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# ANNOUNCEMENT

**UNITED STATES DEPARTMENT OF ENERGY (DOE)**
Scientific and Technical Information (STI) For Financial Assistance Recipients and Non-M&O/M&I Contractors

*OMB Control No. 1910-1400*

## PART I: STI PRODUCT DESCRIPTION

**A. STI Product Identifiers**

1. REPORT/PRODUCT NUMBER(s)
none

2. DOE AWARD/CONTRACT NUMBER(s)
DE-FC36-01ID14016

3. OTHER IDENTIFYING NUMBER(s)
WBS#: 4.2.4.2

**B. Recipient/Contractor**

Amalgamated Research Inc. , Twin Falls, Idaho

**C. STI Product Title**
Industrial Membrane Filtration and Short-Bed Fractal Separation Systems for Separating Monomers from Heterogeneous Plant Material


**D. Author(s)** Kearney, M.; Kochergin, V.; Hess, R.; Foust, T.; Herbst, R.; Mann, N.

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**E. STI Product Issue Date/Date of Publication**
3/31/2005 (mm/dd/yyyy)

**F. STI Product Type** *(Select only one)*

☒ 1. TECHNICAL REPORT
☒ *Final* ☐ *Other (specify)*

☐ 2. CONFERENCE PAPER/PROCEEDINGS
*Conference Information (title, location, dates)*

☐ 3. JOURNAL ARTICLE
*a. TYPE:* ☐ *Announcement Citation Only*
☐ *Preprint* ☐ *Postprint*
*b. JOURNAL NAME*
*c. VOLUME* *d. ISSUE*
*e. SERIAL IDENTIFIER (e.g. ISSN or CODEN)*

☐ OTHER, SPECIFY

**G. STI Product Reporting Period** (mm/dd/yyyy)

January 1, 2001 *Thru* December 31, 2004

**H. Sponsoring DOE Program Office**
Biomass

**I. Subject Categories** *(list primary one first)*
Biomass Products

*Keywords* chromatography; fractals; membrane; filtration; biomass; hydrolysis; ion exchange; acid; sugars; separation


**J. Description/Abstract**
This project focused on development of new methods and equipment for reducing the size and cost of chromatography and ion exchange technologies that support biomass-to-fuels/chemicals conversion processes. This project also focused on development of robust membrane systems for industrial scale biomass suspended solids removal.


**K. Intellectual Property/Distribution Limitations**

*(must select at least one; if uncertain contact your Contracting Officer (CO))*

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☐ 6. SMALL BUSINESS TRANSFER (STTR) DATA
*Release date (Required,*
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☐ 7. OFFICE OF NUCLEAR ENERGYAPPLIEDTECHNOLOGY


**L. Recipient/Contractor Point of Contact** *Contact for additional information (contact or organization name to be included in published citations and who would receive any external questions about the content of the STI Product or the research contained therein)*

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Amalgamated Research Inc.
*Organization*

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## PART II: STI PRODUCT MEDIA/FORMAT and LOCATION/TRANSMISSION

(To be completed by Recipient/Contractor)

**A. Media/Format Information:**

1. MEDIUM OF STI PRODUCT IS:
   - ☒ Electronic Document ☐ Computer medium
   - ☐ Audiovisual material ☒ Paper ☐ No full-text
2. SIZE OF STI PRODUCT 6.7 MB
3. SPECIFY FILE FORMAT OF ELECTRONIC DOCUMENT BEING TRANSMITTED, INDICATE:
   - ☐ SGML ☐ HTML ☐ XML ☒ PDF Normal ☐ PDF Image
   - ☐ WP-Indicate Version *(5.0 or greater)* ______
     Platform/operating system ______
   - ☐ MS-Indicate Version *(5.0 or greater)* ______
     Platform/operating system ______
   - ☐ Postscript ______
4. IF COMPUTER MEDIUM OR AUDIOVISUAL
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   - b. Machine compatibility *(specify)* ______
   - c. Other information about product format a user needs to know: ______

**B. Transmission Information:**

STI PRODUCT IS BEING TRANSMITTED:

- ☒ 1. Electronic via Elink
- ☒ 2. Via mail or shipment to address indicated in award document *(Paper products, CD-ROM, diskettes, videocassettes, et.)*
- ☒ 2a. Information product file name *(of transmitted electronic format)*
  DE-FC36-01ID14016_final report_2001-04.pdf

## PART III: STI PRODUCT REVIEW/RELEASE INFORMATION

(To be completed by DOE)

**A. STI Product Reporting Requirement Review:**

- ☐ 1. THIS DELIVERABLE COMPLETES ALL REQUIRED DELIVERABLES FOR THIS AWARD
- ☐ 2. THIS DELIVERABLE FULFILLS A TECHNICAL REPORTING REQUIREMENT, BUT SHOULD NOT BE DISSEMINATED BEYOND DOE.

**B. DOE Releasing Official**

- ☐ 1. I VERIFY THAT ALL NECESSARY REVIEWS HAVE BEEN COMPLETED AS DESCRIBED IN DOE G 241.1-1A, PART II, SECTION 3.0 AND THAT THE STI PRODUCT SHOULD BE RELEASED IN ACCORDANCE WITH THE INTELLECTUAL PROPERTY/DISTRIBUTION LIMITATION ABOVE.

Released by *(name)* ______

Date ______
(mm/dd/yyyy)

E-mail ______

Phone ______

# FINAL REPORT

# Industrial Membrane Filtration and Short-Bed Fractal Separation Systems for Separating Monomers from Heterogeneous Plant Material

Award Number: DE-FC07-01ID14016

Recipient: Amalgamated Research Inc.

Reporting Period: January 2001 to December 2004

Contact: Mike Kearney
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# Executive Summary

## Purpose and Scope

Large-scale displacement of petroleum will come from low-cost cellulosic feedstocks such as straw and corn stover crop residues. This project has taken a step toward making this projection a reality by reducing capital and energy costs, the two largest cost factors associated with converting cellulosic biomass to chemicals and fuels. The technology exists for using acid or enzyme hydrolysis processes to convert biomass feedstock (i.e., waste cellulose such as straw, corn stover, and wood) into their base monomeric sugar building blocks, which can, in turn, be processed into chemicals and fuels using a number of innovative fermentation technologies. However, while these processes are technically possible, practical and economic barriers make these processes only marginally feasible or not feasible at all. These barriers are due in part to the complexity and large fixed and recurring capital costs of unit operations including filtration, chromatographic separation, and ion exchange.

This project was designed to help remove these barriers by developing and implementing new purification and separation technologies that will reduce the capital costs of the purification and chromatographic separation units by 50% to 70%. The technologies fundamental to these improvements are: (a) highly efficient clarification and purification systems that use screening and membrane filtration to eliminate suspended solids and colloidal material from feed streams and (b) fractal technology based chromatographic separation and ion exchange systems that can substitute for conventional systems but at much smaller size and cost.

A non-hazardous "raw sugar beet juice" stream (75 to 100 gal/min) was used for prototype testing of these technologies. This raw beet juice stream from the Amalgamated Sugar LLC plant in Twin Falls, Idaho contained abrasive materials and membrane foulants. Its characteristics were representative of an industrial-scale heterogeneous plant extract/hydrolysis stream, and therefore was an ideal model system for developing new separation equipment. Subsequent testing used both synthetic acid hydrolysate and corn stover derived weak acid hydrolysate (NREL produced).

A two-phased approach was used for the research and development described in this project. The first level of study involved testing the new concepts at the bench level. The bench-scale evaluations provided fundamental understanding of the processes, building and testing small prototype systems, and determining the efficiency of the novel processes. The second level of study, macro-level, required building larger systems that directly simulated industrial operations and provided validation of performance to minimize financial risk during commercialization. The project goals and scope included:

- Development of low-capital alternatives to conventional crop-based purification/separation processes.
- Development of each process to the point that transition to commercial operation is low risk.

The project reporting period was January 2001 to December 2004. This included a one year extension of the project (without additional funding).

**Project Team:**
DOE-HQ Contact – Amy Manheim
DOE Golden Field Office – Fred Gerdeman
Industry Contact – Dennis Costesso
Principle Investigator – Michael Kearney
DOE Laboratory contact – Richard Hess

**Subcontractor:** Arkenol

**Other Partner:** INEEL

## Key Results

### *High Suspended Solids Filtration*

A primary task of this project was to prepare biomass hydrolysates for subsequent processing with granular media based separation equipment such as chromatography. Because of the nature of biomass, following hydrolysis a significant amount of undissolved material remains. This complicates subsequent processing in media based equipment. The presence of colloidal matter and very fine particles presents a challenge for material removal by filtration. This project's study of particle distribution and characterization of the plant-derived model solution as well as pretreated corn stover indicated that a successful filtration method for handling such streams is a hybrid system capable of inexpensively segregating the larger part of the particle spectrum and a fine filtration system separating particles in the submicron range.

The pretreatment system for removing the larger particles included a clarifier where principles of fractal distribution were applied to reduce turbulence and improve performance. The novel clarifier was followed by a membrane system that demonstrated very high capacity due to the high level of solids removal in the clarifier stage. The membrane system operated at very high concentration factors, thus reducing potential loss of valuable components. The system’s efficiency was demonstrated by continuous operation of a fully automated pilot system processing 600-700 tons/day of raw beet juice for a period of three consecutive processing campaigns. Long-term pilot operation allowed reliable operating data to be collected. As a result, full scale implementation should be low risk.

### *Membrane Erosion/Corrosion*

Both the capital and operating costs of membrane filtration are highly dependent on sustainable membrane performance. Several membranes that demonstrated excellent performance at the beginning of the project were completely eroded in a very short period of time. Catastrophic failure of membranes is not acceptable in industrial operation. This problem was solved by our discovery of the concept of erosion resistant “embedded” membrane where large membrane substrate is impregnated with finer particles which provide fine filtration. The concept was verified by consistent operation of the model membranes for three operating seasons.

A patent has been applied concerning the embedded membrane concept.

### *Novel Suspended Solids Removal*

The completion of this task was the result of combining the work discussed in the two tasks above. The combination of an improved clarifier using fractal technology and an innovative erosion resistant membrane constituted a hybrid liquid-solid separation system providing both high performance and separation efficiency. Resulting product was demonstrated to be successfully processed in subsequent granular media based equipment, including ion exchange and chromatography.

### *Short-Bed Fractal Chromatography Systems*

A key task of this project was to develop simulated moving bed (SMB) chromatography systems based on fractal technology with the goal of significantly reducing the size and cost of such systems applied to biomass processing. The project was successful in this regard. Key results using the fractal systems were:

- Reduction of the size of acid hydrolysate chromatography by 75% (acid-sugars separation).

- Reduction in the size of raw juice chromatography by 50% (model beet raw juice separation).

- Ability to use normally difficult to implement high pressure drop, small or compressible media.

The equipment size reductions appear to have general applicability. Amalgamated Research Inc. (ARi) is now commercially marketing reduced size fractal based chromatography systems.

### *Short-Bed Fractal Ion Exchange Systems*

The project encountered early success with a task involving the use of fractal based ion exchange. In this case a conventional juice ion exchange process was reduced in size by 90%. Due to the very large size decrease and accompanying decrease in system costs, the process was scaled up to a commercial operation and is presently operating at 700 gpm in a plant in Paul, Idaho. This was a clear demonstration of the successful use of fractal technology for enabling process intensification.

ARi is now commercially marketing this technology.

### *Fractal Distribution*

Another completed task involved the use of computational fluid dynamics (CFD) modeling for evaluation and design of the fractal structures used in the chromatography and ion exchange projects. A key aspect of this work was the demonstration of the importance of a variety of factors related to symmetries in the engineered fractal devices. It was determined that key symmetries that must be controlled through proper engineering include a device's geometric symmetries, the bulk hydraulic symmetries of the fluids in motion through the fractals and the internal symmetries of the fluid (such as formation of vortices which can break flow symmetries).

It was demonstrated that engineered fractals are elegant devices for controlling turbulence and greatly reduce energy loss or dissipation by suppressing the formation of large turbulent eddies. Fractals accomplish this in at least two ways:

1. By using channel bifurcation, engineered fractals effectively reduce the mean flow width, which reduces the order of magnitude of the large eddy size.

and,

2. Engineered fractals greatly reduce the negative effects of vortex stretching by orienting the vortex elements of the flow in a manner in which they are not stretched by the mean velocity gradients. Hence vortex stretching effects are greatly reduced in engineered fractals and energy loss in greatly reduced.

The CFD work provided a basis for successfully engineering these devices throughout the project.

### ***Synthesis and Separations of Acid-Sugar Hydrolysates***

As indicated above, a 75% reduction in the size of the acid-sugars chromatographic separator was achieved. This task involved the use of synthetic acid-sugar hydrolysate. Evaluation of system size reduction was made by comparing previous work done with the "Arkenol Process" and, further, by comparing the new system with the size of conventional systems of this type as recommended by resin manufacturers.

Due to the promising results, operation of the pilot fractal chromatography system applied to hydrolysate for acid-sugars separation is continuing independent of this project. An ARi pilot fractal chromatography system has been integrated into a biomass to ethanol pilot process and after one year of successful operation has been upgraded to a larger capacity chromatography system to allow for increased production.

## Recommendations

An optimal filtration system for handling biomass hydrolysates should involve a hybrid system capable of inexpensively segregating the larger part of the particle spectrum and a fine filtration system separating particles in the submicron range. A high efficiency fractal clarifier followed by membrane filtration appears sufficient to prepare hydrolysate for subsequent media based processing such as chromatography.

With respect to ultrafiltration and microfiltration technologies, there is good evidence that the embedded membrane concept developed in this project may offer a number of advantages over current state-of-the-art commercial membranes in the area of biomass filtration. The data and observations indicate that a heterogeneous filter element incorporating a coat material in the support interstices could provide adequate filtration performance (clarity and mechanical strength) while enhancing permeate flux and minimizing degradation of the membrane surface by abrasive mechanisms.

Additional developmental efforts to refine production techniques should be evaluated to provide a more open pore structure and concomitant increase in permeate flux.

The successful results obtained with short bed fractal chromatography and short bed fractal ion exchange technology suggest extending this work. While the project has already resulted in full scale commercial products, the knowledge gained concerning separation of sugars from acid and separation of sugars from background nonsugars forms a basis for expanding the applications from binary to multicomponent separations. This should target the multicomponent production of value added products or building blocks from lignocellulose derived hydrolysates and/or products produced from such hydrolysates.

# Contents

# Project Summary

## Introduction

Large-scale displacement of petroleum will come from low-cost cellulosic feedstocks like straw and corn stover crop residues. This project has taken a step toward making this projection a reality by reducing capital and energy costs, the two largest cost factors associated with converting cellulosic biomass to chemicals and fuels. The technology exists for using acid or enzyme hydrolysis processes to convert biomass feedstock (i.e., waste cellulose such as straw, corn stover, and wood) into their base monomeric sugar building blocks, which can, in turn, be processed into chemicals and fuels using a number of innovative fermentation technologies. However, while these processes are technically possible, practical and economic barriers make these processes only marginally feasible or not feasible at all. These barriers are due in part to the complexity and large fixed and recurring capital costs of unit operations including filtration, chromatographic separation, and ion exchange.

This project was designed to help remove these barriers by developing and implementing new purification and separation technologies that will reduce the capital costs of the purification and chromatographic separation units by 50% to 70%, thus achieving an overall processing plant economic benefit of about 25%. The technologies fundamental to these improvements are: (a) highly efficient clarification and purification systems that use screening and membrane filtration to eliminate suspended solids and colloidal material from feed streams and (b) fractal technology based chromatographic separation and ion exchange systems that can substitute for conventional systems but at much smaller size and cost.

A non-hazardous “raw sugar beet juice” stream (75 to 100 gal/min) was used for prototype testing of these technologies. This raw beet juice stream from the Amalgamated Sugar LLC plant in Twin Falls, Idaho contained abrasive materials and membrane foulants. Its characteristics were representative of an industrial-scale heterogeneous plant extract/hydrolysis stream, and therefore was an ideal model system for developing new separation equipment. Subsequent testing used both synthetic strong acid hydrolysate and corn stover derived weak acid hydrolysate (NREL produced).

A two-phased approach was used for the research and development described in this project. The first level of study involved testing the new concepts at the bench level. The bench-scale evaluations provided fundamental understanding of the processes, building and testing small prototype systems, and determining the efficiency of the novel processes. The second level of study, macro-level, required building larger systems that directly simulated industrial operations and provided validation of performance to minimize financial risk during commercialization. The project goals and scope included:

- Development of low-capital alternatives to conventional crop-based purification/separation processes.
- Development of each process to the point that transition to commercial operation is low risk.

## Summary of Tasks and Conclusions

### *Task 1a: High Suspended Solids Filtration*

A primary task of this project was to prepare biomass hydrolysates for subsequent processing with granular media based separation equipment such as chromatography. Because of the nature of biomass, following hydrolysis a significant amount of undissolved material remains. This complicates subsequent processing in media based equipment. The presence of colloidal matter and very fine particles presents a challenge for material removal by filtration. This project's study of particle distribution and characterization of the plant-derived model solution as well as pretreated corn stover indicated that a successful filtration method for handling such streams is a hybrid system capable of inexpensively segregating the larger part of the particle spectrum and a fine filtration system separating particles in the submicron range.

The pretreatment system for removing the larger particles included a clarifier where principles of fractal distribution were applied to reduce turbulence and improve performance. The novel clarifier was followed by a membrane system that demonstrated very high capacity due to the high level of solids removal in the clarifier stage. The membrane system operated at very high concentration factors, thus reducing potential loss of valuable components. The system's efficiency was demonstrated by continuous operation of a fully automated pilot system processing 600-700 tons/day of raw beet juice for a period of three consecutive processing campaigns. Long-term pilot operation allowed reliable operating data to be collected. As a result, full scale implementation should be low risk.

### *Task 1b: Membrane Erosion/Corrosion*

Both the capital and operating costs of membrane filtration are highly dependent on sustainable membrane performance. Several membranes that demonstrated excellent performance at the beginning of the project were completely eroded in a very short period of time. Catastrophic failure of membranes is not acceptable in industrial operation. This problem was solved by our invention of an erosion resistant "embedded" membrane where large membrane substrate is impregnated with finer particles which provide fine filtration. The concept was verified by consistent operation of the model membranes for three operating seasons.

A method for manufacturing the embedded membrane was proposed and patents applied. Several samples of the new type membrane were tested in bench-scale studies and their operation compared favorably with samples of commercially available membranes.

### *Task 1c: Novel Suspended Solids Removal*

The completion of this task was the result of combining the work discussed in the two tasks above. The combination of an improved clarifier using fractal technology and an innovative erosion resistant membrane constituted a hybrid liquid-solid separation system providing both high performance and separation efficiency. Resulting product was demonstrated to be successfully processed in subsequent granular media based equipment, including ion exchange and chromatography.

### *Task 2a: Short-Bed Fractal Chromatography Systems*

A key task of this project was to develop simulated moving bed (SMB) chromatography systems based on fractal technology with the goal of significantly reducing the size and costs of such systems applied to biomass processing. The project was successful in this regard. Key results using the fractal systems were:

- Reduction of the size of acid hydrolysate chromatography by 75% (acid/sugars separation).

- Reduction in the size of raw juice chromatography by 50% (model beet raw juice separation).

- The ability to use normally difficult to use high pressure drop, small or compressible media.

The equipment size reductions appear to have general applicability. Amalgamated Research Inc. (ARi) is now commercially marketing reduced size fractal based chromatography systems.

Operation of the fractal chromatography system applied to hydrolysate for acid/sugars separation is continuing independent of the DOE work. A pilot system has been integrated with a biomass to ethanol pilot process and after one year of successful operation has been upgraded to a larger capacity system for increased production. The overall process is presently producing sample fuel ethanol.

### *Task 2b: Short-Bed Fractal Ion Exchange Systems*

The project encountered early success with a task involving the use of fractal based ion exchange. In this case the conventional juice ion exchange process was reduced in size by 90%. Due to the very large size decrease and accompanying decrease in system costs, the process was scaled up to a commercial operation and is presently operating at 700 gpm in a plant in Paul, Idaho. This was a clear demonstration of the successful use of fractal technology for enabling process intensification.

ARi is now commercially marketing this technology.

### *Task 2c: Fractal Distribution*

Another completed task involved the use of computational fluid dynamics (CFD) modeling for evaluation and design of the fractal structures used in the chromatography and ion exchange projects. A key aspect of this work was the demonstration of the importance of a variety of factors related to symmetries in the engineered fractal devices. It was determined that key symmetries that must be controlled through proper engineering include a device's geometric symmetries, the bulk hydraulic symmetries of the fluids in motion through the fractals and the internal symmetries of the fluid (such as formation of vortices which can break flow symmetries).

It was demonstrated that engineered fractals are elegant devices for controlling turbulence and greatly reduce energy loss or dissipation by suppressing the formation of large turbulent eddies. Fractals accomplishes this in at least two ways:

- By using bifurcation of channels, engineered fractals effectively reduce the mean flow width, which reduces the order of magnitude of the large eddy size.

and,

-Engineered fractals greatly reduce the negative effects of vortex stretching by orienting the vortex elements of the flow in a manner in which they are not stretched by the mean velocity gradients. Hence vortex stretching effects are greatly reduced in the engineered fractal and energy loss in greatly reduced.

The CFD work provided a basis for successfully engineering these devices throughout the project.

### *Task 3a: Synthesis and Separations of Acid-Sugar Hydrolysates*

As indicated above, a 75% reduction in the size of the acid-sugars chromatographic separator was achieved. This task involved the use of synthetic acid-sugar hydrolysate. Evaluation of system size reduction was made by comparing previous work done with the "Arkenol process" and, further, by comparing the new system with the size of conventional systems of this type as recommended by resin manufacturers.

Due to the promising results, operation of the pilot fractal chromatography system applied to hydrolysate for acid-sugars separation is continuing independent of this project. An ARi pilot fractal chromatography system has been integrated into a biomass to ethanol pilot process and after one year of successful operation has been upgraded to a larger capacity chromatography system to allow for increased production.

