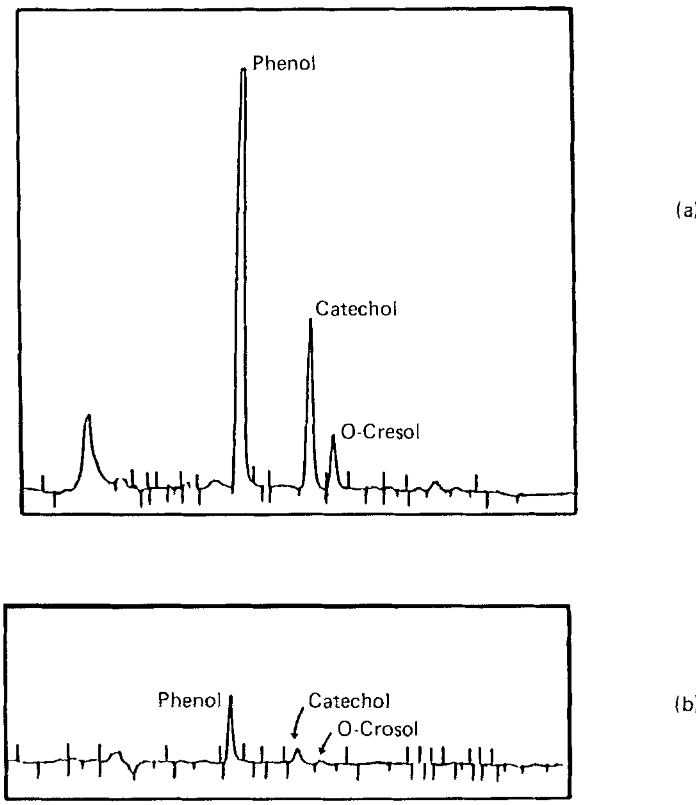

Fig. 4. Typical HPLC Traces of (a) PETC Synfuel Condensate Feed and (b) Permeate from a Hollow-Fiber Membrane Module (vertical scales are equivalent)

Figure 5 shows contaminant rejection (based on HPLC readings) versus recovery[c] for a 2-ft^2 membrane module. These data indicate that rejections of more than 95% can be achieved at recoveries of from 0% to 80%. This indicates the high efficiency of RO when used to treat synfuel condensates.

Figure 6 shows a definite trend for water flux[d] to drop as percent recovery is increased. However, the figure also reveals that the flux decay is eliminated by flow reversal within the fiber lumen at recoveries of up to 40%. This phenomenon was probably due to the presence of suspended solids in the condensate that are larger than the diameter of the fibers or to the concentration of tars and greases over time, resulting in blockage of fiber openings and reduction of the effective membrane area and corresponding flux. By reversing the direction of flow down the fiber lumen, the foulants were swept away. Because the flux returned to the initial value after this simple treatment, it is safe to assume that there was no permanent deposition of oils, greases, or other suspended material on the fiber lumen and that flow reversal can correct the flux decay problem for processing at up to 40% recovery.

At recovery levels higher than 40%, the flux declined steadily and could not be completely restored by flow reversal. This decline was at least partially due to the increase in osmotic pressure of the feed solution at the higher recovery levels. To verify this, the osmotic pressure of the feed solution was determined at various recovery levels using the following equation:

$$J = A(\Delta P - \Delta \pi), \qquad (1)$$

where J is the water flux, A is the membrane constant, ΔP is the applied feed-side pressure, and $\Delta \pi$ is the osmotic pressure (12). These data were generated by measuring the water flux, at a given recovery level, across the membrane as a function of operating pressure—yielding data as shown in Figure 7. The extrapolation of the curve to the abscissa as shown in the figure yields an estimate of osmotic pressure. The fact that the slopes of the two lines shown are not equivalent is probably the result of concentration polarization. Figure 8 shows the osmotic pressure of the feed solution plotted against recovery—each data point corresponding to an extrapolation as shown in Figure 7. As the osmotic pressure of the feed increases, the effective driving force for transport of water through the membrane is decreased. Thus, the permeate flux through the membrane decreases as the recovery level is increased. However, as shown in Figure 6, the data do indicate that an acceptable flux can be maintained even at recovery levels higher than 80%.

---

[c] $$\text{Percent Recovery} = \left(\frac{\text{Total volume of permeate}}{\text{Initial feed volume}}\right) \times 100$$

[d] Flux = The amount of water transported across the membrane per unit area per unit time.