## Milestones

The following table lists the project milestones and completion dates.

| ID Number | Task / Milestone Description | Planned Completion | Actual Completion | Comments |
|---|---|---|---|---|
| 1 | Hybrid membrane pilot-scale system set up | June 2001 | June 22, 2001 | Completed on schedule. (July 31, 2001) |
| 2 | Filtration membranes and operational parameters validated | September 2001 | June 1, 2001 | Operation parameters were validated and presented to the membrane study group in June 2001. This milestone also achieved a decision point, and verified that the hybrid configuration will work for the intended applications. This milestone was completed ahead of schedule and in advance of final alternations to the pilot-scale setup. (July 31, 2001) |
| 3 | Pilot-scale fractal installation | July 2002 | July 2002 | The pilot-scale chromatography unit has been fabricated, and tested for operational readiness. It will be installed and operated during the fall beet juice campaign (July 31, 2002) |
| 4 | Fractal chromatography designs validated | September 2002 | September 2002 | The fractal distributor design has exceeded performance expectations in the chromatographic separator and ion exchange applications, particularly with respect to energy savings (Sept. 30, 2002) |
| 5 | Manufacture optimized fractal | March 2003 | March 2003 | The design, manufacture, and installation of an optimized fractal separation system in the pilot-scale testing facility is completed and in operation at Twin Falls. |

| ID Number | Task / Milestone Description | Planned Completion | Actual Completion | Comments |
|---|---|---|---|---|
| 6 | Pilot-scale acid-sugar hydrolysate separation tests completed | September 2003 | September 2003 | Acid-sugar hydrolysate separation tests complete. |
| 7* | Complete pilot scale operation of the hydrolysate process train running for extended periods of time on the model beet juice system | March 2004 | March 2004 | Completed on schedule. |
| 8* | Identify optimum filter media/configurations for the model beet juice system<br>Identify performance of normally problematic compressible or other high pressure drop media in the fractal chromatography system using product from the model beet juice system | June 2004 | June 2004 | Completed on schedule |
| 9* | Complete comparison of filter throughput of hydrolysate and the model system on selected filter media/configurations | September 2004 | September 2004 | Completed on schedule |
| 10* | Complete comparison of hydrolysate and the model beet juice process on select media to perform optimally in a fractal system<br><br>Develop theoretical basis (derived from experimental and computational performance analysis of data) of fractal operation for improved separation systems<br><br>Complete final project report | December 2004<br><br>December 2004<br><br>Due End March 2005 | December 2004<br><br>December 2004<br><br>March 2005 | Completed on schedule<br><br>Completed on schedule<br><br>Completed on schedule |

* These milestones were added to the extended project to aid in evaluating progress.

# Quarterly Technical Results

This section contains the project technical results by quarter.

## 1st quarter – January 1, 2001 to March 31, 2001

This initial period of time was spent organizing the project and running a large number of preliminary tests.

### Fractal Chromatography

A key unit operation of this project was fractal based simulated moving bed (SMB) chromatography (Appendix 1 describes SMB chromatography). In the first quarter, 20 individual chromatography tests were completed which evaluated ARi's fractal concepts applied to biomass processing. The results appeared favorable and provided direction to this aspect of the project. The testing was continued into the second quarter. The results from this preliminary work were used to design the project's pilot fractal chromatography systems.

### Fractal Ion Exchange

Another key unit operation of this project was fractal ion exchange softening. During this quarter a pilot test was run with an ARi designed fractal ion exchange softener at 600 gpm located at an Amalgamated Sugar LLC factory in Paul, Idaho. The results validated this new approach to reducing the size of ion exchange equipment. The softener is approximately 1/10 the size of a comparable conventional system and was also demonstrated to operate with much lower pressure drop (lower energy use). Because ion exchange softening is a common industrial process, ARi considered this to be a marketable “spin-off” product.

### Membrane Filtration

Another key unit operation of this project was membrane filtration. Three membrane filtration units and necessary pretreatment equipment were operated by ARi during this quarter at the Amalgamated Sugar LLC Twin Falls factory (Fig. 1). Test flow rate was 100 gpm. The main purpose of the testing was to evaluate the performance and durability of several commercial membranes in conditions which simulate industrial operation.

As outlined in the project proposal, raw beet juice was tested as a model system representing filtration of plant derived solutions. Both tubular and spiral type membranes were evaluated. Results of the testing were favorable and enabled a reliable and cost effective configuration to be designed for the project.

Figure 1. Membrane filtration test assembly at Twin Falls, ID.

Figure 2. Bench scale cross flow filtration system for accelerated filter membrane erosion.

Also during this quarter, INEEL configured a bench scale cross flow filtration unit (Fig. 2). This bench scale filtration unit was used by INEEL to develop an understanding of the filtration process including evaluating the effects of aging the membrane surface, primarily due to erosion mechanisms, following extended periods of operation. This allowed evaluation of the effects of erosion by experimental determination of process parameters (permeate flux and transmembrane pressure) under the influence of accelerated surface erosion. Plans were made to pass abrasive slurries of corundum ($Al_2O_3$) and/or ground glass beads through ~2 ft sections of different filter membranes to accelerate the erosion process. Permeate flux, transmembrane pressure, and ultimately SEM analysis will be used to evaluate the effects of erosion on process parameters and surface characteristics. Several 0.1 μm pore size filtration membranes, including $TiO_2$ coated steel, sintered metal stainless steel, and polymer coated resin tubes were obtained by INEEL for the accelerated erosion testing.

### Computational Fluid Dynamics

During this quarter, ARi designed a number of candidate fractal fluid transporting structures which were passed along to INEEL for CFD (computational fluid dynamics) evaluation. At INEEL, turbulence models of various different configurations of pre-distributors were developed. These models provided insight on how effective various configurations were for providing symmetric flow distribution and symmetric axial flow. Models were also developed to determine the best configuration for flow outlet geometry. The best performing CFD candidates were subsequently constructed by ARi and re-evaluated using actual fluids.

Overall, the first quarter of the project proceeded successfully with completion of key preliminary work and early development of a marketable “spin-off” product.

## 2nd quarter – April 1, 2001 to June 30, 2001

### Chromatographic Equipment Design and Procurement

The primary activities at ARi during this time related to design of chromatographic pilot equipment. Based on experimental work from the previous quarter, pilot chromatographic equipment was designed specifically for separation of acid-sugar hydrolysate. Purchase of the pilot components was also begun. Because of the corrosive nature of sulfuric acid, the pilot system design required an in-depth evaluation of practical materials of construction. A wide range of metals and plastics were considered. This information will also be useful for future large-scale construction considerations. The use of sulfuric acid feed material also necessitated a review of handling and processing procedures as the acid and acid by-products must be handled and processed in a safe and environmentally acceptable manner. As a result, a number of safety features were incorporated into the acid separation pilot plant.

### Hybrid Membrane Pilot System

Setup of the hybrid membrane pilot scale system and validation of the filtration membranes and operational parameters were completed. This represented the completion of the first two project milestones. The results of these membrane tests were summarized and presented to the Membrane Study Group (in-kind contributors to this project). Membrane manufacturers were also present at this meeting and discussed equipment and testing for the next processing season. The membranes were operated using raw beet juice as a model system representing filtration of plant derived solutions. The results of a scanning electron microscope (SEM) evaluation of the used membranes provided information needed to design modifications into the existing membrane pilot plant. Required membrane alterations, maintenance and related construction work was begun in June.

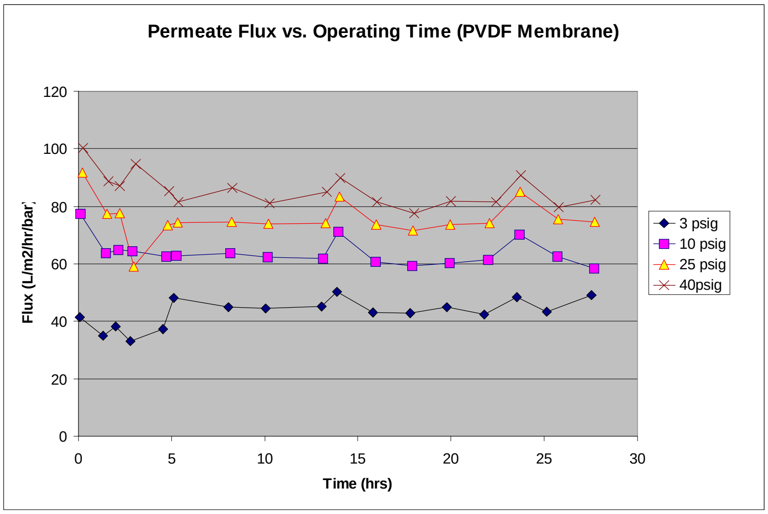



Figure 3. Flux vs. time for the PVDF membrane

Membrane erosion testing commenced at INEEL during the second quarter. Samples of the test membrane filter tubes were received including 0.07 μm $TiO_2$ coated steel (Graver), 70,000 molecular weight cutoff PVDF polymer coated resin (Filter Systems, Inc),and 0.1 μm sintered stainless steel (Mott Corp.). Additionally, samples of the Graver membranes previously used at ARi with ~1700 hours of operating time were obtained. Water fluxes were measured for each of the membranes in the INEEL experimental cross-flow system. The measured fluxes compared favorably with manufacturer water flux data.

Initial erosion testing of a PVDF membrane was initiated with exposure to a 5 wt% solution of 20 μm $Al_2O_3$ (corundum) in water. The abrasive corundum slurry was circulated through a 6 inch length (exposed surface) of the PVDF membrane at 6.5 gpm for ~28 hours. Water flux measurements were recorded as a function of time (Fig. 3). The flux did not noticeably change during the course of the abrasion testing, indicating that the elastomeric or "rubbery" characteristics of the polymer may be resilient to the abrasive conditions.

The PVDF membrane was removed and sectioned for scanning electron microscopy (SEM) analysis. The SEM pictures of the PVDF layer from cross sections of a pristine ("new") and the abraded membranes are indicated in Figures 4 and 5, respectively. The gouging and degradation of the polymer layer is apparent for the

abraded membrane, indicating abrasion was altering the interior membrane surface. The system was likely not operated for a long enough period of time to note changes in the flux characteristics. The results clearly indicated that the experimental system is amenable to degradation of the membrane surface.

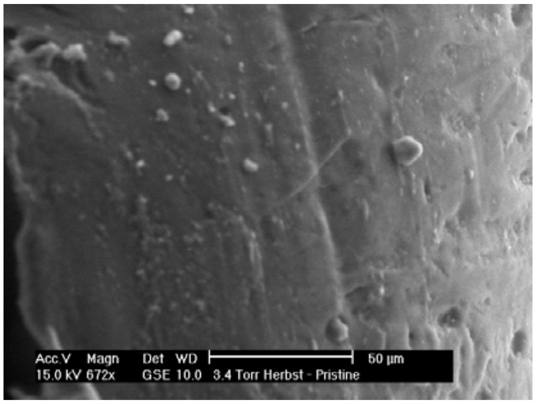



Figure 4. Cross-sectional SEM photograph of a pristine PVDF filter membrane.

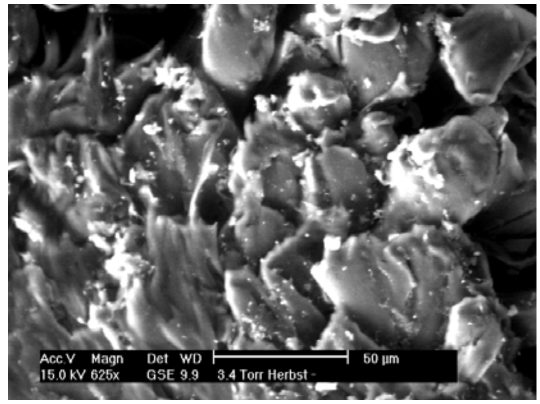
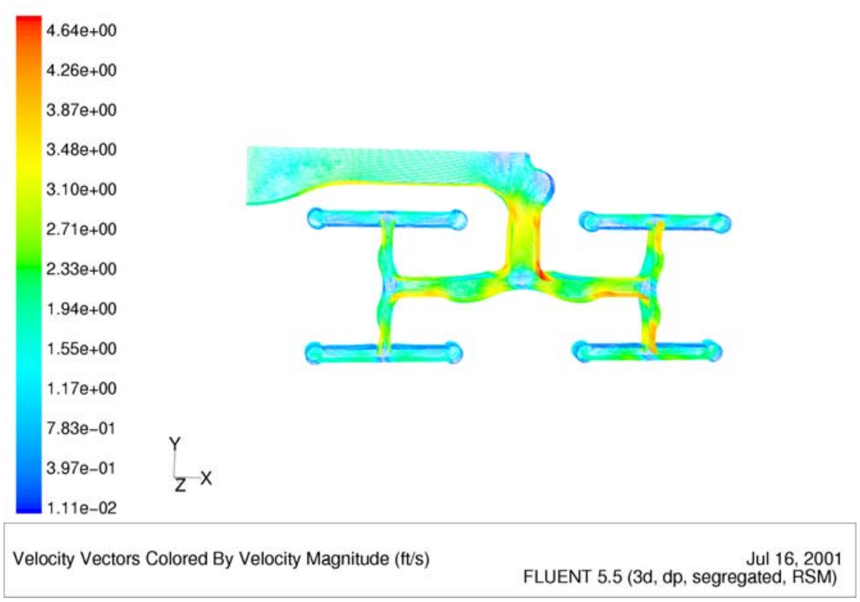



Figure 5. Cross-sectional SEM photograph of the abraded PVDF filter membrane.

## Computational Fluid Dynamics

During the quarter, work continued on the design and evaluation of candidate fractal fluid transporting structures. The structures were evaluated at INEEL using their CFD (computational fluid dynamics) personnel and facilities. A number of various design alternatives were evaluated using a sophisticated turbulence model (Fig. 6). This analysis provided useful insight on how the current design can be improved in order to provide a more uniform exit velocity profile.



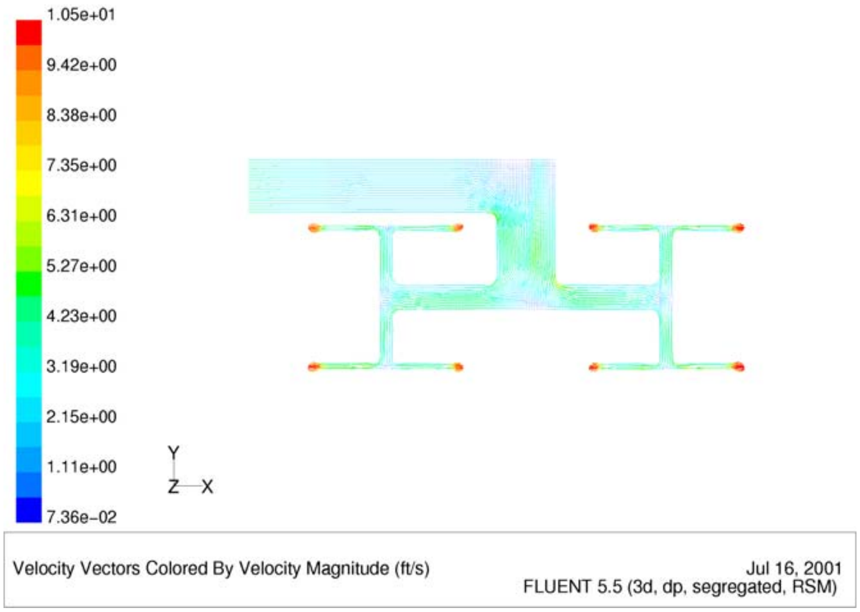



Figure 6. Examples of CFD analysis of fractal flow channels.

## 3rd quarter – July 1, 2001 to September 30, 2001

### Chromatography

During this time period the project's chromatography pilot system was fully assembled. This included the software programming, the communication/control interface and all the system hardware. Parameters for operation were also prepared and entire system was tested with water as feed material.

Safety considerations associated with acid hydrolysates required more hardware than ordinarily used in a chromatography system. Equipment to handle and dispose of corrosive components was installed and tested. Overall, the chromatography system preformed well during water testing and the safety evaluation.

### Membranes

The Twin Falls membrane pilot process was tested using industrially produced raw juice. The pilot system, for suspended solids removal, included two membrane pilot plants which were used to evaluate two different types of membranes. Seven modules used in earlier testing were installed in order to continue longevity studies.

Membrane erosion testing continued at the INEEL during the third quarter. Samples of 0.07 μm $TiO_2$ coated sintered stainless steel membranes were sent to INEEL from ARi for analysis (Figures 7 and 8). These samples were exposed to an abrasive environment during the pilot plant operation (approximately 2000 hours). Detailed inspection of the "2000-hr" membrane samples indicated irregular erosion of the

$TiO_2$ coating and steel support. It is unclear whether the irregularities were present from the beginning of the test. Despite the surface imperfection, ARi observed no noticeable decrease in flux during operation.

The quality of permeate remained unchanged, and microbiological analysis demonstrated that the permeate was always sterile. This conclusion was quite important, because it implied that the surface coating of the membrane is of secondary importance. A SEM photograph of a "2000 hr." membrane (inside edge) is shown in Figure 7. It is of note that the particles of $TiO_2$ are completely filling the pores between the stainless steel particles, thus

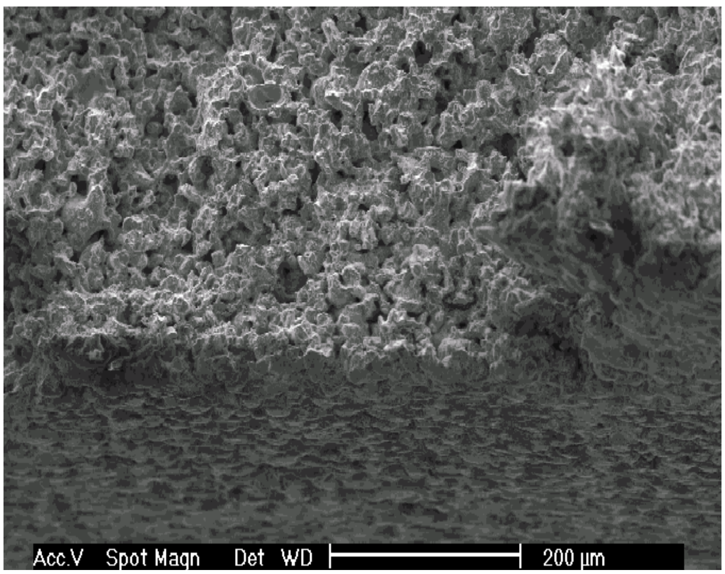



Figure 7. SEM photograph of "2000 hr" membrane (inside edge)

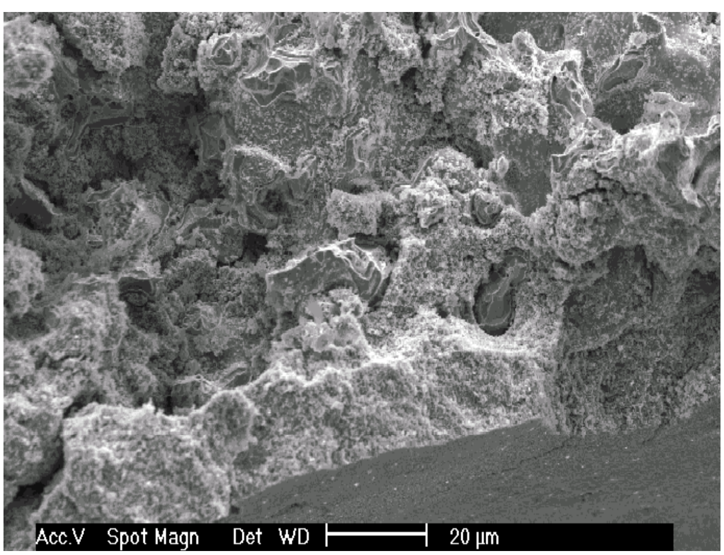



Figure 8. SEM photograph of pristine membrane (inside edge)

forming an "embedding" membrane. A comparative SEM photograph of a pristine membrane (inside edge) with intact $TiO_2$ coating is shown in Figure 8.
Samples of the 2000-hr membranes acquired from ARi were modified for operation and continued abrasion in the Cells Unit Filter (CUF) apparatus. It is worth noting that the ARi membrane had not been subjected to intensive cleaning. Water fluxes were measured for the 2000-hr membranes and compared against new membranes. Results indicated clean water fluxes approximately 3 times lower for the ARi membranes compared to new, pristine membranes (clean water fluxes were measured at crossflow velocities of 0.8 m/sec, 17-20°C, and 2.76 bar transmembrane pressure).

Two different cleaning methods were evaluated for restoring filtrate flux. Each method was followed by a clean water flux measurement. Chemical cleaning was conducted on samples of new and 2000-hr membranes by first soaking in a stirred solution of 0.5 M NaOH at 90°C for 4 hours. The samples were then soaked in a stirred solution of 0.1 M $HNO_3$ at 90°C for 1 hour. The samples were water rinsed and clean water fluxes were measured to evaluate the effect of chemical cleaning. Clean water flux for the 2000-hr membrane sample nearly doubled following chemical cleaning. The samples were then subjected to physical cleaning using an ultrasonic bath with water for approximately 1 hour. Subsequent clean water flux measurements indicated the water flux again nearly doubled after the ultrasonic (physical) cleaning. The clean water flux results are summarized in Table 1.

Table 1. Membrane cleaning results.

| Membrane | Cleaning | Clean Water Flux ($L/m^2/hr/bar$) |
|---|---|---|
| Pristine SS/ceramic Membrane | N/A | 518 [a] |
| 2000-hr SS/ceramic Membrane | N/A | 163 |
| 2000-hr SS/ceramic Membrane | $NaOH/HNO_3$ | 260 |
| 2000-hr SS/ceramic Membrane | Ultra Sonic Bath | 426 |

[a] Measured at an axial velocity of 0 m/sec, i.e., the filter was "dead-headed".

Once clean, the water flux for the 2000-hr membrane was restored to nearly pristine conditions, and erosion testing continued on this sample. A 5 wt. % slurry of $Al_2O_3$ (20 μm) in water was used as the abrasive media. The $Al_2O_3$ slurry was circulated through the membranes at 3.5 gpm for 58 hours. The water flux decreased slightly in the course the test. However, it was difficult to discern whether it was the result of surface damage. The particle size analysis of $Al_2O_3$ slurry showed a gradual decline in particle size. It was unclear if grinding of the corundum particles caused this decrease or fine $TiO_2$ particles from the membrane appeared in the solution and contributed to the shift in particle size analysis.

**New CUF Apparatus**

A second, new CUF apparatus was fabricated for continued abrasion testing. The major modifications of the new system were a different (centrifugal) pump and larger (4 liter) feed vessel. This was anticipated to help eliminate the problems of pump failure from the abrasive corundum slurry and aeration of feed slurry at higher flowrates (4-8 gpm) through the system. The older CUF system continued to be available for use to measure clean water fluxes on the membrane samples in the absence of the corundum particles, which should help alleviate any membrane fouling associated with flux measurements in the presence of solids. Additionally, the older system was available for chemical cleaning of membrane samples under process flow conditions.

### Quantification of Erosion Phenomena

Flux measurements and scanning electron microscopy (SEM) were the methods being evaluated to quantify erosion characteristics. However, the work to date indicated that these techniques may not be an ideal method to evaluate erosion. This is because of the inherent problem associated with forming a protective layer of abrasive material at the surface of the membrane or blinding the membrane pores (fouling) as a result of applying transmembrane pressure (necessary to measure flux) in the presence of the abrasive corundum solids.

Although the use of SEM analysis provided an indication of the effects of abrasion on the membrane surface, the method suffered from the inherent drawbacks of being a destructive method, and provided only qualitative data regarding the abrasive mechanism. An additional method of quantifying erosion was required. Porous Materials Inc. (PMI) was been contacted in regards to a filtration media analyzer. The filtration media analyzer provides fully automated analysis of several membrane tests such as bubble point, pore-size, integrity, gas permeability and liquid permeability. The applicability of such methods to characterize erosion was investigated.

### Computational Fluid Dynamics

As in the previous quarter, work continued on the design and evaluation of candidate fractal fluid transporting structures. The structures were evaluated at INEEL using their CFD (computational fluid dynamics) personnel and facilities.

### Membrane Filtration Pilot Plant

Support processes for the Twin Falls membrane system were designed during the quarter. These support processes were necessary to complete the overall integrated biomass processing pilot plant and involve feed treatment prior to membranes and subsequent concentration of product

## 4th quarter – October 1, 2001 to December 31, 2001

### Industries of the Future Award

Idaho's Energy Division's Industries of the Future program in partnership with the U.S. Department of Energy Honored Amalgamated Research, Inc. and INEEL with the "2001 Idaho Innovation in Industry Agriculture and Food Industry Award." Researchers at Amalgamated Research, Inc. (Dennis Costesso, Mike Kearney, Vadim Kochergin, John Cox, Gene Rearick, Mike Mumm, Ken Petersen, Bill Jacob, and Larry Velasquez) and INEEL (Eric Peterson, Thomas Foust, Nick Mann, Richard Hess, and Scott Herbst) won the award for their work on this project (Industrial Membrane Filtration and Fractal Separation Systems).

The award presentation was made in Boise, ID at the Idaho Industrial Summit and Expo on November 13, 2001, which was "Idaho Industries of the Future Awareness Day" as proclaimed by Dirk Kempthorne, Governor of the State of Idaho.

In addition to the award, the fourth quarter of the project proceeded with no delay in reaching milestones.

**Pilot Scale Raw Juice Purification**

A pilot raw juice purification system consisting of juice pretreatment and two membrane filtration systems were operated successfully. The system used about 100 gallons per minute of fresh beet diffusion juice. One of the main objectives of the test was to evaluate the effective lifetime of the polymeric and stainless steel membranes. Total operating time since the beginning of beet campaign for stainless and polymeric membranes reached 1700 hours and 800 hours, respectively. Brief membrane surface inspection did not reveal significant changes in surface condition. Cleaning of the polymeric membranes appeared to present more difficulties, therefore, the operating time was lower comparing to stainless membranes.

The pretreatment system comprised a Tekleen self-cleaning filter/screen with a 100-micron opening size. After several modifications to adapt the screen for treating sugar solutions, the installation demonstrated reliable operation. The filter was especially efficient removing fibrous material from beet juice.

Several tests were performed with concentration factors of 50 and 100X. A positive displacement pump was installed on the concentrate line to avoid control problems at low flowrate. Typically it takes considerable time to concentrate solids in a single stage membrane system. Calculations show that it can take about 40-50 hours to reach 50X concentration factor. Therefore, the control program was modified to reduce transition time and make sure that the results were meaningful. The flux was about 90 GFD for 50X and 70 GFD for a 108X test. It was of interest to observe the viscosity change in the concentration loop. Viscosity of 100 X concentrate measured at 25$^{o}$C was almost 10 times higher than that of feed material. This may have been due to a large concentration of suspended particles since the permeate samples showed viscosity similar to feed material. Dextrans rejected by membranes may also contribute to viscosity increase.

**Membrane Erosion Testing**

Membrane erosion testing continued at the INEEL during the fourth quarter. A statistical parametric study using 0.01 $\mu$m polymeric membranes and solutions containing $Al_2O_3$ was initiated. The statistical parametric study varying parameters such as temperature, axial velocity, particle size and solids loading was evaluated for their effects on membrane stability and filtrate flux. Data and SEM analysis obtained from testing was used to detemine which parameters have the greatest effect on membrane erosion.

Additionally, the fabrication of a second Cells Unit Filter (CUF) apparatus was completed during this quarter. A (4 liter) feed vessel was also added to the old system. The larger feed vessel has been shown to eliminate aeration of feed slurry at higher flowrates (4-8 gpm) through the system.

### Pilot Fractal Chromatography

Operation of the newly constructed pilot fractal chromatography system was begun. By the end of the quarter it was demonstrated that the fractal chromatography system could enable at least a 75% reduction in the size of the acid hydrolysate separation process compared with conventional process size recommendations by chromatographic resin suppliers (Dow Chemical) and compared with previous conventional configuration pilot studies by Arkenol and ARi.

Combined with the fractal ion exchange results obtained earlier in this project, it was demonstrated that both the ion-exchange and the chromatography processes can be significantly reduced in size and capital cost. A major goal of the project was to demonstrate that such a reduction is possible.

Construction of the fractal chromatography support equipment for the biomass processing pilot plant was begun. This included a pilot fractal ion exchange system and an evaporator.

### Publications/Presentations

Kearney, M., V. Kochergin, D. Costesso, J. Cox, G. Rearick, M. Mumm, K. Petersen, B. Jacob, and L. Velasquez. Engineered Fractal Structures for Fluid Processing. *Exhibit – Idaho Industrial Summit and Expo.* Boise, ID. November 3, 2001.

## 5th quarter – January 1, 2002 to March 31, 2002

### Pilot scale raw juice purification

All pretreatment systems including heat exchange, clarification and pre-screening operated consistently to the end of campaign in February.

Spiral membranes were not in operation during the month of January and the beginning of February. At this time the decision was made to analyze a module from the skid. The main purpose of the test program was to evaluate the useful life of the membranes. It was known that cleaning is responsible for normal gradual membrane aging. Multiple cleanings would eventually reduce the life of the test membranes without answering the question of their longevity. This was another motivation for temporarily stopping the testing.

The manufacturer performed an autopsy on the removed membrane and came to the conclusion that overall the membrane appeared to be in good condition. No signs of chemical damage were observed. Scanning electron microscopy showed the presence of some possible fouling. IR spectrometry analysis was also performed and the results were sent to ARi for evaluation. According to ARi specialists the peaks indicated the presence of both organic and inorganic materials. A sample of the membrane was also analyzed for total nitrogen using the Kjeldahl method. The total estimated amount of protein was several grams per 15 square meters of membrane surface.

Tubular membranes were operated throughout the quarter and continued to demonstrate reliable performance. However some drop in performance was observed which may have been related to juice quality. Total operating time (including last campaign) reached 4500 hours. Permeate quality was always acceptable.

As a part of the cooperation with the Idaho National Engineering and Environmental Lab, tests were carried out in a separate membrane system using samples obtained from several sources. Following operation these membrane samples were found to exhibit different degrees of wear. The main purpose of this testing was to determine if membrane performance changes depending on the condition of the membrane coating.

The new evaporator and softener unit operations operated well during the month of January. As a result, it was possible to supply sufficient quantities of treated material as feed for the fractal chromatography system.

**Membrane Erosion Testing**

The two Cells Unit Filter (CUF) systems were taken to ARi during this quarter and several membrane filters with different degrees of age and erosion were tested on raw beet juice. The tests were conducted in conjunction with the the larger pilot operated on raw juice at ARi for comparative purposes. The filter membranes tested were $TiO_2$ coated stainless steel and samples were obtained which had been in operation for approximately 2000 hours, 1 year, 2 years, 3 years. A sample of “pristine” membrane was also evaluated for comparision. Samples of the tubular filter membranes were qualitatively evaluated using a Scanning Electron Microscope (SEM) to examine the interior membrane surface, providing a relative method to compare the condition of the interior surfaces of the different samples. The condition of the membranes varied in terms of the visible condition of the interior surface, and therefore in the degree of erosive wear present in the various samples. The 3 year sample was extremely eroded, containing no discernable $TiO_2$ coating and the stainless steel substrate being highly polished. Erosion observed in the samples was related to the process conditions and feed stream under which the filter membranes were operated; the associated time frame of operation (1, 2, or 3 years), while convienent for sample labelling, in no way reflects the anticipated life span of similar membranes under the process conditions anticipated in the application associated with this project.

During testing with raw juice, one of the two CUF systems was set up and operated with the sole purpose of cleaning samples of filter membranes. Cleaning efficiency was evaluated in this system by determining the clean water flux (before and after cleaning) through the filter sample under a standard set of process conditions. The cleaned samples were then installed into the second CUF and raw beet filtered through the system. The juice flux was measured as a function of time under standard process conditions. Data were collected until the filter flux achieved approximate or semi-steady state condition. This data allowed comparision of filter performance as a function of membrane condition.

The statistical abrasion tests were halted since the data did not indicate a quantifiable degree of abrasion under the test conditions developed. Additional testing of this type may be continued in the future, pending the development of appropriate test conditions.

### Pilot Fractal Chromatography

In the previously reported quarter it was demonstrated that the pilot fractal chromatography system was capable of significantly reducing the size of the acid hydrolysate process compared with conventional process size. This work was continued in the present quarter and it was demonstrated that a similar reduction in the size of the chromatography process could be achieved with permeate feed from the membrane process. Therefore, it could be concluded that the fractal chromatography approach allows significant size reduction for both acid/sugars separation and for the separation of the components of plant extracts.

## 6th quarter – April 1, 2002 to June 30, 2002

### Pilot scale raw juice purification

Following the 2001-2002 raw beet juice campaign, the membrane systems were inspected and serviced to ready the membrane processing systems for fall 2002 operation.

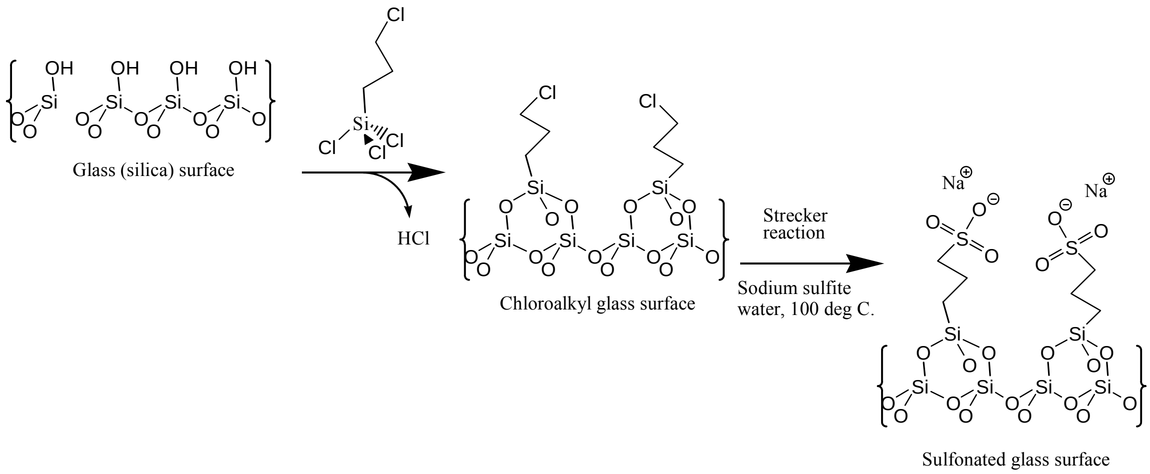
An annual report was prepared and presented to the project sponser group on May 13-14, 2002. Planning for the next campaign as well as ARi’s proposal and budget for the next season were discussed. A final decision was made on the specific membrane systems to be evaluated in the fall 2002 pilot system.

### Membrane Erosion Testing

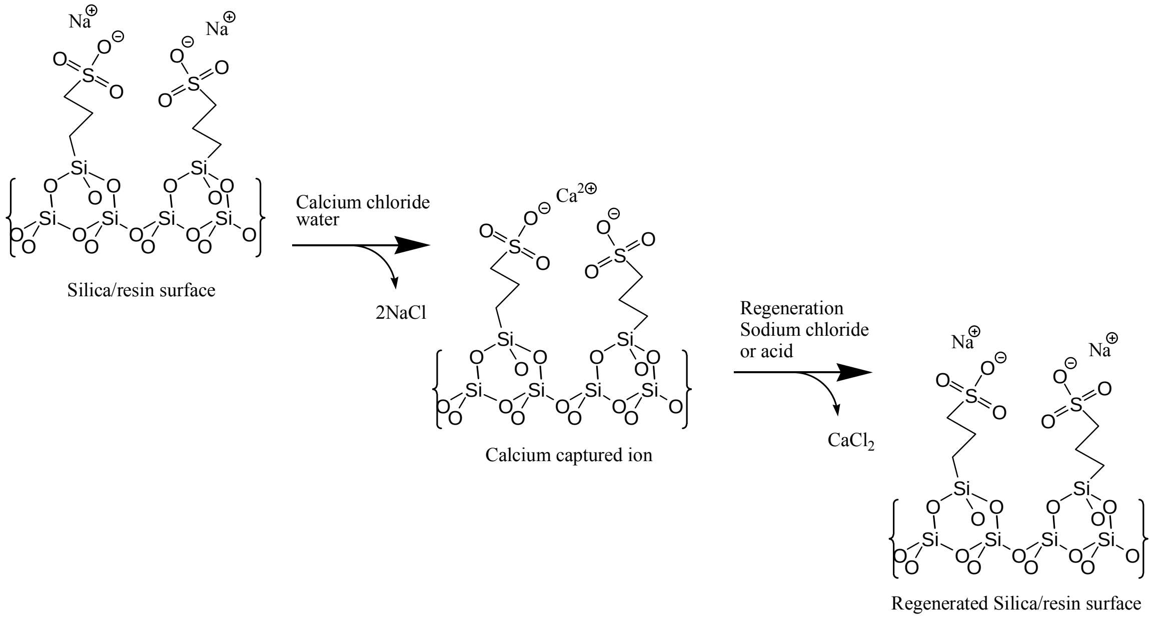
Data from the errosion studies were analyzed and an invention disclosure record was prepared for a new membrane design concept. The sintered metal membranes were proven to be very resistant to abrasive conditions and not likely to experience catastrophic membrane system failures.

### Softener Resin Development

Development began on a silica based softener resin that would be optimized for use in fractal softener columns used on the model beet juice system. Synthesis of the new silica resin is accomplished using the following process.




The ion capture and regeneration mechanism of the resin are as follows.




Using a test column containing 3 grams of modified silica resin, the capacity using saturated sodium chloride as an eluant was:

- Column capacity for copper and calcium was 300 micrograms of metal per gram of modified silica.
- Sodium chloride removes approximately 80% of absorbed metal per strip cycle.

The advantages of this system are an inexpensive stripping agent and operation at neutral pH (7.0). The disadvantages are absorbed cations are not entirely removed and only partial regeneration of column.

Using a test column containing 3 grams of modified silica resin, the capacity using 1% nitric acid as eluant:
- Column capacity for calcium was 770 micrograms of metal per gram of modified silica.

- 1% nitric acid removed 100% of absorbed metal per strip cycle.

The advantages of this system are complete removal of absorbed cations, higher capacity, and total regeneration of column. The disadvantages are low pH (1.0) and eluant cost is slightly higher than saturated sodium chloride.

**Pilot Fractal Chromatography**

Work to reduce the size of the acid hydrolysate chromatographic separator was continued. Planning and design work for the integration of fractal chromatography into the integrated model system was proceeding.

**Publications/Presentations**

Kochergin et al. 2002. Progress on Development of Membrane Filtration Systems. Membrane Study Group Presentation, Twin Falls, ID May 13-14, 2002.

Foust, T.D., M.M. Kearney, V. Kochergin, E.S. Peterson, R.S. Herbst, N.R. Mann, and J.R. Hess. 2002. Industrial Membrane Filtration and Fractal Separation Systems. 24th Symposium on Biotechnology for Fuels and Chemicals, Gatlinburg, TN, April 28-30, 2002.

## 7th quarter – July 1, 2002 to September 30, 2002

**Project Annual Review**

The project annual review was held at the ARi research facility in Twin Falls, ID on July 25, 2002. Conducting the review was Mark Paster and Amy Manheim from DOE headquarters and Matea McCray the DOE Idaho contracting officer. The two main points of discussion were the developments on the embedded membrane concept that is considerably improving membrane performance and longevity under the harsh conditions of raw crop extracts, and the higher than expected performance efficiencies of the fractal chromatographic separator.

Also of specific mention were the variety of energy savings experimentally observed with the fractal systems. These energy savings include reduced distribution and collection pressure drop, reduced media pressure drop (with a 700 gpm fractal ion exchange application, the pressure drop was 1/70$^{th}$ the drop across a conventional system), reduction of turbulence which reduces the energy losses due to the turbulent dissipation of energy, and post processing savings due to sharper cut-off of rinse cycles which subseqently require concentration.

**Pilot scale raw juice purification**

All planned maintenence and automation projects were completed before the end of the quarter.

### Membrane Erosion Testing

Computational fluid dynamics analysis was performed to evaluate the embedded membrane concept for pressure drop and flux rate. Initially a macro-scale analysis was performed, which proved to be inconclusive for the purpose of evaluating different embedded membrane configurations. A new micro-scale approach was being developed that would overcome the inaccuracies of the computational assumptions made at the macro-scale.

### Softener Resin Development

INEEL scientists completed synthesis of small amounts of silica-based ion capturing materials. The materials were tailored for the ions that are specified in the beet juice model system. The materials were to be evaluated at bench scale for their throughput and ion capturing properties/capacities at INEEL.

### Pilot Fractal Chromatography

Chromatography work was primarily directed towards preparation of the pilot systems for integration into the model system which will be operated in the next quarter.

### Publications/Presentations

Foust, Thomas D., Michael M. Kearney, Vadim Kochergin, Eric S. Peterson, R. Scott Herbst, Nick R. Mann and J. Richard Hess. 2002. Industrial Membrane Filtration and Fractal Separation Systems for Separating Monomers from Heterogeneous Plant Material. Bioenergy 2002, Boise, ID, September 22- 26, 2002.

## 8th quarter – October 1, 2002 to December 31, 2002

### Pilot scale Raw Juice Purification and Separation Processing Train

During this quarter the entire raw juice processing train was completed. Previous operation was somewhat piecemeal in order to clearly evaluate each unit operation. The train now included: clarification, filtration, membrane skids, ion exchange, evaporation and chromatography. The entire train was operating by January 2003. The processing train (minus chromatography) operated reliably October through December. Incoming flow rate of raw juice was 100 gpm.

At the end of the quarter, a particular candidate membrane had operated a total of 6300 hours (includes previous campaign). This result was important in that this membrane, together with the pre-processing steps, appears to provide a practical manner to filter biomass derived solutions.

An existing pilot chromatography system was retrofitted to allow fully automated operation with the material produced from the juice processing. The completed train now provides an overall demonstration of the concept of biorefining. All pilot equipment in the processing train is large enough to allow scale-up to commercial size equipment.

Figure 9. Location of the pilot testing. Amalgamated Sugar Co. plant In Twin Falls, Idaho.

Figure 10. The pilot plant enclosure with raw juice delivery from the plant.

Figure 11. Raw juice tank. Typical flow rate to filtration = 100 gpm.

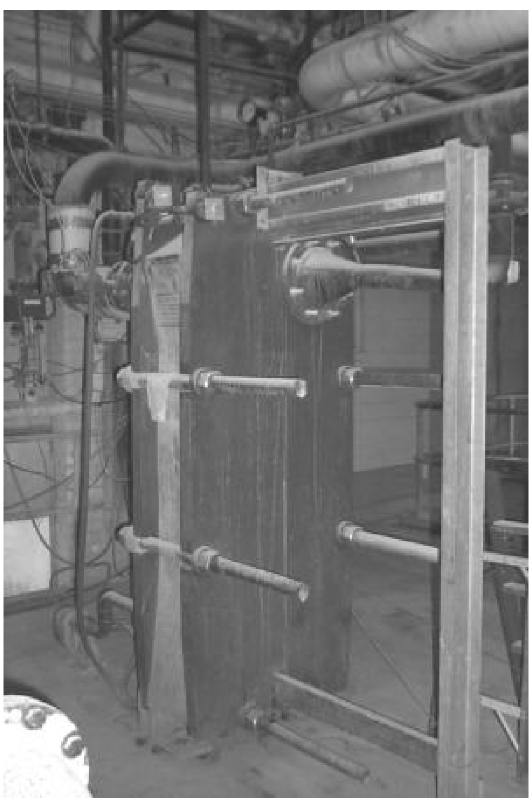


Figure 12. Raw juice heat exchange.

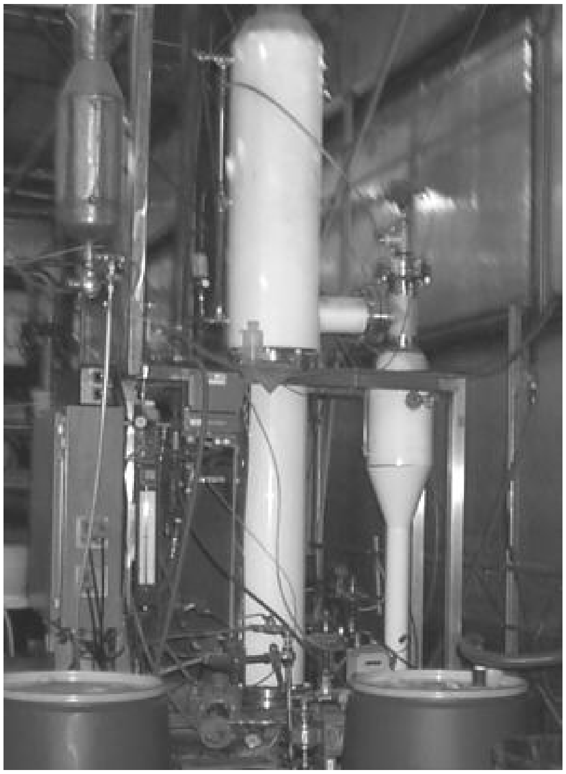


Figure 13. Treated juice evaporator prior to chromatography.

Figure 14. One of several candidate membrane skids.

## Engineered Fractals for Gas-Liquid Systems

As the present DOE project proceeded, it was recognized that fractal technology could be applied to additional unit processes required for biorefining. These processes include distillation and scrubbing equipment (gas-liquid applications).

With the permission of the DOE, $20,000 of the project funding was diverted to finance a joint program with TU Delft and the Separation Research Program (SRP) at the University of Texas at Austin The purpose was to investigate the applicability of fractals to these processes. Both Universities are recognized centers for gas-liquid research and are fully qualified to carry out investigation of the required projects. The work plan is shown in the following table.