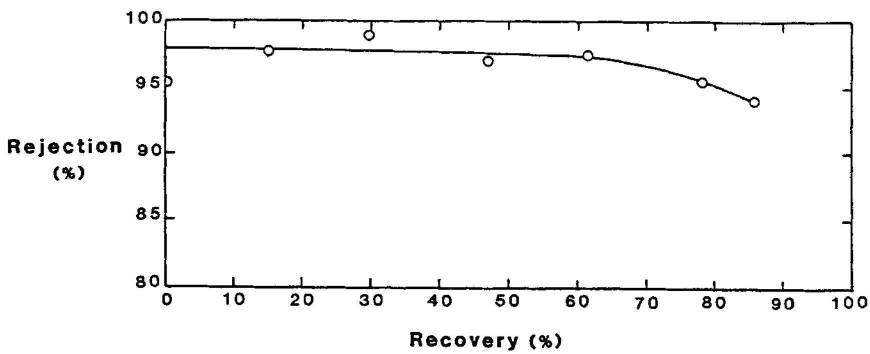

Fig. 5. Contaminant Rejection Versus Recovery for a 2-ft^2 Hollow-Fiber Membrane Module
Test Conditions: PETC synfuel condensate, 400 psi
24°C, pH 11, velocity down the fiber lumen = 20 cm/sec

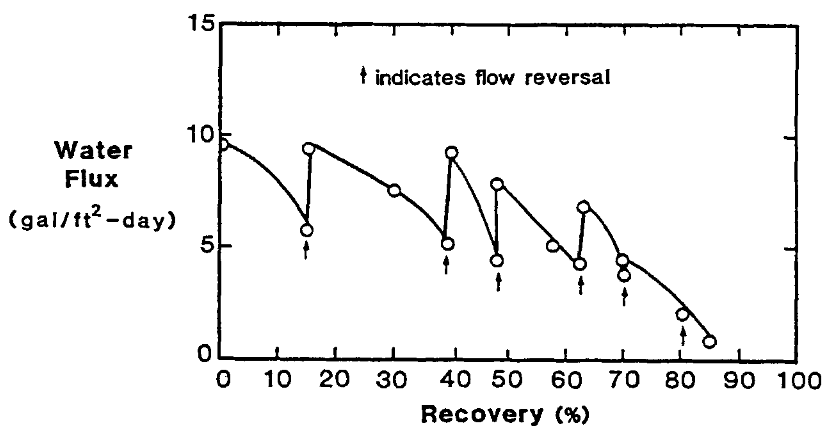

Fig. 6. Flux Versus Recovery for a 2-ft^2 Hollow-Fiber Membrane Module
Test Conditions: PETC synfuel condensate, 400 psi, 24°C,
pH 11, velocity down the fiber lumen = 20 cm/sec

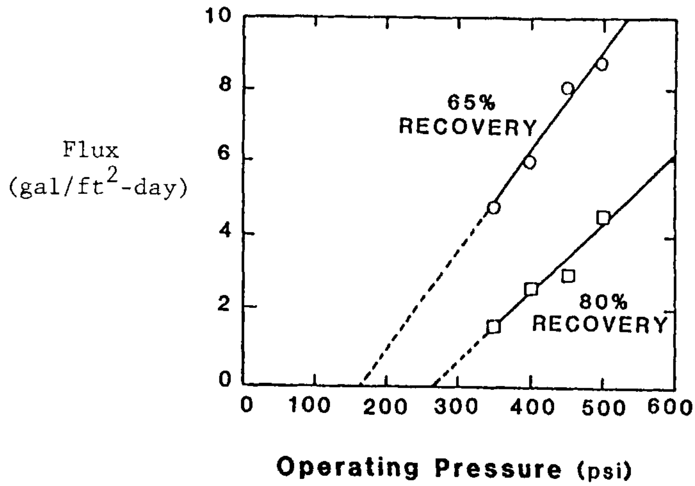

Fig. 7. Water Flux Versus Feed-Stream Pressure for a 2-ft^2 Hollow-Fiber Membrane Module
Test Conditions: PETC synfuel condensate at 65% and 80% recovery, 25°C, pH 11, velocity down the fiber lumen = 20 cm/sec

Long-term tests were conducted to study the effects of phenols on a 10-ft^2 membrane module. In these experiments, a feed solution containing 5000 ppm phenol was used. As Figures 9a and 9b show, the flux and rejection of this module exhibited little change during 43 days of operation. Experiments to determine the life of these modules are currently being conducted; however, based on experience and these data, it is expected that hollow-fiber membrane modules will have a one-year lifetime when operated on harsh synfuel condensate.