Table 2. Fractal work plan.

| Test | Goal | Model system | Collaborator /est. cost |
|---|---|---|---|
| 1. Hydraulic test with mass transfer packing | Compare distributors (conventional vs. fractal). To include measurement of mass transfer area | Caustic – $CO_2$<br>18" diameter column | SRP/U of Texas at Austin<br>$10,000 |
| 2. Hydraulic test with mass transfer packing | Initial distribution vs, packing distribution at various gas loads | 5' diameter Column<br>air - water | Delft/Netherlands<br>$10,000 |

SRP completed their work in this quarter and a report was submitted to ARi. Results demonstrated that engineered fractals provide superior performance compared with conventional equipment. The Delft testing was completed in the first quarter of 2003.

## Publications/Presentations

Amalgamated Research Inc. attended the AIChE 2003 annual meeting and presented a paper and poster concerning the present DOE project. These were included as part of the Separations 2020 sessions.

Paper title: "Reducing Capital Costs and Facilitating Scale-Up of Bioseparations Using Fractal Technology"

Author: Mike Kearney

Poster title: "Amalgamated Research Inc. Bioseparations Technology"

Author: Vadim Kochergin

## 9th quarter – January 1, 2003 to March 31, 2003

### Pilot scale Raw Juice Purification and Separation Processing Train

During this quarter, for the first time, the entire raw juice processing train was operated. This included clarification, filtration, membrane skids, ion exchange, evaporation and chromatography. All equipment operated reliably.

The most reliable candidate membrane had been operated for 7500 hours. At the end of the quarter, the clarification through evaporation steps were shut-down and maintenance begun (the end of the beet processing campaign was reached). The chromatography operation was extend into subsequent quarters by using stored material from the evaporation step.

### Ultra-Filtration Testing using NREL Hydrolysate

Ultra-filtration testing using samples of NREL hydrolysate was performed at ARi during March 2003. The scope of testing was to provide a preliminary estimate of the overall filterability of actual hydrolysate and examine the performance of three different ultra-filtration membranes on this feedstock.

Three ultra-filtration membranes, a Mott (0.1 mm, symmetric, industrial grade), GKN Sitka (0.1 mm, asymmetric) and Graver Scepter (0.1 mm, asymmetric, $TiO_2$ coated), were tested in the Cells Unit Filter (CUF) system using actual hydrolysate provided by NREL. All membranes tested had an inside diameter of 0.375 inches and were comprised of sintered 316 stainless steel. Prior to testing, the Mott and GKN membranes were pretreated to remove any residual organics present from previous testing. This was accomplished by processing a 2% caustic solution containing 200 ppm chloride (bleach) for 0.5 hours. The Scepter membrane followed a separate pretreatment process, as specified by Graver. This was accomplished by processing a 2% caustic solution at >85 °C for 10 minutes followed by a 0.01 nitric acid (pH=2-3) at >85 °C for 10 minutes.

Once the pretreatment step was complete, the system was thoroughly rinsed and prepared for testing. Approximately 3-Liters of stock NREL hydrolysate was added to the CUF apparatus for each test. Hydrolysate solutions were heated to approximately 65 °C (NREL suggested a operating temperature of 65-80 °C) using an immersion heater. Testing was performed at 20 TMP and 3.7 gpm. Permeate flux was recorded in 10 minute intervals. Since flux rates were relatively high, flux was obtained by collecting a given volume of permeate (100-300 mLs) in a graduated beaker and recording the time. Filtrate flux as a function of time for the Mott, GKN and Graver membranes are shown in the Figure 15.

At various stages during testing, samples of the feed solution and permeate were taken to measure turbidity. The average turbidity measurements (NTU) for the Mott, GKN and Graver membranes are shown in Table 3. In addition, during the GKN membrane test, samples of stock unfiltered hydrolysate and permeate (after two hours of operation) were measured in absorbance units using a Beckman DU-65 photo spectrometer. Both permeate and stock feed solution displayed an absorbance of 3.967. No change in color was observed.

The data obtained in these tests definitely indicated there may advantages to evaluating other commercially available membranes for pilot and large scale testing of hydrolysate solutions. Substantial increases in permeate flux have the net effect of reducing the size of filter equipment and/or increasing throughput of industrial scale systems, thereby enhancing the process economics. Aspects such as flux as a function of solids loading, ability to clean the media, long-term stability of flux, and filter life was addressed during additional testing.

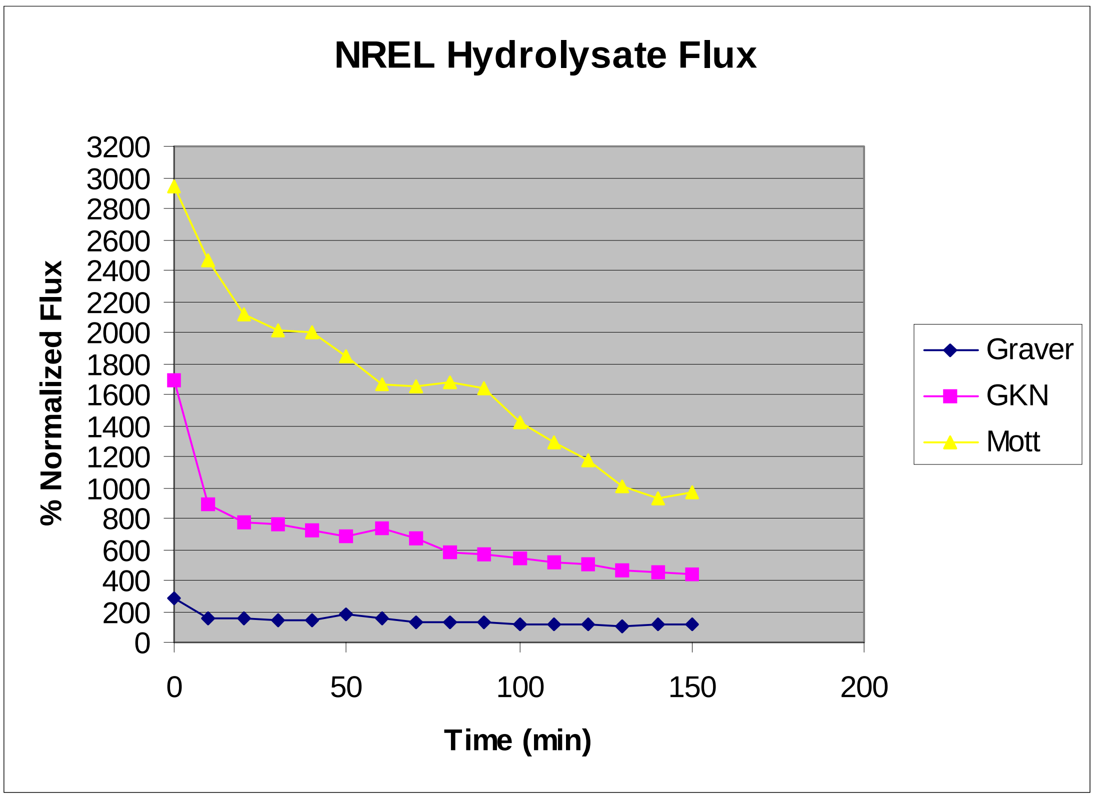



Figure 15. Flux as a function of time for the Mott, GKN, and Graver 0.1 micron, industrial grade commercial membranes.

Table 3. Average turbidity measurements for Mott, GKN and Graver membranes.

| Mott | GKN | Graver | |
|---|---|---|---|
| Permeate | 0.18 NTU | 0.37 NTU | 0.27 NTU |
| Feed | 83.6 NTU | 92.3 NTU | 127.5 NTU |

### Engineered Fractals for Gas-Liquid Systems

Due to the success evaluating a fractal distributor by the Separation Research Program (SRP) at the University of Texas at Austin, the decision was made to design and construct an aluminum fractal for additional testing.

### Publications/Presentations

The AIChE (American Institute of Chemical Engineers) requested that ARi present the fractal concepts being developed in this project at the AIChE Spring "Process Intensification" sessions. This was an appropriate forum because engineered fractals narrow the distribution of fluid properties in a controlled manner and can therefore result in significantly smaller equipment, less energy use and more homogeneous processes. These characteristics are associated with process intensification.

## 10th quarter – April 1, 2003 to June 30, 2003

In this quarter, the majority of the test equipment was temporarily shutdown following completion of scheduled testing. Evaluation was begun on the data collected during the 9th quarter pilot testing. Results of the on-going project were prepared and presented at meetings and in publications.

### Pilot scale Raw Juice Purification and Separation Processing Train

Although the raw juice purification and separation processing train was shutdown, as scheduled, the chromatography of processed and stored raw juice continued during the 10th quarter. It was demonstrated in these tests that the fractal oriented raw juice chromatographic separator could be operated at twice the baseline capacity thus reducing the separator size in half for this application. This corresponds well with the results determined earlier in this project wherein the synthetic hydrolysate chromatography system was also significantly reduced in size.

### Engineered Fractals for Gas-Liquid Systems

Due to the success evaluating a fractal distributor by the Separation Research Program (SRP) at the University of Texas at Austin, the decision was made to design and construct an aluminum fractal for additional testing. During this quarter the device was manufactured and some preliminary testing was completed.

### Publications/Presentations

Data collected during the operation of the pilot plant during the beet processing season was presented to the group of companies sponsoring the membrane part of the project.

A paper titled, “A Concept for Enhanced Flux, Erosion Resistant Membranes for Biomass Separations,” was presented at the American Filtration and Separations Society 16th Annual Technical Conference and Exposition, held in Reno, Nevada June 18-21. Numerous professionals working in the field of filtration, including academic, industry and manufacturing, attended the conference. The paper, as well as the embedded membrane concept, was well received.

A paper was requested by the American Institute of Chemical Engineers (AIChE) for presentation at the Spring National Meeting. This involved our use of fractals and the concept of "Process Intensification". The paper was prepared including an industrial example developed in the present DOE project (ion exchange using fractal equipment). The paper was presented in April. Because the paper presents key results of this project, it is included in this technical report as Appendix 1.

## 11th quarter – July 1, 2003 to September 30, 2003

During this quarter, the majority of test equipment was placed in stand-by and planning mode. Operation will resume in the next quarter.

### Hydrolysate testing

Continued testing of hydrolysate solutions was scheduled to resume in October or November. Planned testing included the continued investigation of alternative ultrafiltration membranes. In addition, membranes enhanced with the embedded membrane concept were to be tested.

### Publications/Presentations

A paper was prepared by the University of Texas (Lewis, Fair and Seibert) for presentation at the American Institute of Chemical Engineers (AIChE) 2003 annual meeting. This paper presented the results from testing a fractal distributor developed in this project for application to distillation applications:

### Paper [307d] Abstract

Mass transfer performance in random and structured packing beds is based on several mitigating factors. One of the most important factors is the initial distribution of the liquid because it determines how evenly the liquid will spread and make use of the packing’s available surface area. This is especially critical when using a high surface area structured packing which are often used in short beds.

The Separations Research Program is investigating a new device for liquid distribution called a fractal distributor. This distributor is distinguished from a trough drip-tube distributor and an orifice pipe distributor because its liquid flow paths are hydraulically equivalent. This enables the device to distribute liquid more uniformly across the bed which maximizes mass transfer efficiency.

Initial distribution testing at the SRP was performed in an 18" air/water absorption column packed with 10 feet of perforated, shallow-embossed, high surface area (500 m2/m3), structured packing. A caustic solution was used to scrub CO2 from ambient air. The nature of the chemical absorption

2NaOH + CO2 --> Na2CO3 + H2O

also allows an estimation of the effective mass transfer area provided the distributor/packing system. The paper will compare the performance of orifice pipe, trough drip-tube and fractal distributors.

## 12th quarter – October 1, 2003 to December 31, 2003

### Model biomass hydrolysate processing

During this quarter a feedstream of 100 gallons/minute model biomass hydrolysate was treated on a continuous basis through all steps of clarification, membrane filtration, ion exchange and chromatographic separation. This was carried out on two pilot plants located at Amalgamated's Twin Falls, Idaho location. Crystallization was also added to the process for this quarter's testing. Of particular note, the low pressure characteristics of the reduced size fractal chromatographic separation system allowed the use of a normally difficult to use compressible media. By enabling the use of this media, the recovery of separated sugar was increased from a previous best of 97% to 99.5%.

Figure 16 illustrates the pilot flow and unit processes evaluated this quarter. The process was operated October through December. Figure 17 illustrates the vacuum crystallizer added to the system. Obtaining crystalline product demonstrated the successful use of this equipment to obtain purified, value added material from the processing train. This project had now demonstrated both a chromatographic oriented pathway for fermentable product (for ethanol production) and a chromatographic oriented pathway for recovery of value added biomass components.

Other project work included the determination of heat transfer coefficients for the pilot forced circulation rising film evaporator.

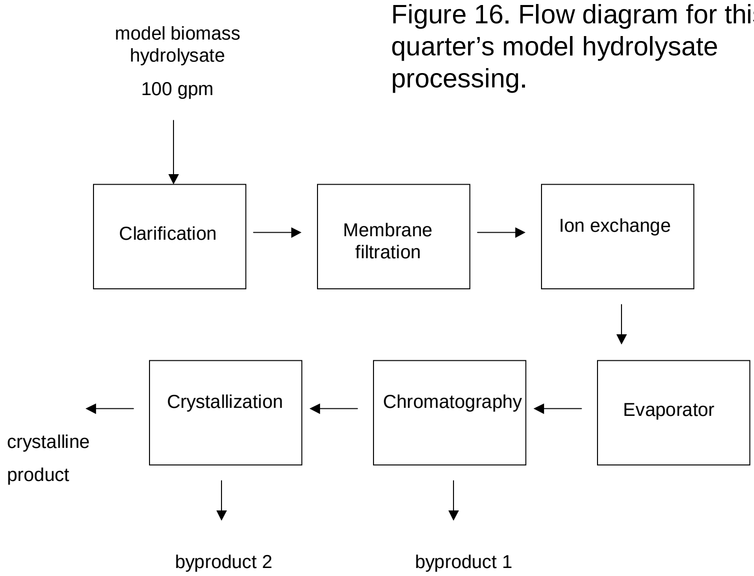



Figure 16. Flow diagram for this quarter's model hydrolysate processing.

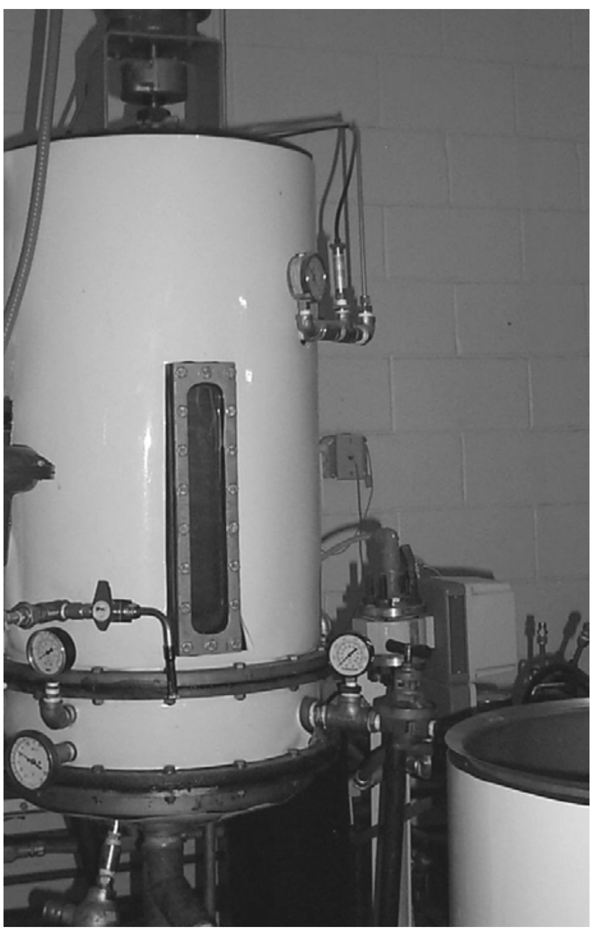


Figure 17.
Pilot vacuum crystallizer added in quarter 12 to the processing train.

### Fractal development

New fractal designs continued to be evaluated during the quarter. Evaluation included CFD work and
manufacturing feasibility. The successful results obtained so far in this project for ion exchange, chromatography and, most recently, the project's distillation study suggested a general beneficial applicability of fractal structure for biomass processing.

## 13th quarter – January 1, 2004 to March 31, 2004

Note: A one year extension was granted for this project (no additional funding). The extension included quarters 13 through 16.

### Engineering bottleneck identification

During this quarter possible bottlenecks were identified which relate specifically to the large scale engineering and implementation of the technology. Solutions to these problems were determined. These solutions included the development of a new vessel design and the implementation of an innovative fractal manufacturing technique. These advancements allow the pilot work to be properly scaled for industrial implementation.

### Model biomass hydrolysate processing

During this quarter the operation of the 100 gallons/minute model biomass hydrolysate pilot system was continued. This included treatment on a continuous basis through all steps of clarification, membrane filtration, ion exchange, chromatographic separation and crystallization. This work was carried out at two pilot plants located at Amalgamated's Twin Falls, Idaho location. The complete system testing was completed by the end of the quarter. Partially treated material was also concentrated and stored for additional experimention planned for the next quarter. This was done because the biomass feedstock is only seasonally available.

Tests with the low pressure, reduced size fractal chromatographic separation system were continued with additional difficult to use media candidates (high pressure drop media). The results of these tests further demonstrated the successful use of normally high pressure drop media in the fractal system.

Figure 18 illustrates the pilot flow and unit processes evaluated this quarter (continued from last quarter). The project continued to demonstrate both a chromatographic oriented pathway for fermentable product (for ethanol production) and a chromatographic oriented pathway for recovery of value added biomass components.

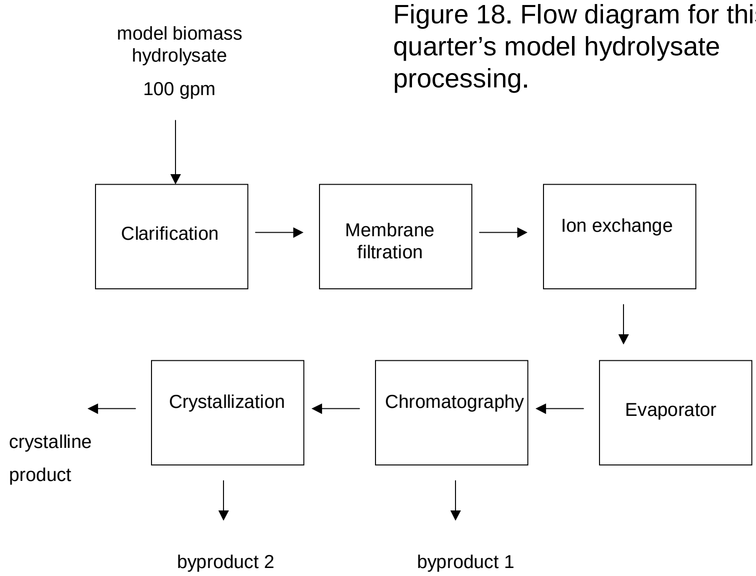



Figure 18. Flow diagram for this quarter's model hydrolysate processing.

With respect to membranes used in the pilot process, a proprietary product continued to show the same level of performance as observed last year. The concept of erosion resistant membranes for this biomass application was proven.

**Alternative ultra-filtration testing**

Several alternative, commercially available ultrafiltration membranes were tested by INEEL with raw sugar juice. Raw sugar juice was used as a model or surrogate feedstock for actual hydrolysate and was shown to be very similar in both solids loading and particle size. The scope of testing was to compare the filter performance (permeate flux) of six different ultrafiltration membranes using raw sugar juice. Potential increases in filter performance could have the effect of reducing the size of filter equipment and/or increasing throughput of industrial scale systems, thereby enhancing the process economics. Similar testing was performed in March 2003; however, several commercial membranes, not available during initial testing, were obtained for testing in 2004.

In an effort to obtain beet juice that was homogeneous (particles size, solids loading), samples of raw juice were obtained and frozen for testing.

The CUF apparatus was used for membrane testing. A statistical test matrix, which varies transmembrane pressure (TMP) from 5-35 psig and axial velocity (AV) from 2-12 ft/sec, was used to evaluate the different membranes. Confirmation of the best performing membranes is planned later this year with samples of hydrolysate that will be obtained from NREL.

Preliminary statistical evaluation of the data indicated that, in the presence of solids, flux was independent of TMP and dependent on AV (i.e. wall shear stress). These observations conform to cross-flow filtration theory; the resistance to filtrate flow through the membrane is constrained by the thickness of the solids layer at the interior surface, which varies with AV.

### Fractal development

New fractal designs continued to be evaluated during the quarter. Evaluation included CFD work and manufacturing feasibility.

## 14th quarter – April 1, 2004 to June 30, 2004

### Identify optimum filter media/configurations for the model beet juice system

The results of the long-term study of membrane filtration of raw beet juice containing abrasive particles demonstrated that membranes exhibiting “embedded” characteristics are able to best sustain filtration capacity over long periods of time. Gradual erosion of a non-embedded filtration layer in such cases is not detrimental to membrane performance. Membrane modules were configured in a way to minimize the overall transmembrane pressure due to characteristics of the raw juice. Hydrolysate streams are expected to behave in a similar manner to the optimized model system.

### Identify performance of normally problematic compressible or other high pressure drop media in the fractal chromatography system using product from the model beet juice system

During this quarter the pilot chromatography separator was operated in a fractal configuration which demonstrated very good performance with normally difficult to use high pressure drop media. Benefits of this type of operation were observed to be increased chromatographic kinetics for simulated moving bed separations. This can lead to smaller chromatographic separation systems for equivalent processing capacity. It was demonstrated that the fractal chromatography system is constrained very little by highly compressible media.

High pressure drop media results in high energy use (due to the pressure drop). The testing demonstrated that energy required for this factor can be much reduced since pressure drop is significantly reduced.

### NREL hydrolysate

Experimental design and preparation for future separation testing has been ongoing during the second quarter. A series of tests were planned. Testing would include membrane ultra-filtration, ion exchange and chromatography on actual NREL hydrolysate. Discussions with NREL personnel led to an agreement that NREL would provide approximately 6-10 drums of hydrolysate for future testing.

### Fractal development

New fractal designs continued to be evaluated during the quarter. Evaluation included CFD work, cell design and manufacturing feasibility. Application to gas liquid processes continued.

### Publications/Presentations

During this quarter a paper was presented at the Proceeding of the American Filtration and Separations Society (9th World Filtration Congress, New Orleans, LA, April, 2004). The paper presented the embedded membrane concept developed during this project.

### Patents

N. R. Mann, R. S. Herbst, T. Trowbridge, V. Kochergin, "Fabrication of embedded membrane for micro or ultrafiltration." Filed for patenting 5-15-04.

## 15th quarter – July 1, 2004 to September 30, 2004

### NREL hydrolysate preparation

During this quarter, the National Renewable Energy Lab (NREL) produced several drums of weak acid hydrolysate from corn stover feedstock in their pilot plant for subsequent testing at the ARi lab facility. ARi testing would continue into the next quarter with this material and include ultra-filtration, ion exchange, chromatography and fermentation tests.