Using the above data, a plant was designed that could treat 100,000 gal/day (gpd) of a synfuel condensate that contained 5000 ppm phenols. Table II gives the values used to design the plant, and a schematic of this design is shown in Figure 10. Conventional design of an RO plant typically relies upon a pyramid or tapered configuration. However, the design shown here is in block form to allow for the inclusion of the flow reversal needed in treating synfuel waste streams. To achieve approximately 79% recovery of the feed water, 11,350 ft^2 of membrane area would be required. The combined permeate stream would contain approximately 470 ppm phenols (90% overall rejection), which would be removed in a final carbon-adsorption polishing step. The reject stream would contain approximately 22,000 ppm phenols. Depending on the total composition of the feed stream, this stream could either be burned as-is, or further concentrated using a solvent-extraction step prior to being burned.

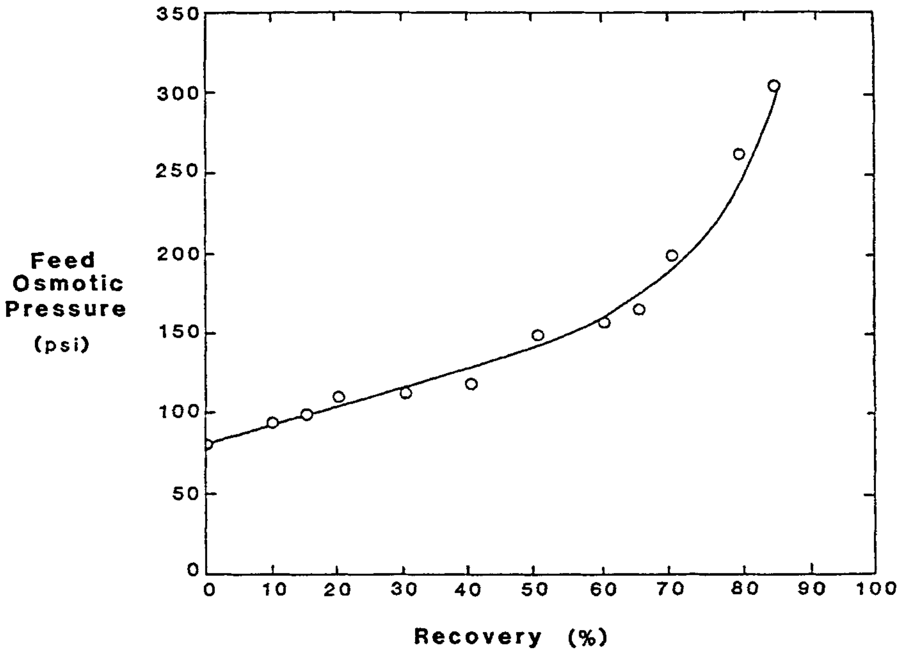

Fig. 8. Feed Osmotic Pressure Versus Recovery
Test Conditions: PETC synfuel condensate, 25°C, pH 11, velocity down the fiber lumen = 20 cm/sec

TABLE II
Input Valves used in the Design of a 100,000-gpd RO Plant to Treat Synfuel Condensate

Item	Value
Feed Stream:	
Flow rate	100,000 gpd
Composition	5,000 ppm phenols
Temperature	25° C
Hollow-Fiber-Membrane Module:	
Module area	50 ft^2
Distilled water flux at 400 psi	9 gal/ft^2-day
Phenol rejection	95%
Operating Conditions:	
Feed inlet pressure	500 psi
Maximum velocity down fiber lumen	40 cm/sec
Minimum velocity down fiber lumen	20 cm/sec

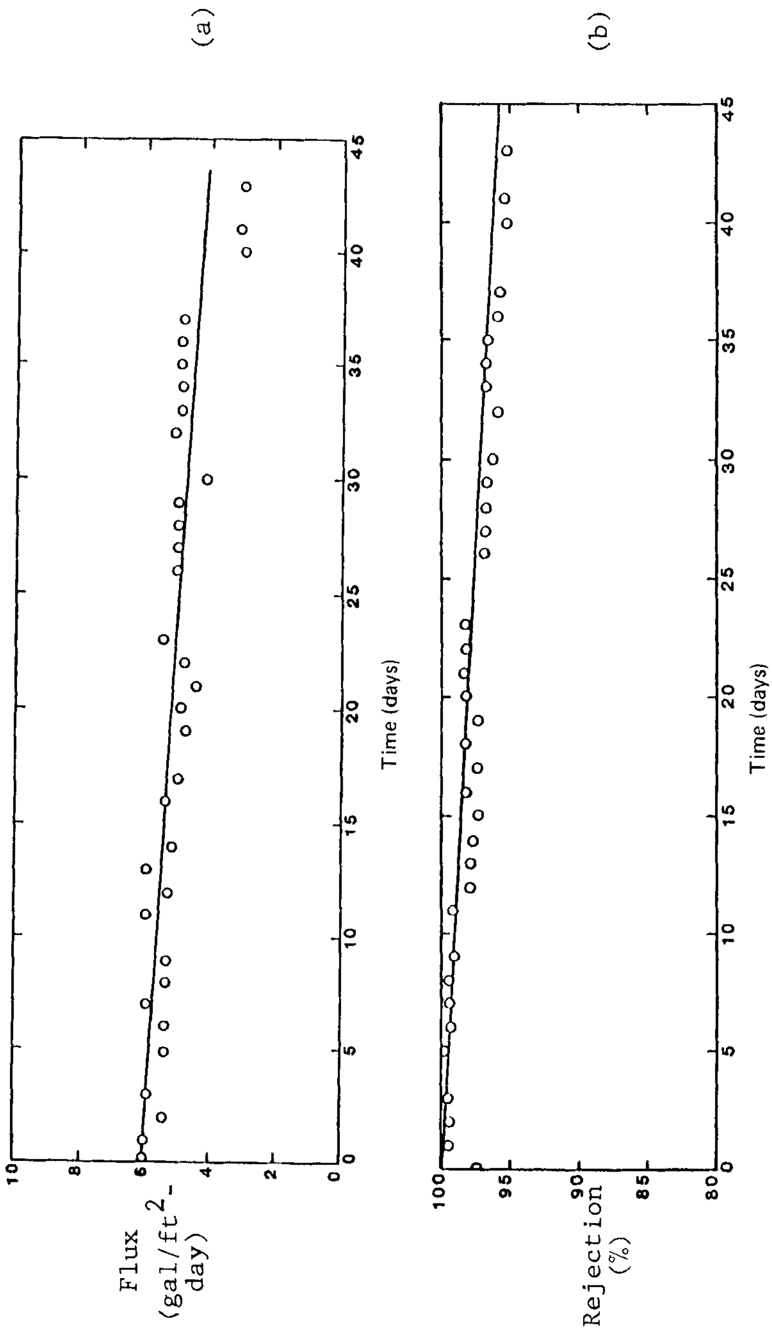

Fig. 9. Flux (a) and Rejection (b) of a 10-ft^2 Hollow-Fiber Membrane Module
Test Conditions: 5000 ppm phenol, 400 psi, 25^{o}C, pH 11, velocity down the fiber lumen = 20 cm/sec