### Complete comparison of filter throughput of hydrolysate and the model system on selected filter media/configurations

Operating data from the membrane filtration of raw beet juice was compared with membrane performance on corn stover hydrolysate obtained from the National Renewable Energy Lab (NREL) pilot plant. Initially, the general characteristics of beet juice and hydrolysate were shown to be similar in terms of particle size distribution. The total amount of dissolved and suspended solids in hydrolysate was found to vary significantly depending on the conditions of pretreatment and the quality of the removal of suspended solids prior to membrane filtration. Fluctuations in permeate flux were mainly due to differences in total dissolved and suspended solids content. The quality of permeate from both microfiltration of the model system and hydrolysate using stainless/ceramic membranes was shown to meet the requirements of downstream operations - such as chromatography and ion exchange. Furthermore, ARi/INEEL's concept of embedded membranes was demonstrated to be applicable to both the model and hydrolysate streams. A primary conclusion was that general membrane operating results determined during this project with the model system are transferable to hydrolysate streams.

### Fractal development

New fractal designs continued to be evaluated during the quarter. Evaluation included CFD work, cell design and manufacturing feasibility. In addition, a project involving comparison of a fractal prototype versus conventional distribution equipment was proceeding.

## 16th quarter – October 1, 2004 to December 31, 2004

This was the last quarter for this project.

### NREL hydrolysate evaluation

During this quarter, weak acid hydrolysate produced by the National Renewable Energy Lab (NREL) was subjected to suspended solids removal, ultra-filtration and chromatography prior to fermentability tests. The purpose was to determine clean-up and chromatography requirements which could lead to possible elimination of the expensive and environmentally problematic "over-liming" step used in the typical lignocellulose to ethanol process. This testing was performed by ARi and INEEL personnel and demonstrated that it is possible to clean-up hydrolysate for subsequent chromatographic separation. Fermentability tests on chromatographic product indicated that materials toxic to fermentation can be removed from the hydrolysate. This experimental work suggested the possibility of eliminating over-liming.

### Complete comparison of hydrolysate and the model beet juice process on select media to perform optimally in a fractal system.

This milestone was completed and represents an accumulation of results collected throughout this project. Data obtained from pilot testing of chromatographic separation of the model beet juice system and hydrolysate demonstrate that the general chromatographic operating size reductions obtained with the model solution are transferable to hydrolysate streams. Furthermore, the results suggest that the fractal approach to chromatographic system size reduction may be applicable to biomass chromatographic separations in general.

### Develop theoretical basis (derived from experimental and computational performance analysis of data) of fractal operation for improved separation systems.

This milestone was completed and represents an accumulation of experimental and CFD (computational fluid dynamics) information collected and evaluated throughout the project. A key aspect of this work was the demonstration of the importance of a variety of factors related to symmetries in the engineered fractal devices. It was determined that key symmetries that must be controlled through proper engineering include a device's geometric symmetries, the bulk hydraulic symmetries of the fluids in motion through the fractals and the internal symmetries of the fluid (such as formation of vortices which can break flow symmetries). This work provides a practical basis for successfully engineering these devices.

## Publications/Presentations

A joint paper authored by ARi and INEEL was presented at the November 2004 AIChE meeting in Austin Texas. "Challenges for Membrane Filtration of Biomass Derived Solutions" was presented in the "Envisioning Biorefineries: Chemicals and Materials from Renewable Feedstocks" conference. The following abstract describes the paper which was based upon the present DOE sponsored project:

"The emerging industry of fuels and chemicals from renewable sources creates challenges for chemical engineers in many areas. Most current efforts are focused around optimization of pretreatment methods, which “solubilize “ biomass for further processing. However, the cost and efficiency of separation technologies applied to fractionation and purification of biomass constituents may play a decisive role in technical and economic viability of the proposed processes. In addition to well-developed technologies, such as distillation for ethanol recovery, affinity based technologies such as adsorption or chromatographic processes will most likely be applied. Since these unit operations involve passing fluids through beds of fine granulated particles, the presence of suspended solids is undesirable. Because most plant -derived hydrolysates contain significant amount of suspended solids and colloidal matter with a broad range of particle sizes, membrane filtration (within MF/UF range) appears to be the most suitable unit operation for clarification of the process solutions.

As a part of a DOE-funded effort, Amalgamated Research Inc. and the Idaho National Engineering and Environmental Laboratory have demonstrated that cross flow filtration coupled with newly developed chromatography and ion exchange systems can substantially enhance the efficiency and reduce the size of conventional separation and purification equipment. Several commercially available membranes have been tested with model plant-derived solutions as well as with hydrolysate streams. Results indicate that membranes with nominal cutoff of less than 0.1-micron produce permeate of sufficient quality to be treated with e.g. ion exchange or adsorption media. However, analysis of the operating cost and durability of the available membrane products suggests that improved membrane products will be needed to meet the challenges of hydrolysate filtration. The tests also identified the challenges for membrane manufacturers related to corrosive and erosive characteristics of process solutions."

# Membrane Study - Additional Technical Discussion

Separation processes account for 40 to 70% of both capital and operating cost for all separation-dependent industries (Humphrey and Keller, 1997). Because of the complex nature and composition of biomass feedstocks, the cost of separation processes is expected to be even greater for the crop-based renewable resources industry. Humphrey and Keller (1997) evaluated the technological maturity of various separation technologies, and found maturity values for membrane, chromatographic and ion-exchange technologies ranging from 20 and 30%, whereas crystallization and distillation processes exceeded 65%. Therefore, there is a definite need for technology development efforts. Some technologies and equipment need to be modified to meet the challenges of the emerging industry of renewable crop-based resources.

One such challenge is the relatively high quantities of suspended and dissolved solids present in biomass feed stocks. Following a course solids removal or pre-filtration step, such as with a filter press, these solutions consist of fiber, soil, colloidal materials (typically on the order of 0.01 to 1 wt % loading in the size range of ~0.01 to 10 µm), and other contaminants. Membrane filtration will be necessary to remove the small residual mass of solids. These residual solids are detrimental to effective operation of downstream chemical separations (typically ion exchange and chromatography). Furthermore, these residual colloidal and other small particles are detrimental to the membrane filters and will tend to foul the membrane, resulting in the need for frequent cleaning cycles, and ultimately membrane replacement. More importantly, suspended solids, such as soil particles, could erode the interior membrane surface resulting in either catastrophic failure or reduced performance after extended periods of operation time.

The objectives of this portion of the research were to overcome the challenges presented by these fine and abrasive residual solids through the study of abrasion mechanisms and the development of innovative membranes technologies. The processes to complete this objective are as follows:

1) Define the effects of erosion on membrane performance on numerous candidate UF/MF membranes.
2) Perform bench-scale accelerated abrasion studies
3) Perform bench-scale filtration tests using actual National Renewable Energy Laboratory (NREL) hydrolysate and raw sugar juice using commercially available membranes.
4) Perform bench-scale filtration tests using actual NREL hydrolysate using novel experimental prototype embedded membranes.

### Scoping Studies (Membrane Selection)

In an effort to define the effects of erosion on membrane performance, a series of tests were performed to identify a preferred commercial membrane for the ultra-filtration/micro-filtration (UF/MF) application under consideration. Small-scale and long-term studies led to the evaluations of numerous commercially available UF/MF membranes, including polymeric, ceramic, and sintered metal products. Both short duration (2-4 hour bench scale tests) and long-term (2 to 3-year pilot scale) evaluations were performed using a model system of raw beet juice taken as a slip stream from the diffusers in an operating beet sugar plant. Based on the results of those efforts, sintered metal membranes were chosen as the best all-around choice. This recommendation was based on the following observations:

1) Commercially available ceramic membranes tested on the raw juice system were rapidly eroded resulting in a loss of filtrate clarity; with a concomitant increase in permeate flux. Furthermore, the ceramic membranes were rather fragile and easily broken, making them susceptible to catastrophic failure under processing and maintenance conditions.
2) Commercially available polymeric (PVDF) membranes were rapidly fouled and could not be effectively cleaned to restore juice flux to acceptable levels. Additionally, such membranes were susceptible to rapid erosion by small particulates in the feed stream, which could result in the potential for catastrophic failure unless the elements were routinely and frequently replaced.
3) Commercially available, ceramic-coated sintered stainless steel (CSS) membranes were found to combine the desirable qualities of erosion resistance and excellent structural integrity, resulting in extended membrane life with a low probability of catastrophic failure. Additionally, the excellent chemical resistance of these membranes allows the use of rather harsh chemical cleaning regimes to restore permeate flux to initial levels without degradation of the membrane or filtrate clarity. The obvious drawback of these types of membranes is their rather expensive price relative to the polymeric or ceramic analogues.

**Accelerated Abrasion Tests**

With the various candidate membranes narrowed down, the study of the effects of erosion commenced. The initial approach was the combination of two methods: 1) to operate candidate membranes industrially for extended periods of time and qualitatively evaluate the long-term effects of wear on the membranes, 2) develop experimental methods to accelerate and study abrasive wear on candidate membranes. The first method qualitatively monitored operational data for an extended period of time at the pilot scale with the actual raw beet sugar juice. The second method, designed to accelerate the abrasive wear, was performed by processing a 5 wt.% slurry of 20 µm corundum ($Al_2O_3$) in water through short (6" effective length) pieces of CSS tubular membrane samples under true crossflow conditions using a bench scale apparatus. Corundum was selected as the abrasive material due to its hardness (9 on the Mohs hardness scale). The $Al_2O_3$ slurry was recirculated at 3.5 gpm for 58 hours through a sample of membrane tube which had been previously operated for 2200 hours on raw sugar juice. Detailed SEM inspection of the sample indicated no discernable erosion of the ceramic surface coating or steel support and only minor decrease in flux was observed over the course of the abrasion test. During this attempt to accelerate the erosion of the CSS samples, the corundum particles resulted in a far more abrasive effect on the pump than on the filter membrane. The pump failed several times (after as little as 20-30 hours of operation) due to erosion of the pump internals composed a chrome plated steel rotor and rubber stator. As a result of the poor results obtained in these experiments to accelerate the erosion phenomenon, it was apparent that alternative methods of accelerating and characterizing wear effects were required for the CSS samples.

## Cells Unit Filter (CUF)

The CUF pictured in Figure 19 is a bench scale crossflow filter apparatus (Mann, Todd 2000). The system consists of a 4 L feed vessel, which feeds a Monyo/Oberdorfer hybrid progressive cavity pump driven by a variable speed direct current (DC) motor. The feed solution (either water, cleaning solution, or raw juice, etc) is recirculated from the feed vessel through a flowmeter, heat exchanger, the interior of the tubular filter membrane sample, and back to the feed vessel. Maximum volumetric flow through the system is ~9 gpm, and depends on the pressure head at the pump outlet. The discharge throttle valve, located on the discharge side of the filter membrane, is used to control transmembrane pressure by controlling pump head (and flow rate). The permeate side of membrane is at ambient pressure (0 psig) and transmembrane pressures of 40-50 psig can be easily achieved with this arrangement. The permeate exiting on the low pressure side of the membrane is collected in the sample holder, routed through a graduated cylinder that can be used to manually measure permeate flow rate, and is typically re-routed back to the feed vessel.

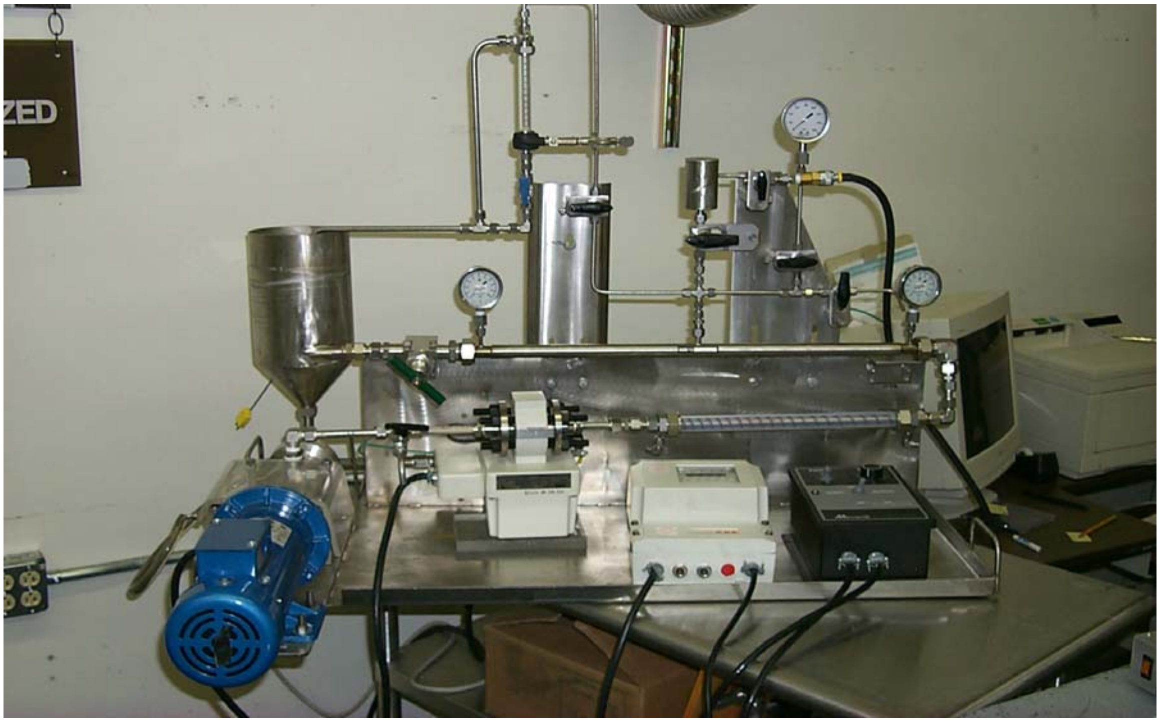


Figure 19. Photograph of the CUF system used for UF/MF testing.

## Alternative Approach to Abrasion Testing

The experimental method designed to accelerate erosion and ascertain the long term effects of wear on membrane performance failed for the CSS samples; an alternative approach to accelerating the natural wear process of the membrane inner surface was necessary. A fortuitous turn of events occurred when a colleague provided samples of CSS membranes that were run industrially, presumably on a similar feed stock to the raw beet juice, for various, but extended periods of time. Three such CSS membranes, identical to those being evaluated at our facilities, were provided. One sample had been run for approximately 1 year of industrial operation, another for approximately 2 years, and a third sample that was extraordinarily abused, under harsh conditions, to filter a solids heavy, very abrasive stream. The unfortunate nuance associated with obtaining these three CSS membrane samples is that quantitative data were unavailable about the feedstock (liquid properties, solids loading, solids rheology, etc.) or operating history (axial velocity, temperature, transmembrane pressure) of these samples.

Included in the comparison of the above industrially operated samples of membranes were membranes operated for 2200 hours in the pilot skid with raw juice and newly manufactured (pristine) membranes. It should be noted that all CSS membranes obtained for observation and testing were from the same manufacturer and of the same porosity and size. The operating history and condition of the interior membrane surfaces were the only discernable physical differences. Consequently, all observations and measurements related to their performance were qualitative and could not be related back to actual operating conditions or history. However, our observations were useful from the standpoint that filter performance could be related to the condition of the interior membrane surface, which varied between the available samples. The nomenclature adopted and used for labeling the different samples and their description are summarized in Table 4. All samples were provided in tubular form, 2 to 4 feet in length, which were cut and prepared for the visual examinations and use in the CUF system.

Table 4. Summary and labeling of the CSS UF/MF membranes available for study.

| Sample Designation | Description |
| --- | --- |
| New | Pristine membrane - As received from the manufacturer. |
| 1P | Operated with raw juice in our pilot installation for ~2200 hours. |
| 2I | Provided by industrial colleague, ~1 year operation w/unknown operating history. |
| 3I | Provided by industrial colleague, ~2 year operation w/unknown operating history. |
| 4I | Provided by industrial colleague, 2+ year operation in a harsh, abusive environment. |

**Visual Inspections**

The interior surfaces of the various membrane samples were first characterized and evaluated by visual inspection. Sections of the tubular CSS membranes were cut approximately in half down the length of the membrane (pieces up to several feet in length were cut open). The ceramic material on the interior membrane surface was clearly discernable by its much darker color, readily distinguishable from the shiny, metallic surface of the sintered metal. Visual inspection indicated that the thickness of the interior ceramic layer or coating was noticeably inconsistent, both axially and circumferentially in a specific membrane sample, and also between the different samples. Variations in the thickness of the ceramic layer were most prominent in the new membrane; at points it appeared there were drops or even runs (such as would be observed in an overly thick coat of paint) of excess ceramic material on the interior surface. "Bald" spots, which appeared completely free of ceramic coating, were visually prevalent in the different membranes. The bare areas were even apparent in the new membrane, although these areas were less prevalent than in the other samples. Most notably in the aged samples, the ceramic appeared eroded from the surface of the membrane during normal operations and in places looked as though the ceramic had been scratched from the surface by a dull instrument, exposing the underlying metal substrate. The most striking contrast was of the 4I membrane, which had been operated extensively under severe conditions. The interior surface showed a very highly polished metallic luster, visually appearing completely free of any traces of ceramic material; the interior surface appeared as though it had been thoroughly polished with fine grit abrasive. Visual inspection qualitatively indicated that the exposed surface area of sintered metal substrate (the total area with the ceramic layer missing) increased in the order:

$$\text{New} < 1P < 2I < 3I < 4I$$

**SEM & EDS Analysis**

Small pieces (~1 cm$^2$) were carefully cut from the above samples of the different membranes. These were used to study the interior membrane surface in closer detail using a Scanning Electron Microscope (SEM) and Energy Dispersion Spectroscopy (EDS) techniques. In order to examine the subsurface structure of the membranes, samples were carefully prepared by breaking off pieces of the membrane along the length; the cross-section of the membrane thickness could be examined in these samples. Figures 20 and 21 pictorially indicate a representative summary of several SEM results. Figures 22 and 23 indicate axial cross-sections of the new and 2I membranes, respectively. The ceramic surface layer on the inner, porous sintered metal support is clearly enunciated in these SEM photographs. The SEM was used to evaluate the thickness of the ceramic coating on those samples where this layer existed and appeared intact. In the new membrane, actual measurements indicated a 10 - 30 µm thick coating of ceramic on the metallic substrate. The inner surface of a bald area from the 1P membrane is shown in Figure 22 and of the 3I membrane in Figure 23. The dark areas indicate the presence of the ceramic coating; the lighter areas indicate the porous sintered metal substrate protruding from the ceramic layer. The composition of the different regions was also verified by chemical analysis using the EDS technique during SEM analyses. The evidence based on SEM, EDS, and visual inspection indicates the ceramic coating on pristine membranes is extremely inconsistent in terms of both thickness and consistency (the inner coating of new membranes was often observed to be cracked and non-homogeneous). Despite these observations, each of the membrane samples typically indicated consistent performances relative to permeate flux and clarity.

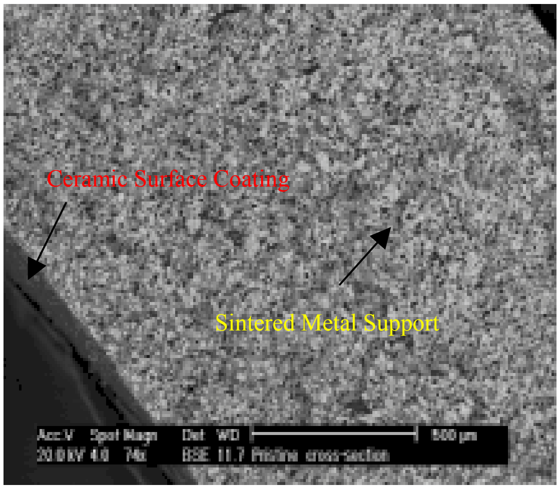



Figure 20. Cross-section of a new membrane.

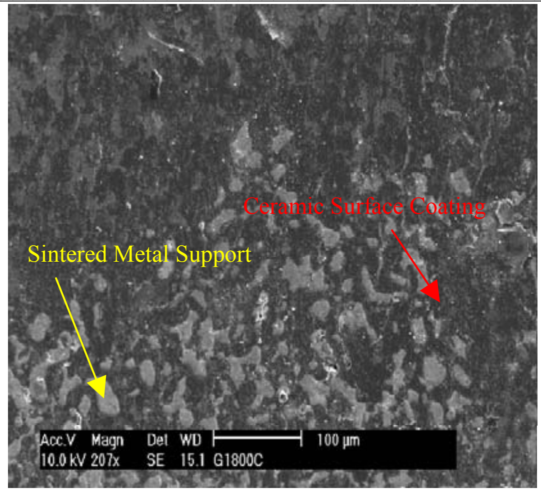



Figure 21. Inner surface of the 1P membrane.

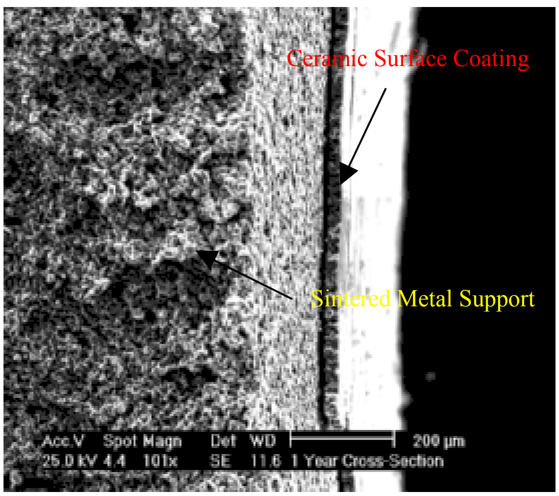



Figure 22. Cross-section of the 2I CSS. membrane.

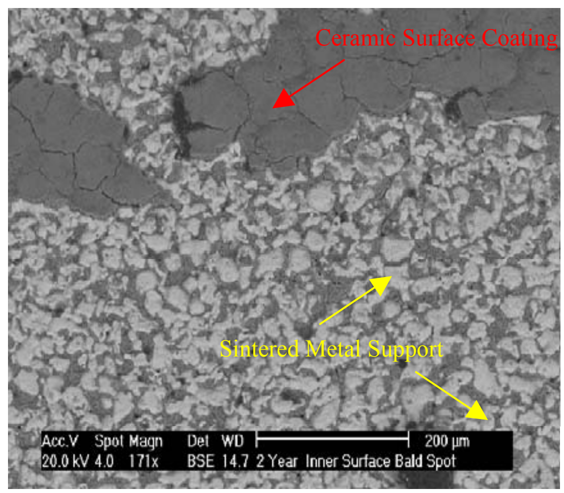



Figure 23. Inner surface of the 3I CSS membrane.