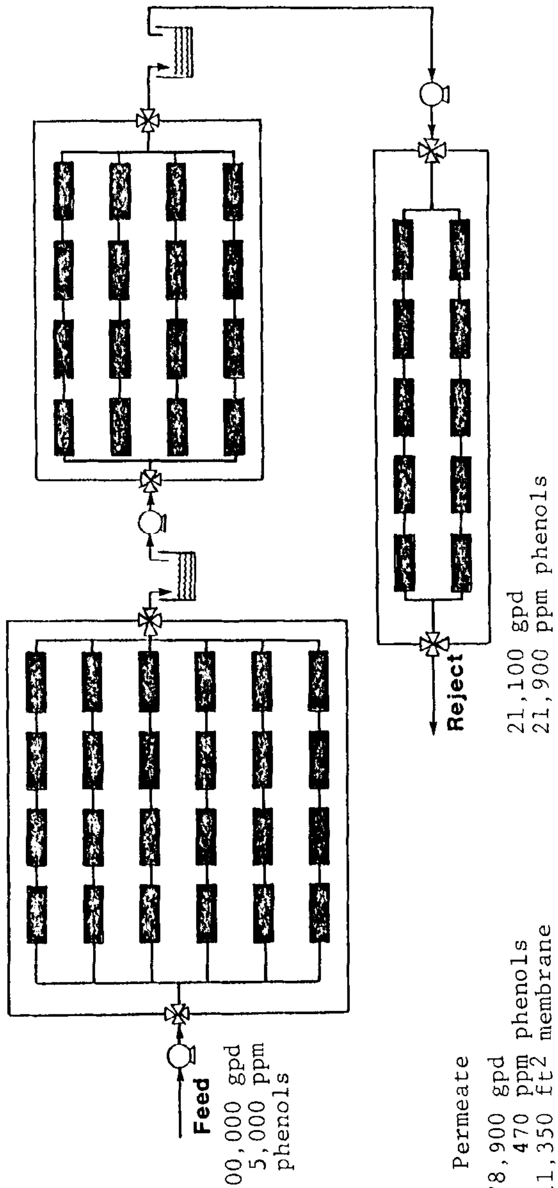

Fig. 10. RO Plant Capable of Treating 100,000 gpd of Synfuel Condensate [note that 1) a contingency is included for flow reversal, and 2) for simplicity, permeate streams for each module are not shown]

TABLE III
Estimated Costs for Treatment of
Synfuel Condensate

Treatment Method	Estimated Costs (1) ($/1000 gal treated)
Steam stripping	12 - 20
Solvent extraction	7 - 20
Biotreatment	7 - 50
Carbon adsorption	8 - 50
Total treatment train:	$25/1000 gal to $90/1000 gal

TABLE IV
Solvent-Extraction Economics
Basis: 100,000 gpd (1) of synfuel
condensate treated

Capital Cost	$503,000
Total Operating Cost	$8.2/1000 gal
Amortization Costs	
Depreciation (5-yr, 50% tax)	$1.4/1000 gal
Interest on Capital (10%)	$1.4/1000 gal
Total	$2.8/1000 gal
Total Treatment Costs	$11.0/1000 gal

ECONOMIC ANALYSIS

The process economics for conventional treatment of synfuel process condensates and for an RO treatment process were estimated and compared. Table III shows estimated costs (1) for a conventional treatment train such as that shown in Figure 1. The cost of the total treatment train is estimated at $25 to $90 per 1000 gallons of waste water.

Table IV shows the estimated cost (1) of a solvent-extraction plant capable of treating 100,000 gpd of condensate. The depreciation was calculated on a 5-year straight line, assuming a 50% tax break. The interest on the capital was assumed to be 10%, straight line. The total cost of treatment by solvent extraction is estimated to be $11/1000 gallons.

Table V shows the estimated cost of the RO plant shown in Figure 10. The total cost for an RO plant capable of treating 100,000 gpd of 5000 ppm phenol in water is $7.4/1000 gal--substantially lower than the cost of treatment by solvent extraction.

However, as stated above, a subsequent solvent-extraction step may be required downstream from the RO stage to further concentrate the reject stream. If the RO plant is assumed to operate at 80% recovery, this solvent-extraction unit need only treat 20,000 gpd of waste water. Table VI compares the economics of a solvent-extraction unit with those of a hybrid plant that combines RO and solvent extraction. This table indicates that the hybrid plant would require $110,000 more capital than would the solvent-extraction plant. However, the

TABLE V
Reverse-Osmosis Economics
Basis: 100,000 gpd of synfuel condensate treated

Capital Costs:	
Membranes (installed)[a]	$380,000
Main feed pump (installed)	$ 14,000
Booster pumps (installed)	$ 8,000
Total	$402,000
Operating Costs:	
Membrane replacement[b] (1-yr membrane life)	$4.3/1000 gal
Electricity[c]	$0.8/1000 gal
Maintenance (10%)	$1.1/1000 gal
Total	$6.2/1000 gal
Amortization Costs:[d]	
Depreciation (5-yr, 50% tax break)	$0.6/1000 gal
Interest on capital (10%)	$0.6/1000 gal
Total	$1.2/1000 gal
Total Treatment Costs	$7.4/1000 gal

[a] Installed membranes = $33.5/ft^2
[b] FOB membranes = $14/ft^2
[c] Electricity at $0.05/kW-hr
[d] Based on FOB-membrane-free capital cost

TABLE VI
Cost Comparison of a Solvent-Extraction Plant and a Hybrid RO/Solvent-Extraction Plant

	Solvent Extraction 100,000 gpd	RO 100,000 gpd	Solvent Extraction 20,000 gpd	Total Hybrid Plant
Total Capital ($)	503,000	402,000	211,000	613,000
Total Operating Costs ($/year)	299,000	226,000	43,000	269,000
Total Amortization Costs ($/year)	101,000	44,000	42,000	86,000
Total Treatment Costs ($/yr)	400,000	270,000	85,000	355,000

operating costs for the hybrid plant are estimated to be $145,000 per year lower than those of the solvent-extraction plant, yielding a payback period of 2.7 years. Ray, et al. (13) have shown that hybrid processes can be optimized by varying the percentage of the waste water treated by the membrane unit. The usual optimization criterion is the total production cost; however, other criteria, such as capital cost, maintenance costs, size, reliability, or operational constraints (such as high osmotic pressures) may be used. The data required to perform an optimization on the RO/solvent-extraction hybrid process presented here are currently not available. When these data are obtained, it is believed they will show that a hybrid unit will offer significant advantages over conventional processes for the treatment of synfuel wastes.