Another very interesting observation was derived from the visual, SEM, and EDS analyses of the 4I sample of the highly eroded membrane, as indicated in the SEM photograph of the interior surface of the membrane indicated in Figures 24 and 25. This photo indicates that the sintered metal substrate was heavily worn and actually "flowed", or was smeared (as in plastic deformation) across the interior surface of the membrane; the individual metal particles observed at the interior surface of the previously examined samples (Figures 23 and 24) are not observed in the 4I sample. The larger pockets of ceramic material embedded in the metallic matrix have also largely disappeared in this sample, and are replaced by much smaller penetrations or imperfections into the predominately metallic surface. Thus, it is postulated that the interior surface of this membrane represents that which would be observed in the advanced stages of wear by erosive processes, and is indicative of the condition of the interior surface as the membrane as it reaches the end of its useful life.

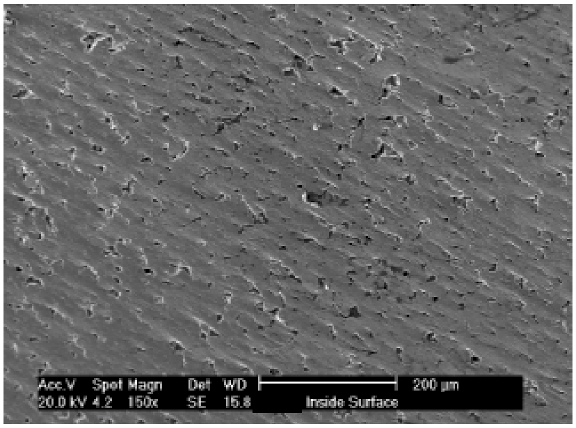



Figure 24. Inner surface of the 4I (150X).

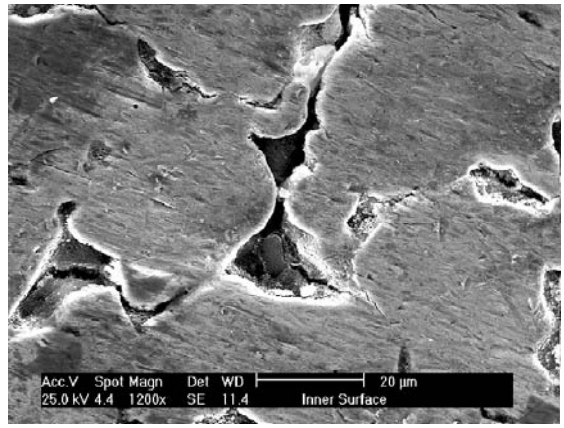



Figure 25. Inner surface of the 4I (1200X).

The above observations for the various membrane samples beg the question: "How were these membranes functioning efficiently in the absence of the ceramic layer, which is attributed the filtration properties of the CSS membranes?" In an attempt to answer this question, the interior surfaces of the membrane samples were probed via EDS analysis. The EDS spectra indicated that in each of the membrane samples, ceramic material was still prevalent in the interstices of the sintered metal support, and in some cases was measured to be present at depths of 20 to 30 µm into the sintered metal support structure. This feature is in fact prevalent in the SEM photographs as indicated in Figures 24 and 25. Furthermore, EDS spectra taken inside the small imperfections of the 4I membrane (right hand photo in Figure 25) indicated that ceramic material was indeed prevalent in the small imperfections or depressions of this membrane.

**Flux Measurements**

In order to further understand why the membranes were still operating efficiently without the interior ceramic coating, flux measurements were performed with both water and raw beet juice on samples of each CSS membrane using the CUF systems. The objective was to evaluate permeate flux with respect to the condition of the interior membrane surface. Triplicate samples of each membrane were prepared for the flux measurements, with the exception of the pristine (new) membrane; only sufficient lengths of this material was available to prepare two pieces of sample for testing. Initially, clean water flux for each sample was measured in the CUF system under identical operational conditions. The samples were then chemically cleaned and rinsed (in situ) and the water flux re-measured. The samples were placed in a second, identical CUF apparatus and the flux measured as a function of time with raw juice, until semi-steady state flux was achieved.

Permeation rates were measured for raw juice on the samples after cleaning and water flux determinations. The permeation rates for raw juice were consistently and substantially lower than those measured for clean water (not shown). This was expected and is attributed to the presence of solids forming a boundary layer at the membrane surface.

Comparative graphs shown in Figures 26 and 27 depict the average raw juice flux vs. time for all samples at 30 TMP and the average steady-state raw juice flux. With the exception of the abused sample, all permeate curves are similar, but slight differences in juice flux are observed. Furthermore, if the values of the semi-steady state flux are compared, the abraded membrane samples (with the exception of the abused membrane) all appear to be higher than for the new P1 membrane. In addition, in all cases, solids were not detected in the permeate samples indicating that there was no measurable degradation in filter efficiency coinciding with the higher permeation rates.

Data indicate that the ceramic coating on the surface of the sintered metal serves little utility to the filtration process and is actually an impediment to filtration by providing an unnecessary flow resistance and thereby inhibiting permeate flux across the membrane. For the CSS membranes (with reduced surface coatings) examined, the apparent conclusion is that the filter efficiency is actually provided by ceramic particles residing in the interstices of the macroporous support.

It is based on these observations that the concept of an embedded membrane was propagated. The concept relies on removing the surface coating and embedding smaller particles of one material (e.g. ceramic such as $TiO_2$) into the interstices of a macroporous support (e.g., sintered metal such as sintered stainless steel). This arrangement is believed to provide increased flux without any decrease in filter efficiency. More importantly, the resulting embedded membrane is resistant to erosion processes since only the support material is subjected to the harsh hydrodynamic properties of the flowing bulk process fluid. Furthermore, the finer embedded particles that provide the necessary filtration efficiency are protected from the bulk process fluid.

In general, the observations associated with the highly abused membrane leads to a general theory regarding the long-term effects of erosion on CSS type membranes in abrasive environments: The long term effect of abrasion at the interior CSS membrane surface is to initially remove the ceramic coating and expose the sintered metal substrate to the abrasive particles in the bulk fluid. The results are pockets of the ceramic embedded in the interstices between the larger metallic substrate particles of the support. The abrasive particles in the bulk fluid then, over time, begin to erode or abrade the exposed metallic surface, which tends to flow or smear across the surface due to the malleable nature of the metal. This effect tends to fill in the ceramic containing pockets resulting in a net reduction in the available porosity at the membrane surface. It is unfortunate that details of the operational history for this membrane are unknown; information regarding the bulk fluid properties, entrained solids loading and rheology, and the operational parameters (axial velocity, transmembrane pressure, temperature, operation time, etc) are unavailable. Without this key information, only general conclusions regarding the effects of erosion on membrane performance (flux and efficiency) can be postulated and it is impractical to estimate membrane life based on actual process conditions. However, it may be postulated that the long term effects of membrane wear would likely not result in a catastrophic failure mode (rupture), rather it would result in a substantial deterioration of filtrate flux, without a decline in filtrate clarity.

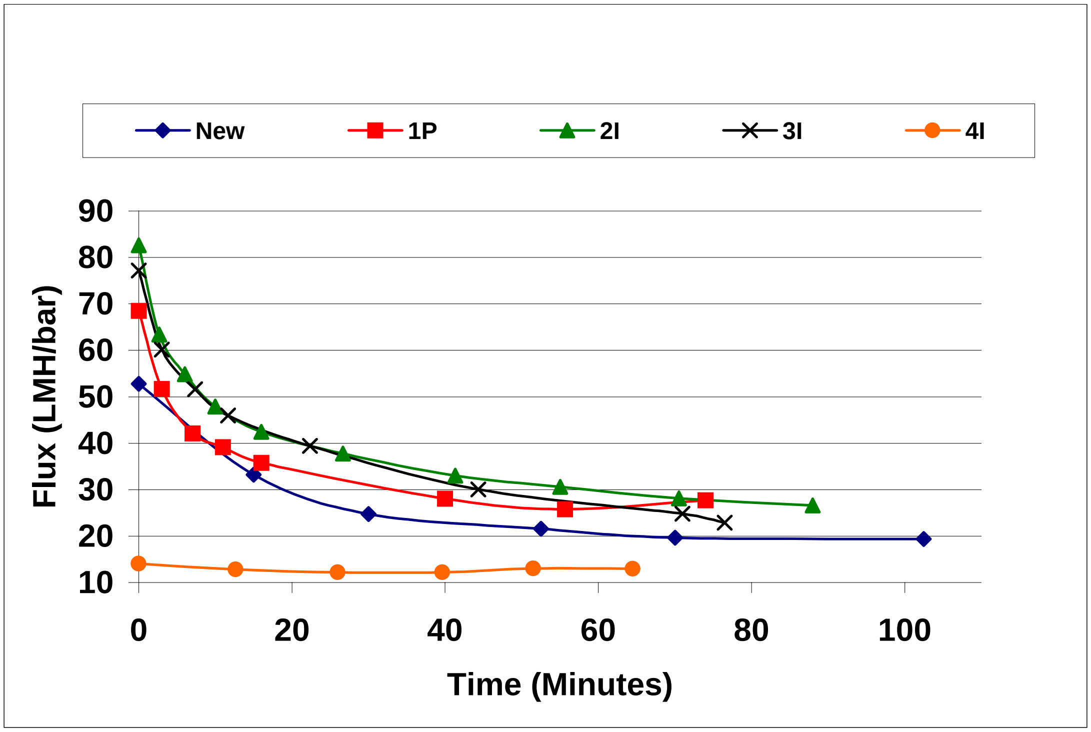



Figure 26. Raw juice flux vs. time for the different membrane samples.

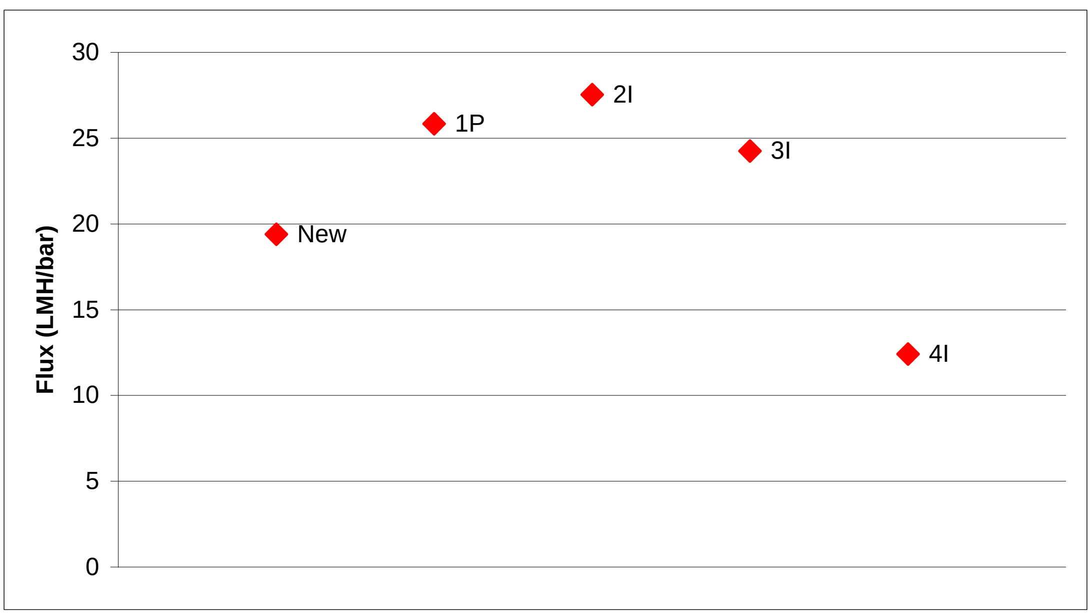



Figure 27. Steady-state fluxes of raw juice for the membrane samples.

Observations regarding the permeate flux and filtration efficiency on asymmetric composite ceramic coated sintered metal membranes and the long-term effects of erosive wear on the interior surfaces have qualitatively led to several observations. The postulated sequence of physical changes to the interior of the CSS membranes and the observed effects are as follows:

1) New or as-received membranes have largely intact surface coatings that act as a resistance to permeate flow, resulting in lower fluxes without impacting filter efficiency in terms of particulate removal.
2) During the course of extended industrial operation, the surface coating tends to wear away from the substrate by erosive wear mechanisms. This erosion exposes the substrate to the process fluid and flow properties. The exposed substrate tends to protect or shield a layer of embedded surface material that resides in the substrate as a nuance of the manufacturing process from the flow properties of the bulk fluid. Permeate flux is enhanced as a function of time, coinciding with the resistive surface layer being removed. Solids retention (filter efficiency) is not impacted since the material embedded within the substrate pores serves to reject the bulk solids.
3) With continued, extended operation, wear mechanisms continue to erode the substrate material. In the case of the sintered metal, deformation tends to smooth the rough membrane surface and the substrate begins to fill the interstices containing the effective filter media. As this process occurs, permeate flux decreases with time corresponding to a reduction in porosity at the interior surface. Filter efficiency is therefore not impacted over the course of the useful membrane life due to embedded particles filling the interstices of the macroporous support.

The above series of events result in the eventual failure of the membrane due to a decline the permeate flux. This failure mode is not catastrophic, i.e., a sudden breach of the filter media does not result in contamination of the product fluid with solids. The time frame in which the above series of events occur is currently unknown, but certainly is dependent on two factors, the physical properties of the membrane surface (hardness, roughness) and the properties of the bulk slurry being filtered, primarily the rheology of the solids (hardness, density, size, etc). The observations associated with this work provide a scenario of what may be expected during long-term operation of these types of membranes; however, detailed understanding or modeling of the long term effects of erosive mechanisms on membrane performance is a complicated problem, likely to be better understood only upon examination and data that becomes available following extensive, documented operational history (Mann., et. al, 2004).

### Alternative Membrane Testing Using NREL Hydrolysate

As alternatives to the previously studied CSS membranes, two additional sintered metal membranes were evaluated using actual biomass hydrolysate produced from weak acid pretreatment of corn stover by the National Renewable Energy Laboratory (NREL). The scope of testing was to provide a preliminary estimate of the overall filterability of actual hydrolysate using the CSS membranes and examine the performance of two alternative ultra-filtration membranes as a basis of comparison. Prior to testing, course filtration was performed using a basket centrifuge to remove the bulk of the solids from the NREL hydrolysate.

Membranes chosen for UF/MF testing included a Mott (0.1 μm, symmetric, industrial grade), GKN Sitka (0.1 μm, asymmetric) and Graver Scepter, otherwise known as the CSS membrane, (0.1 μm, asymmetric, $TiO_2$ coated). The Cells Unit Filter (CUF) system was used for bench-scale testing. All membranes tested had an inside diameter of 0.375 inches and were comprised of sintered 316 stainless steel. It should be noted that the Graver and GKN membranes were of the asymmetric type, indicating a finer, secondary coating above the larger sintered metal support. The asymmetric coatings found on the Graver and the GKN membranes consist of a $TiO_2$ and finer sintered metal, respectively.

Prior to testing, the Mott and GKN membranes were pretreated to remove any residual organics present from previous testing. This was accomplished by processing a 2% caustic solution containing 200 ppm chloride (bleach) for 0.5 hours. The Scepter membrane followed a separate pretreatment process, as specified by Graver. This was accomplished by processing a 2% caustic solution at >85 °C for 10 minutes followed by a 0.01 nitric acid (pH=2-3) at >85 °C for 10 minutes.

Once the membrane pretreatment step was complete, the system was thoroughly rinsed and prepared for testing. Approximately 3-Liters of stock NREL hydrolysate was added to the CUF apparatus for each test. Hydrolysate solutions were heated to approximately 65 °C using an immersion heater. Testing was performed at 20 TMP and 3.7 gpm. A higher flowrate would have been desirable, however, the increased temperature and relatively low recirculating volumes aerated permeate and cavitated the helical rotor pump. Permeate flux was recorded in 10 minute intervals. Filtrate flux as a function of time for the Mott, GKN and Graver membranes are shown in the Figure 28.

When referring to the Figure 28, the Mott membrane displayed an initial flux of 2203 LMH/Bar followed by a gradually declining flux. A gradual step down in flux can be observed at 40, 90 and 120 minutes. One possible theory, which may explain the gradual step down, is an increase in solids loading due to evaporation over the course of the test. It is believed that had the hydrolysate maintained its original solids loading, the Mott would have reached a steady state flux at approximately 40 minutes at a flux of 1500 LMH/Bar. The final flux recorded at 150 minutes was 596 LMH/Bar. The GKN membrane displayed an initial flux of 1270 LMH/Bar followed by an immediate and rapid decrease in flux. Flux is relatively steady for one hour after which a gradual decrease is observed. The final flux recorded at 150 minutes was 333 LMH/Bar. A gradual stepping down in flux can also be observed with the GKN membrane. However, the step is less pronounced.

The Graver membrane displayed an initial flux of 286.23 LMH/Bar followed by an immediate and rapid decrease in flux. Flux is relatively steady throughout the test, but a downward trend is visible. It is believed that the tighter porosity of the Graver membrane (as evidenced by lower flux) is less affected by evaporation and subsequent increasing solids loading than the Mott and GKN membranes. This is most likely due to the tighter asymmetric coating.

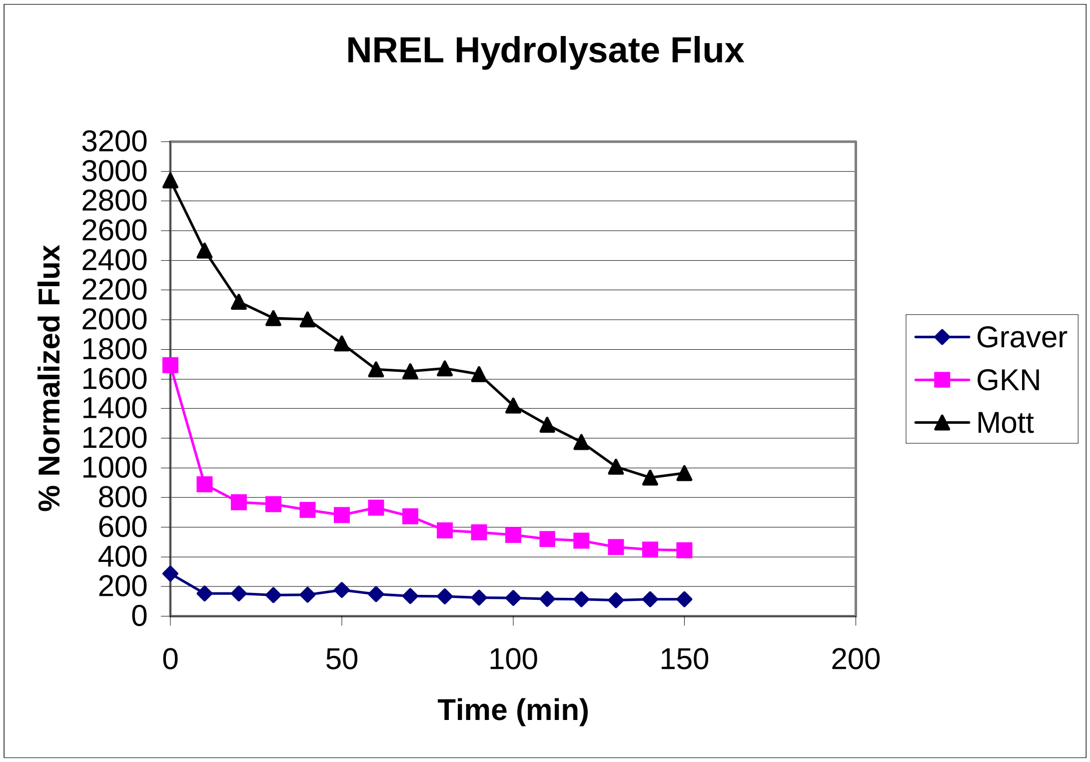



Figure 28. Flux as a function of time for the Graver 0.07 µm, Mott 0.1 µm and GKN 0.1 µm membranes using NREL hydrolysate.

Data indicates that alternative membranes may provide substantial increases in permeate flux over the Graver (CSS) membranes. However, additional, detailed testing is required to determine the ramifications of selecting other filter media. Aspects such as flux as a function of solids loading, ability to clean the media, long-term stability of flux, and filter life should be evaluated.

**Embedded Membrane Testing**

The embedded membrane concept was ultimately developed by leveraging funding obtained through the INEEL Laboratory Directed Research and Development (LDRD) program. The concept of the embedded membrane was validated and a methodology for manufacturing embedded membranes was developed. To date, multiple, working prototypes have been developed and have been tested using actual hydrolysate solutions. Several drums of weak acid hydrolysate, from corn stover feedstock, were provided by NREL for testing. Actual hydrolysate solutions, as received by ARi, were prefiltered using a basket centrifuge and the retentate washed using a standard centrifugal filter. The final working solution consisted of 60% hydrolysate permeate and 40% wash solution.

The scope of testing the novel embedded membranes was to compare the filter performance (permeate flux) of the prototype membranes using actual hydrolysate. Two prototype embedded membranes were evaluated using NREL hydrolysate based on previous water and strontium carbonate testing. These membranes were labeled EM30-950 and EM10-800 based on their manufacturing methodology. In addition, two commercial ultra-filtration membranes were also tested as a basis of comparison. The commercial membranes have been extensively tested over the past several years at the pilot scale (ARi) and in bench scale tests (INEEL).

Commercial membranes selected for comparison are as follows:

- Graver Scepter (Nominally rated at 0.07 μm, asymmetric, $TiO_2$ on stainless steel)
- Pall (Absolute rated at 0.1 μm, asymmetric – $ZrO_2$ on stainless steel)

Note that both commercial products consist of an asymmetric ceramic coating on a stainless steel support. The embedded membrane prototypes have removed this ceramic surface layer and embedded it within the support structure. It should also be noted that, the nominal porosity of the embedded membrane prototypes were not determined. Nevertheless, it is postulated that the embedded membrane prototypes have a nominal porosity < 0.1 μm, (based on clean water flux measurements). All membranes had inside diameters of 0.375 inches. The active membrane length for the Graver and Pall membranes was 24 inches. The active membrane length for the embedded membrane prototypes was 11.5 inches.

As with earlier testing, the Cells Unit Filter (CUF) apparatus was used for membrane testing. Operating parameters consisted of an axial velocity of 11 ft/sec (3.7 gpm) and transmembrane pressures of 10, 20, 30 and 40 psid. Test solutions were preheated to 50°C in accord with the process design (NREL/TP-510-32438). Performance, (filtrate flux) for each membrane, was determined by measuring a volume of permeate over a given period of time. Each test parameter was held for 30 minutes with samples being taken every ten minutes.

A graph depicting flux (LMH) vs. TMP (psid) for all membranes is shown in Figure 29. All membranes, including the two prototypes, indicated excellent filtration efficiency as solids were not detected in the filtrate (based on turbidity measurements). Prototype EM30-950 displayed a ~30% higher flux compared to the second prototype, EM10-800, presumably due to differences associated with production methods. The higher flux prototype indicated fluxes ~35 to 50% lower than the commercial membranes. This is likely attributed to significant differences in porosity, with the prototype membranes having a lower (or "tighter") nominal porosity relative to the commercial membranes. Additional characterization of the prototypes are required to confirm this hypothesis, and it is certain that the production techniques can be modified for a more open pore structure and concomitant increase in permeate flux.

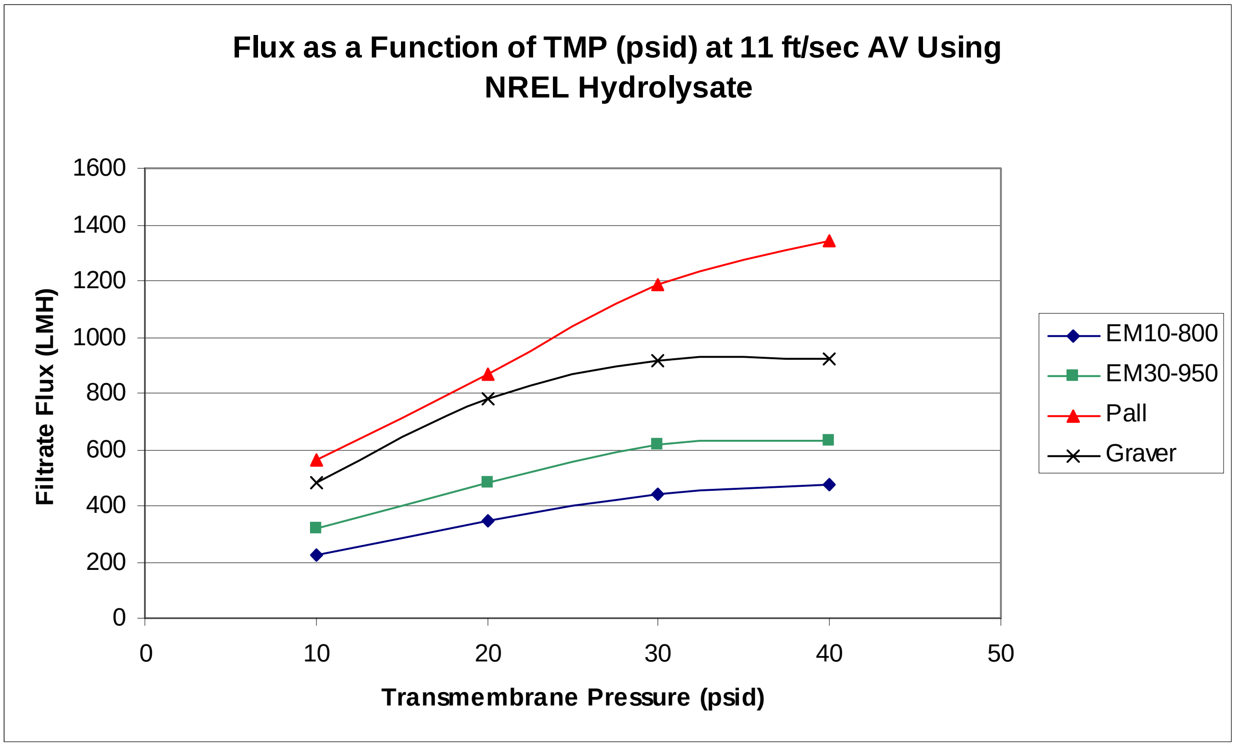



Figure 29. Flux as a Function of TMP (psid) at 11 ft/sec AV using NREL hydrolysate.

Based on the preliminary results of these studies, ceramic-coated sintered stainless steel membranes were the best overall choice for ultrafiltration of biomass hydrolysate solutions. Qualitative evaluation and bench-scale testing have shown that erosion mechanisms will most likely not lead to catastrophic failure, (i.e., a sudden breach of the filter media, resulting in contamination of the product fluid with solids), but rather will result in gradual membrane failure due membrane deformation and concomitant decline of permeate flux.

These studies have propagated the concept and development of the embedded membrane. The concept relies on removing the surface coating and embedding smaller particles of one material (e.g. ceramic such as $TiO_2$) into the interstices of a macroporous support (e.g., sintered metal such as sintered stainless steel). This arrangement is believed to provide increased flux without any decrease in filter efficiency. More importantly, the resulting embedded membrane is resistant to erosion processes since only the support material is subjected to the harsh hydrodynamic properties of the flowing bulk process fluid. Furthermore, the finer embedded particles that provide the necessary filtration efficiency are protected from the bulk process fluid. Bench-scale testing using INEEL manufactured embedded membranes indicate a flux ~35 to 50% lower than commercial analogues using NREL hydrolysate. This is likely attributed to significant differences in porosity, with the prototype membranes having a lower (or “tighter”) nominal porosity relative to the commercial membranes. Additional characterization of the prototypes are required to confirm this hypothesis, and it is certain that the production techniques can be modified for a more open pore structure and concomitant increase in permeate flux.

Bench-scale testing using commercially available alternative membranes and actual NREL hydrolysate indicate that alternative membranes may provide substantial increases in permeate flux. However, additional, detailed testing is required to determine the ramifications of selecting other filter media. Aspects such as flux versus solids loading, ability to clean the media, long-term stability of flux, and filter life should be addressed during additional testing.

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N. R. Mann, R. S Herbst, T. L. Trowbridge, V. Kochergin, "Development of the Embedded Membrane Concept," proceedings of the American Filtration and Separations Society, 9th World Filtration Congress, New Orleans, LA, April, 2004

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**Patents**

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## Fractal Discussion - Turbulence Control

Turbulence is prevalent in practically all-engineering gaseous or liquid flows of interest. It occurs when the Reynolds number of the flow, a primary parameter correlating the viscous behavior of fluids, increases to a point where the viscous stresses are overcome by the fluid's inertia and the laminar motion becomes unsteady. Rapid velocity and pressure fluctuations appear and the motion becomes inherently three dimensional and unsteady. When this occurs the fluid motion is described as turbulent.

Turbulence consists of a continuous spectrum of scales ranging from largest to smallest, as opposed to a discrete set of scales. In order to visualize and analyze turbulent flows with a spectrum of scales it is useful to think of these scales in terms of eddies. A turbulent eddy can be thought of as a local swirling motion whose characteristic dimension is the local turbulence scale. These eddies overlap in space, large ones carrying smaller ones. Turbulence features a cascade process whereby, as the turbulence decays, its kinetic energy transfers from larger eddies to smaller eddies. Ultimately, the smallest eddies dissipate into heat through the action of molecular viscosity and represent an energy loss and hence, turbulent flows are highly dissipative.

Turbulent flow is dominated by the large energy bearing eddies. The large eddies are primarily responsible for the enhanced diffusivity and stresses observed in turbulent flows. Because large eddies persist for long distances, the diffusivity and stresses are dependent upon flow history, and cannot necessarily be expressed as functions of local flow properties. Also, while the small eddies ultimately dissipate turbulent flow energy through viscous action, the rate at which they dissipate is controlled by the rate at which they receive energy form the largest eddies. Hence the key to controlling turbulent flow is by controlling the formation of the large energy bearing eddies. A useful mathematical description of this phenomenon is as follows:

$$E(\kappa) = kl\,\mathrm{g}(\kappa l)$$

$$k \sim (\varepsilon l)^{2/3}$$

where

$E(\kappa)$ is the turbulence energy spectral density

$k$ is the kinetic energy of turbulent fluctuations per unit mass

$l$ is the turbulence length scale or large characteristic eddy size

Hence, both turbulent energy spectral density and turbulent kinetic energy are directly proportional to the turbulence length scale or large eddy size. Since it is desirable to minimize energy density, which represents a loss, it is necessary to minimize the turbulence length scale or large eddy size. The large eddies are typically the same order of magnitude as the dimension of the object governing the flow or mean flow width (e.g. pipe diameter for pipe flow).

Another process that leads to significant energy dissipation in turbulent flows and hence is undesirable is vortex stretching. Vortex stretching leads to increased turbulent energy gains, and occurs when the vortex elements are primarily oriented in a direction in which the mean velocity gradients can stretch them. This process has the most profound effect on large eddies, since vortex stretching has the most effect when eddy size is on the same order of magnitude as the mean flow width. Consequently, the larger scale turbulent motion carries most of the energy and is mainly responsible for the enhanced diffusivity and attending stresses. In turn, the larger eddies randomly stretch the vortex elements that comprise the smaller eddies, increasing the rate at which energy is cascaded to them. Energy is lost or dissipated by viscosity in the smallest eddies, although the rate of dissipation of energy is set by the large eddy-wavelength motion at the start of the cascade.

The engineered fractal is an elegant device for controlling turbulence and greatly reducing energy loss or dissipation by suppressing the formation of large turbulent eddies. The fractal accomplishes this in two ways:

1) By using the bifurcation method of channel division, the engineered fractal effectively reduces the mean flow width, which reduces the order of magnitude of the large eddy size.
2) The engineered fractal greatly reduces the negative effects of vortex stretching by orienting the vortex elements of the flow in a manner in which they are not

stretched by the mean velocity gradients. Hence vortex stretching effects are greatly reduced in the engineered fractal and energy loss in greatly reduced.

In summary the engineered fractal is an elegant method of turbulence control and suppression that is based on fundamental sound theory.

## Project Recommendations

An optimal filtration system for handling biomass hydrolysates should involve a hybrid system capable of inexpensively segregating the larger part of the particle spectrum and a fine filtration system separating particles in the submicron range. A high efficiency fractal clarifier followed by membrane filtration appears sufficient to prepare hydrolysate for subsequent media based processing such as chromatography.

With respect to ultrafiltration and microfiltration technologies, there is good evidence that the embedded membrane concept developed in this project may offer a number of advantages over current state-of-the-art commercial membranes in the area of biomass filtration. The data and observations indicate that a heterogeneous filter element incorporating a coat material in the support interstices could provide adequate filtration performance (clarity and mechanical strength) while enhancing permeate flux and minimizing degradation of the membrane surface by abrasive mechanisms.

Additional developmental efforts to refine production techniques should be evaluated to provide a more open pore structure and concomitant increase in permeate flux.

The successful results obtained with short bed fractal chromatography and short bed fractal ion exchange technology suggest extending this work. While the project has already resulted in full scale commercial products, the knowledge gained concerning separation of sugars from acid and separation of sugars from background nonsugars forms a basis for expanding the applications from binary to multicomponent separations. This should target the multicomponent production of value added products or building blocks from lignocellulose derived hydrolysates and/or products produced from such hydrolysates.

## Appendix 1: Process Intensification Using Engineered Fluid Transporting Fractals.

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Prepared for presentation at the 2003 AIChE Spring National Meeting

April 2003

**Abstract**

We have determined that engineered fluid transporting fractals can be used to accomplish many of the goals of process intensification. The fractals are used to control the scaling and distribution of fluids. Fractals allow fluid properties, such as eddy size or concentration distributions, to be adjusted in a highly controlled manner. This control is obtained by introducing symmetries into the fractal structures. In some cases benefits can include order of magnitude reductions in process size, energy use and device design pressure.

Target applications include control of single and multi-phase flows in chromatography, ion exchange, distillation, adsorption, aeration, extraction, mixing and reaction.

**Background**

As a simple definition, fractals are self similar objects whose pieces are smaller duplications of the whole object. Examples are ubiquitous in nature and include coastlines, clouds, river beds, trees and the blood circulation system (1,2). Fractals are, for the most part, absent from engineered devices.

The usefulness of fractals lies in their controllable scaling characteristics. Scaling, for example from large to small or vice versa, is a common requirement in a number of disparate unit processes. For example, fluid scaling is required when the geometry of a fluid is altered. Fluid entering a large column must be scaled and distributed to approximate a surface. The opposite operation is performed for fluid collection from a column. Mixing is a unit operation with a very different purpose but also requires fluid scaling as a key characteristic wherein fluids are scaled to smaller and smaller parts and interspersed.

It is not ordinarily recognized that scaling is such a central requirement of fluid processes and, as a result, the common methods used for scaling are not generally recognized as inefficient or lacking control. For example, mixing is usually accomplished using turbulence for scaling. The use of an impellor is a typical example of using turbulence to scale and distribute fluids. Turbulence results in broad distributions of fluid properties such as eddy size, bubble size, concentration bands, etc. The use of engineered fractals can narrow the distribution of these fluid properties in a controlled manner and can therefore result in significantly smaller equipment, less energy use and more homogeneous processes (3,4). These results are associated with process intensification.

Figure 1 illustrates a partial view of a fractal structure which can be used to introduce a fluid to a column oriented process. (5,6). Characteristics include:

- Scaling is accomplished using engineered symmetry. A uniform surface of fluid is introduced. This is in contrast to nozzle or orifice pipe type distributors which usually depend upon the uncontrollable characteristic of turbulent scaling to spread a fluid.

- The device is dependent upon fractal scaling and symmetry for proper flow distribution. As a result, the fractal has low energy requirements. Most distributors (such as orifice pipe) are designed using pressure drop to provide proper flow to all exit points.

- Due to symmetry, all the flow paths of the fractal are hydraulically equivalent. The hydraulic path to an exit point near the center is equivalent to the hydraulic path to a point at the outer edge. Therefore, unlike distributors designed using pressure drop criteria, the fractal has a very large turn- down (1 to 10 easily obtained).

- Fractals by definition are scaling structures. As a result, the often difficult problem of process scale-up is alleviated. Figure 2 illustrates how the smallest fractal structure used in small scale tests is maintained as larger fractal iterations are added to create the larger scale device. This method tends to maintain the process characteristics observed at the smallest scale.

Note that as the center of the device is approached, the fractals are scaled by a different percentage depending upon the direction. The fractals appear to be stretched more in one direction than the other. This type of stretched fractal is referred to as self-affine. Self-affine fractals are used in this case to best match the geometric constraints of the vessel.

Fractal manufacturing and use is a practical reality. We have installed over 45,000 $ft^2$ of the fractal similar to that in figure 1.

Figure 1: A section of a fractal distributor for fluid introduction/collection.

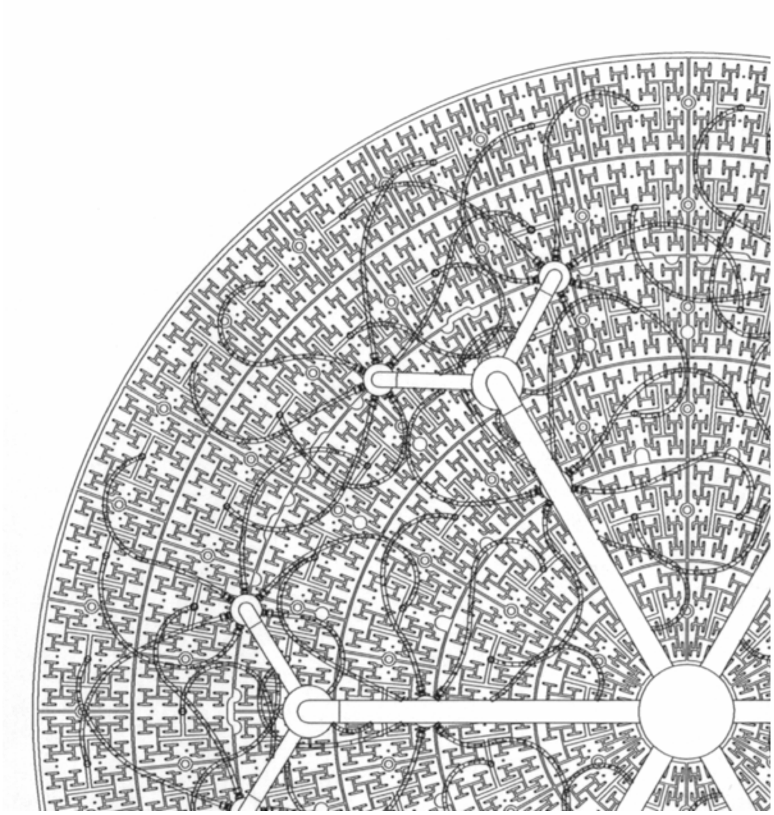
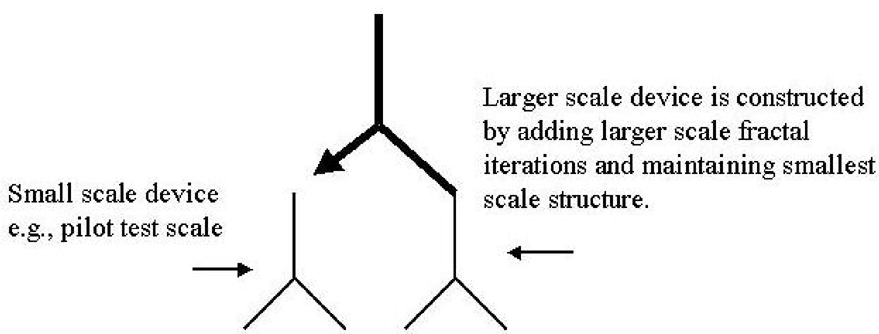


Figure 2: The concept of process scale-up using engineered fractals.




## Process intensification example

Figure 3 is a photo of an ion exchange application using fractal distribution and collection. The vessel is 5 ft. diameter x 1 ft. height. The process is weak cation softening of a biomass derived material (juice from sugar beets). The process involves regeneration of the ion exchange resin with sulfuric acid and exhaustion of the resin to $Ca^{+2}/Mg^{+2}$ form. Steps of the process include exhaustion, sweet-off, regeneration, regeneration rinse and backwash. The larger scale fractal structure can be seen above and below the vessel. Layers of progressively finer fractal structure are located inside the vessel.

The fractal introduction and collection of fluid allows extremely high flow rates to be used without turbulent disturbance of the resin bed. This characteristic also allows the bed to be very flat (only 6 inches). Table 1 lists a comparison of operation of the fractal ion exchange vessel and a conventional vessel operating in the same factory. Of particular note is the order of magnitude decrease in resin requirement and the near complete elimination of pressure drop. Other advantages include safety since the fractal vessels operate at low pressure. The low pressure also allows feed by gravity rather than by pump. Small space requirement is another benefit.

Another interesting characteristic concerns the flow in the freeboard above the resin bed. Six inches of freeboard was provided to allow 100% expansion during resin backwash. The Reynolds number associated with the flow through this free area is about 85,000 (700 gpm at 85 C). However, the fractals introduce the fluid in a very controlled, non-turbulent manner. All the fluid momentum across the introductory surface is in the same direction so that the processing can be carried out without the development of visible large scale turbulence. This is an example where a fractal can beneficially introduce a temporary stability into a process operating in the turbulent regime.

Figure 3: A fractal ion exchange vessel.

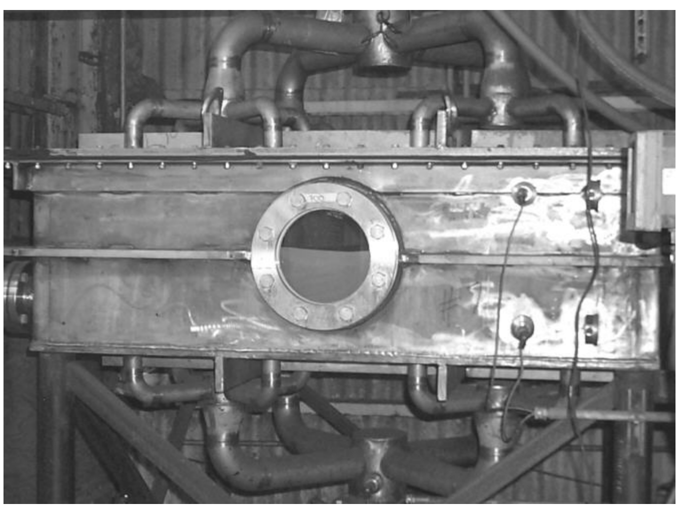


Table 1: A comparison of conventional ion exchange and fractal ion exchange.

| | Conventional IX | Fractal IX |
|---|---|---|
| Resin bed depth (inches) | 40 | 6 |
| Exhaustion flow rate (Bed volumes/hour) | 50 | 500 |
| Maximum resin bed pressure drop (psi) | 50-70 | 1 or less |
| Relative process size | 10 | 1 |

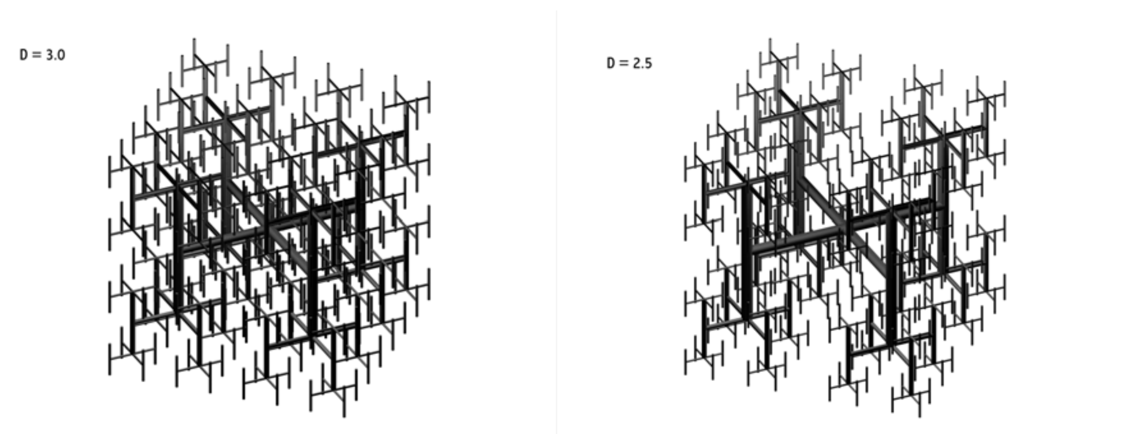
**<u>Flexibility of fractal design</u>**

As noted, engineered fractals allow for precise control of the geometry of fluid scaling. Reference 7 describes several ways that fractals can be varied to provide desired scaling and distribution geometry. These methods include:

1. Variation of scale-down factors to modify space filling characteristics.

The fractal dimension is a measure of the space filling characteristics of a fractal. As the calculated dimension is reduced, space is less filled by the object, as can be seen by comparing the fractals in figure 4 with D = 3.0 and 2.5. Therefore, the fractal dimension of an engineered structure is a key design criteria. Because fractals have a dimension associated with them, certain aspects of design are straightforward. Using the fractal dimension, fractals can be designed in a logical manner to approximate surfaces, volumes and non-integer patterns (8).

Figure 4: A comparison of space filling characteristics at different fractal dimension.




2. Variation of the fractal cut-off.

Smaller and smaller iterations of structure are added to an initiator to produce a fractal. The space filling characteristics can be altered by adjusting the number of iterations. The smallest scale used in a device is referred to as the fractal cut-off. In some cases, the cut-off may be constrained by manufacturing limits and cost restrictions rather than design intentions.