CONCLUSIONS

Laboratory results indicate that treatment of synfuel condensates by RO is feasible. Contaminant rejections higher than 95% can be achieved using tube-side-feed hollow-fiber modules, which resist fouling even when operating at high recovery levels. Both small- and large-scale field tests of this technology are planned.

Preliminary cost estimates indicate that RO/solvent-extraction hybrid processes offer a significant economic advantage over nonhybrid processes. The total treatment cost for a hybrid unit capable of treating 100,000 gpd of synfuel condensate waste is $60,000/yr less than that of a solvent-extraction process of the same size. Once the necessary data to perform a detailed optimization of the hybrid process are obtained, it is believed that the optimum hybrid process will show an even greater economic advantage over conventional processes for the treatment of synfuel wastes.

ACKNOWLEDGMENTS

This work was funded by the U.S. Department of Energy under a Small Business Innovation Research contract. We would like to thank Dr. Richard Noceti of The DOE Pittsburgh Energy and Technology Center for his technical assistance during this project.

REFERENCES

1. University of California Department of Chemical Engineering, Processing Needs and Methodology for Wastewaters from the Conversion of Coal, Oil Shale and Biomass to Synfuels. DOE/EV-0081, available through NTIS, Springfield, Virginia (1980).

2. Witmer, F.E., "Coal Conversion Wastewater Treatment/Reuse--An Overview," presented at U.S. Environmental Protection Agency Symposium, Environmental Aspects of Fuel Conversion Technology--VI, Denver, Colorado, October 26-30, 1981.

3. Oswald, G.E., J.F. Walker, C.H. Brown, J.A. Klein, R.K. Genung, Development and Evaluation of Wastewater Treatment Processes at the H-Coal Site in Catlettsburg, Kentucky, Volume I: Design Summary and R&D Task Identification. Available from NTIS as Report No. ORNL/TM-8213.

4. Brown, C.H., Jr., G.E. Oswald, M.T. Harris, S.G. DeCicco, and J.D. Hewitt, Operation of the Wastewater Treatment PDU at the H-Coal Site in Catlettsburg, Kentucky, During the Period June 14-25, 1982, Oak Ridge National Laboratory, Oak Ridge, Tennessee, August 17, 1982.

5. Singer, P.C., F.K. Pfaender, J. Chinchilli, A.F. Maciorowski, J.C. Lamb, III, and R. Goodman, Assessment of Coal Conversion Waste Waters - Characterization and Preliminary Biotreatability. EPA Report EPA-600/7-78-181, September, 1978.

6. Drummond, C.J., R.P. Noceti, J.G. Walters, "Treatment of Solvent-Refined Coal Wastewater, "Environ. Prog., 1:1(1982)73.

7. Chou, C.L., and F.H. Verhoff, "Process for Power Generation from Wet-Air Oxidation with Application to Coal Gasification Waste Waters, "Ind. Eng. Chem. Proc. Des. Devel., 20(1981)12-19.

8. Reverse Osmosis Technical Manual, prepared for the Office of Water Research and Technology by Burns and Roe Industrial Services Corporation, Paramus, New Jersey. Available as NTIS PB80-186950, July, 1979.

9. Channabasappa, K.C., "Status of Reverse Osmosis Desalination Technology, "Desalination, 17(1975)31.

10. Sudak, R.G., and A.M. Desai, "Reverse Osmosis for Yuma Desalting Plant, "Desalination, 19(1976)389.

11. Porter, M.C., and A.S. Michaels, "Membrane Ultrafiltration, "Chem. Tech., 2(1972)56.

12. Lonsdale, H.K., "The Growth of Membrane Technology, "J. Membrane Sci., 10(1982)81-181.

13. Ray, R.J., J. Kucera-Gienger, and S. Retzlaff, "Membrane-Based Hybrid Processes for Energy-Efficient Waste-Water Treatment," submitted for publication to the J. Membrane Sci., 1985.