3. Variation of the structure with respect to symmetry.

Fractals can be engineered with variations of the object's scaling symmetry. For example, the scaling factor can be different in different directions. The self-affine fractals in figure 1 are an example of this. The scaling factor can also change with change in iteration number. Another related technique is to vary the symmetry characteristics of the initiator. Note that the initiator is the original large scale structure geometry duplicated in the smaller descendent generations.

4. Variation of the structure with respect to the number of branches per node.

Figure 4 illustrates fractals with 8 branches per node. Altering the branch count is a useful design parameter. Techniques 1-4 can, of course, be used in combination.

## Offset fractals

Fractals can be constructed such that two or more fractals are offset. This allows design of devices wherein two or more fluids can be scaled simultaneously prior to interaction. In such configurations the separate fractals can scale in the same flow direction or from differing directions before combining. Used as mixers and/or reactors, offset fractals can provide precise control of scaling and distribution of all fluid components.

## Combining the use of engineered fractals with process turbulence

While fractals can be thought of as highly controlled functional alternatives for the scaling and distribution feature of turbulence, they can also be used together with turbulence to take advantage of its beneficial characteristics (7). Some examples:

- Fractals can be used to provide an advantageous first stage of distribution prior to final turbulent mixing.

- Fractals can be placed in motion and thus cause turbulence while concurrently distributing fluid.

- Fractals can be used in a turbulent fluid flow passing through the fractal.

- Fractals can be designed to provide turbulent jetting.

- Similarly, fractals can be used as fluid collection devices from turbulent flows.

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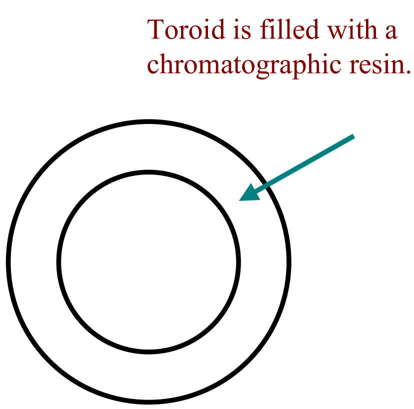
## Appendix 2: Amalgamated Research Inc. Simulated Moving Bed Chromatography (SMB).

In the following discussion, True Moving Bed chromatography will first be described (a very difficult process to put into practice) and from this, the more practical Simulated Moving Bed Chromatography (SMB) process can be derived and understood.

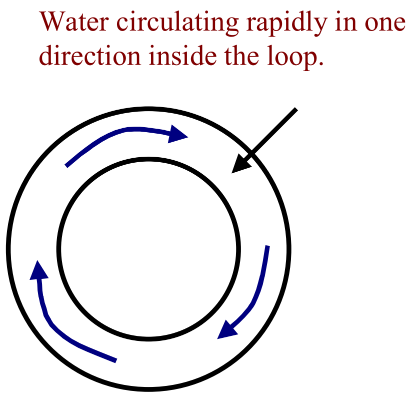
### True Moving Bed Chromatography - an imaginary process.

As opposed to conventional batch chromatography, the true moving bed process (while imaginary) employs some unusual operating principles and a number of valuable benefits. For purposes of clarity, we will assume that the chromatographic eluent is water and the chromatographic media is a resin.

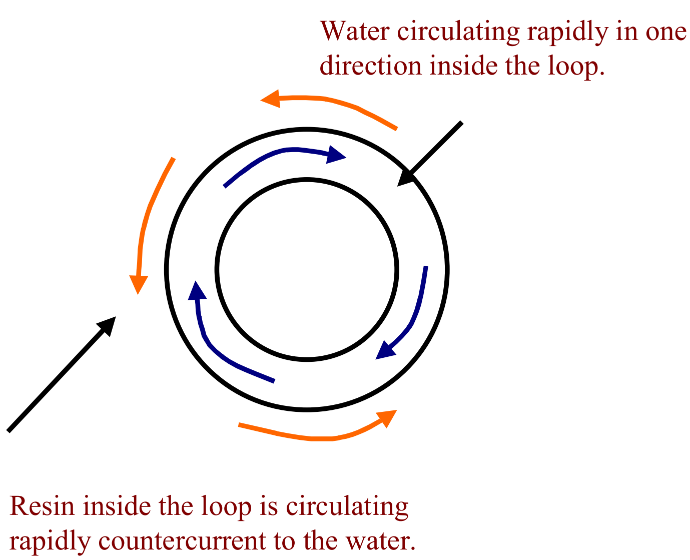
First imagine a resin filled column formed as a toroid:




Now imagine a rapid, continuous flow of water (eluent) in one direction inside the loop:



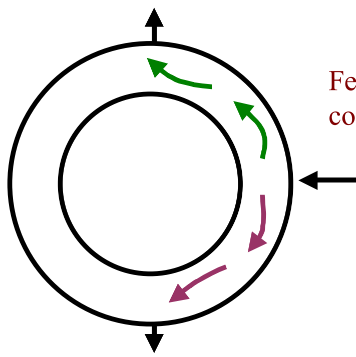

Now imagine that the chromatographic resin contained in the toroid is rapidly circulating in the loop in the opposite direction from the water circulation:




Recall that this process is, for the time being, imaginary so how the two opposing flows of water and resin are enabled need not be explained. Setting up these two opposing internal flows results in a key characteristic of a true moving bed. If a binary mixture to be separated is added continuously at one point of the loop, the component

more readily adsorbed by the resin will tend to move with the resin and the component less readily
adsorbed will move with the water. If the two opposing internal flows are balanced carefully, the two components can be continuously separated and recovered.

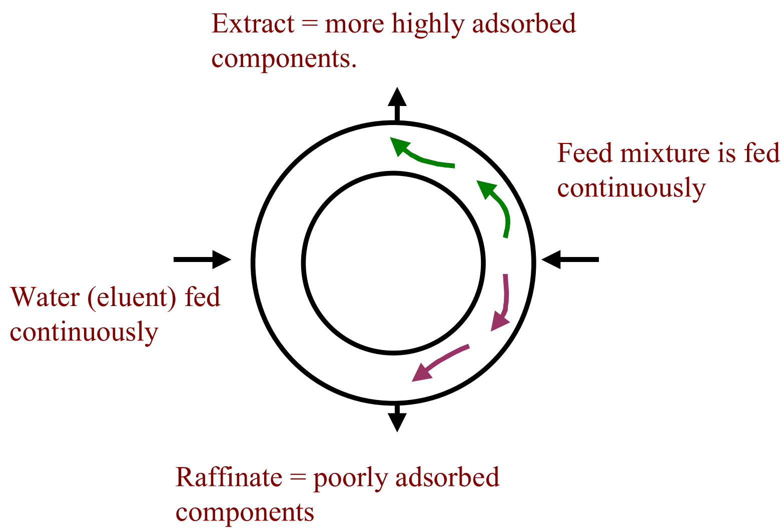
More highly adsorbed components tend to move with the resin and can be taken out of a valve downstream from the resin flow direction.



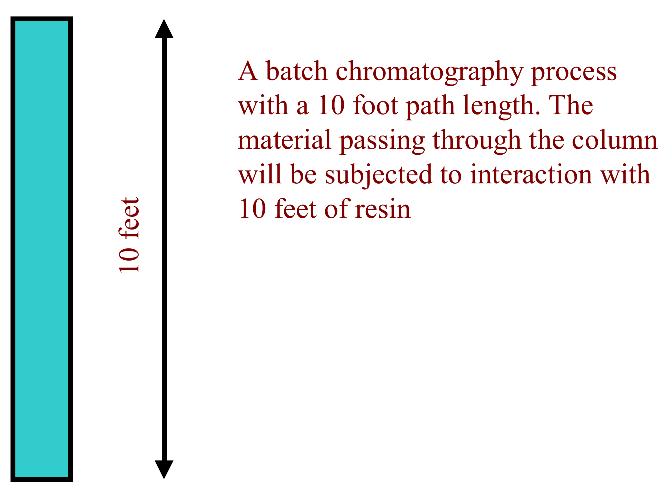
Feed mixture is fed continuously

Poorly adsorbed components move with the water and can be taken out of a valve downstream of the water flow direction.

So here we have a type of continuous chromatography. The benefits observed, in addition to continuous operation, are less eluent and less resin than used for batch chromatography. Eluent must also be added continuously to the system so the overall process looks like the following figure. Note that the highly adsorbed component is commonly called "extract" and the less adsorbed component is called "raffinate".

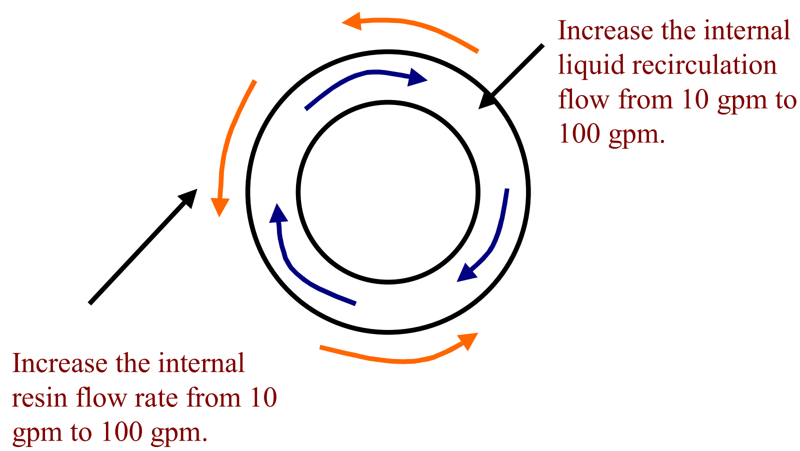



Unlike batch chromatography which can separate many components from a mixture, the moving bed method is a binary separation technique - the material which moves with the
circulating water and the material which moves with the circulating resin. There are some unusual characteristics of moving bed technology which cannot be accomplished with batch chromatography. For example, there is a useful path length effect. With a batch system which has, for example, a column with a 10 foot path length, the entering mixture will interact with a path of 10 feet of resin.



A longer path length will generally improve the chromatographic separation because additional equilibrium steps, or "theoretical plates" will be available. With moving bed technology the path length of resin which interacts with the feed mixture can be increased beyond the length of the resin in the system by increasing the internal flow rate of the resin. It may at first appear that this will just move the highly adsorbed component more quickly to its outlet valve, but to avoid this, the water flow in the opposite direction is also increased. This tends to move components back in the other direction.

Increasing internal flows in both directions means the entering mixture will interact with a much longer path of resin before exiting. So instead of being constrained to a path length as observed with batch chromatography, the moving bed system can increase path length without increasing the amount of resin used. This is one reason why moving bed technology can use significantly less resin than a batch system. The resin path can be increased in this way until constraints such as pressure drop or adsorption kinetics are reached. An example of increasing path length in this manner is shown in the following figure:



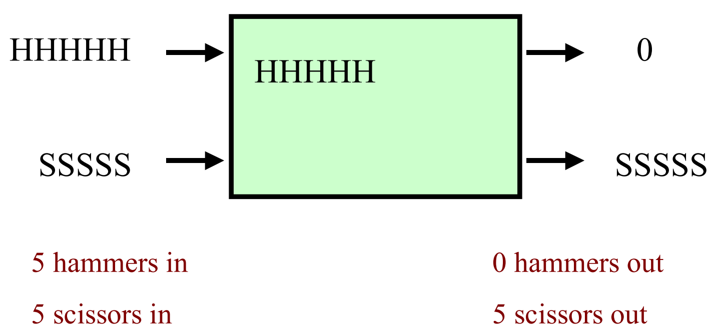

Another unusual advantage of moving bed technology is control of the internal inventory. At ARi we refer to this as control of "differential inventory". This means that with a moving bed it is possible to operate the system, in many respects, like a storeroom so that a targeted imbalance of components internal to the system can be realized prior to operating in steady state. This can be understood by referring to a storeroom wherein initially an imbalance between components is maintained so in ≠ out for one component. This will result in an differential inventory of one component forming in the storeroom.

Subsequently, if the storeroom is operated in a balanced condition such that in = out, then the previously stored inventory results in the component remaining in the storeroom longer than other components since the inventory in the storeroom must be continuously displaced. With respect to moving bed technology, this results in some dramatic effects not observed with batch chromatography. For example, a particular component entering with the feed mixture can be differentially inventoried so it is subjected to a longer residence time in the system than other components.

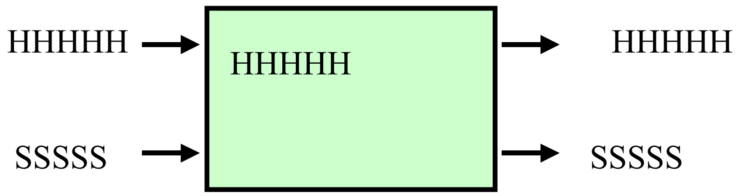
This can be useful if the longer residence time will be helpful to separate a particular component. This is a method that can be used to subject a component to a longer resin path than other components. Note how different this is from batch chromatography. As one example of the possibilities, at constant feed and eluent rate, a particular component can be inventoried in such a manner that it exits at a higher or lower target % dissolved solids.

The inventory effect is illustrated below for a storeroom:

Initial unbalanced storeroom operation.



Equilibrated, balanced storeroom operation, but with a buffer of hammers due to the initial short-term unbalanced operation. An entering hammer will have a longer residence time in the storeroom before exiting since it must wait in line for the inventory to be displaced.




5 hammers in

5 scissors in

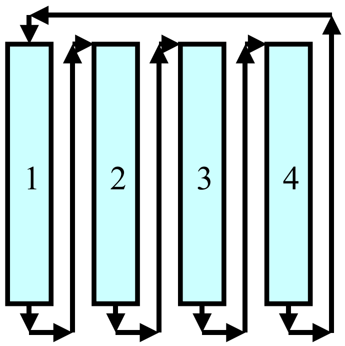
5 hammers out

5 scissors out

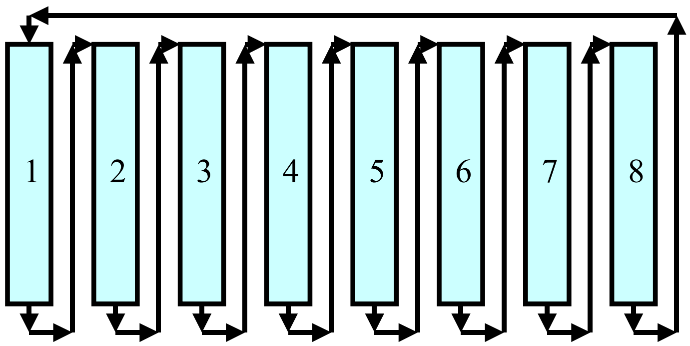
## Simulated Moving Bed Chromatography (SMB) - A practical process.

Simulated moving bed technology is used to implement a very close approximation of true moving bed chromatography. SMB exhibits the same valuable characteristics of the true moving bed concept. The following discussion will develop the SMB concept based on the previous discussion.

When encountering SMB in the literature, often a set of cells or columns is illustrated:



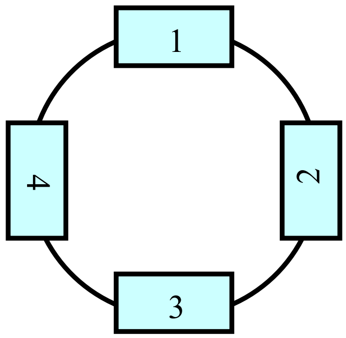

4 cells or columns




8 cells or columns

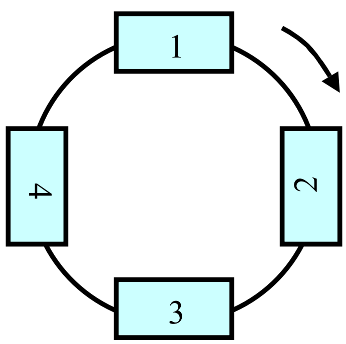
Note that the exit from each cell enters the top of the next cell and all the cells are linked in this manner into a loop. In order to understand how the imaginary true moving

bed can be simulated, it is useful to draw the common depiction of an SMB as a loop. In the following figure, the concept is still the same, i.e., the exit from each cell enters the top of the next cell and all the cells are linked in this manner into a loop. We are just drawing the SMB differently to make a correspondence with our discussion of true moving bed technology:




Drawing the SMB system like this it is easy to see how we can start with a continuous rapid circulation of liquid flow in one direction - the same as in the true moving bed discussion. This flow is accomplished with circulation pumps between cells:

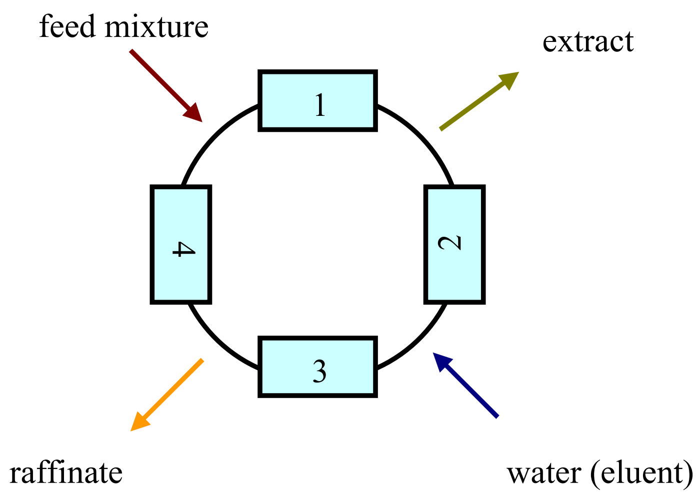
Rapid internal liquid recirculation in one direction.



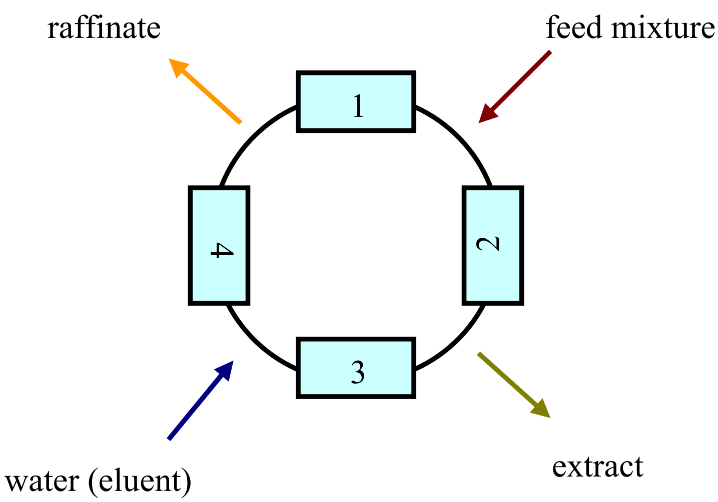

However the resin is residing in cells and is therefore stationary. Unlike the true moving bed, we have no way to move the resin in a direction opposite to the circulating

liquid. If a feed mixture is added at a point between cells, everything will simply move in the direction of the liquid flow. This is not what we want. The secret of SMB operation is that the resin movement can be simulated in the direction opposite to the internal circulation if the feed valve is occasionally switched in the same direction as the liquid flow. The other 3 valves - eluent, extract and raffinate, must also move in this manner.

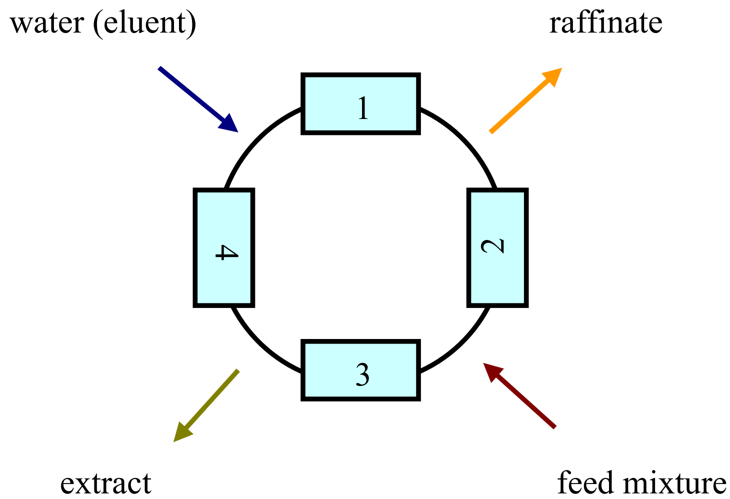
With respect to the figures below, for a person standing in the frame of reference of the feed mixture valve (not aware that it is moving around the loop but thinking it is stationary and the loop itself is moving), it would appear that the circulation liquid is moving ahead and the resin is moving back. This is the same as a true moving bed.



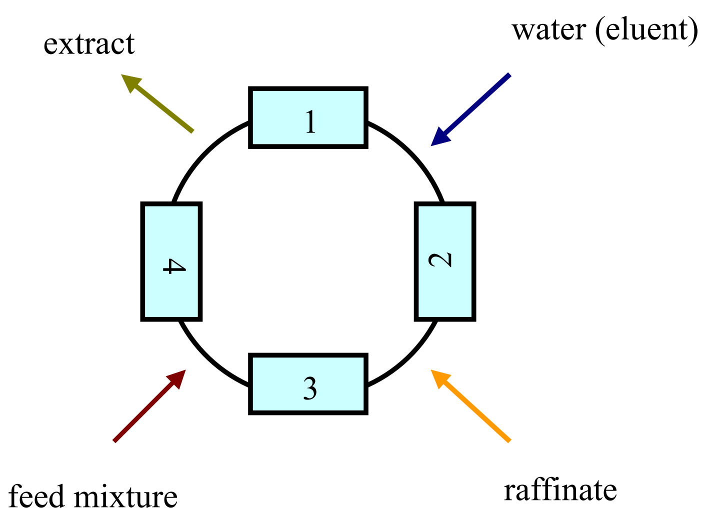

Step 1




Step 2




Step 3




Step 4

Note, therefore, that for SMB operation the switching of valve locations takes the place of the internal resin flow.

Important: You can best understand how a true moving bed is simulated by placing yourself in the frame of reference of the rotating valves and assume that the presently working valves (feed, water, extract or raffinate) for a given material are always in the same location in space and the rest of the SMB equipment - cells etc. - moves relative to you, or in other words, the resin appears to move counter-current to the internal liquid flow because of your frame of reference.

SMB operation is not a perfect simulation of true moving bed operation. The reason is that the resin movement simulation (by valve switching) is not accomplished in a continuous manner around the loop, but rather, jumps intermittently between cells. This means that as more cells are added to an SMB, a true moving bed is more closely simulated. An infinite number of cells would be needed for an exact simulation. Fortunately, 4 to 12 cells are typically enough to obtain most of the benefits of a true moving bed.

In this project, ARi's fractal technology was used to improve the efficiency of SMB technology applied to biomass processing.

An Amalgamated Research Inc. simulated moving bed chromatography system.