FINAL CRADA REPORT

BP Amoco Chemicals
Acetyls and Aromatics
Naperville IL

Argonne National Laboratory
Energy Systems Division
Argonne IL

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CRADA Number: C0201501
CRADA Title: Scaleable Production and Separation of Fermentation-Derived Acetic Acid
CRADA Start/End Date: March 2003 – September 2007

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Summary of Major Accomplishments:

Half of U.S. acetic acid production is used in manufacturing vinyl acetate monomer (VAM) and is economical only in very large production plants. Nearly 80% of the VAM is produced by methanol carbonylation, which requires high temperatures and exotic construction materials and is energy intensive. Fermentation-derived acetic acid production allows for small-scale production at low temperatures, significantly reducing the energy requirement of the process.

The goal of the project is to develop a scaleable production and separation process for fermentation-derived acetic acid. Synthesis gas (syngas) will be fermented to acetic acid, and the fermentation broth will be continuously neutralized with ammonia. The acetic acid product will be recovered from the ammonium acid broth using vapor-based membrane separation technology. The process is summarized in Figure 1. The two technical challenges to success are selecting and developing 1) microbial strains that efficiently ferment syngas to acetic acid in high salt environments and 2) membranes that efficiently separate ammonia from the acetic acid/water mixture and are stable at high enough temperature to facilitate high thermal cracking of the ammonium acetate salt.

- **Fermentation:** Microbial strains were procured from a variety of public culture collections (Table 1). Strains were incubated and grown in the presence of the ammonium acetate product and the fastest growing cultures were selected and incubated at higher product concentrations. An example of the performance of a selected culture is shown in Figure 2.

- **Separations:** Several membranes were considered. Testing was performed on a new product line produced by Sulzer Chemtech (Germany). These are tubular ceramic membranes with weak acid functionality (see Figure 3). The following results were observed:
  - The membranes were relatively fragile in a laboratory setting.
  - Thermally stable @ 130 °C in hot organic acids
  - Acetic acid rejection > 99%
  - Moderate ammonia flux

Summary of Technology Transfer Benefits to Industry:

The advantages of producing acetic acid by fermentation include its appropriateness for small-scale production, lower cost feedstocks, low energy membrane-based purification, and lower temperature and pressure requirements. Potential energy savings of using fermentation are estimated to be approximately 14 trillion Btu by 2020 from a reduction in natural gas use. Decreased transportation needs with regional plants will eliminate approximately 200 million gallons of diesel consumption, for combined savings of 45
trillion Btu. If the fermentation process captures new acetic acid production, savings could include an additional 5 trillion Btu from production and 7 trillion Btu from transportation energy.

Other Information/Results: (Papers, Inventions, Software, etc.)

One invention was developed as part of this CRADA: ANL-INV-02-007.

TITLE:
PROCESS FOR PRODUCTION AND PURIFICATION OF FERMENTATION DERIVED ORGANIC ACIDS

INVENTORS:
Argonne: Rathin Datta, Michael Henry, Edward St.Martin

The invention was reduced to practice and a patent was filed on June 2, 2004 by Emrich & Dithmar (Serial No. 10/859,259).

This is a CRADA-subject invention that includes inventors from the Contractor.

On September 9, 2006 all claims were rejected citing prior art. The prior art was a project announcement on the US Dept of Energy, Industrial Technologies Program website (ITP Chemicals: Production and Separation of Fermentation-Derived ... http://www.eere.energy.gov/industry/chemicals/pdfs/acetic_acid.pdf)

<table>
<thead>
<tr>
<th>Table 1: Example Acetogens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetobacterium woodii</td>
</tr>
<tr>
<td>Acetobacterium wieringa</td>
</tr>
<tr>
<td>Thermoanaerobacter kivui</td>
</tr>
<tr>
<td>Clostridium aceticii</td>
</tr>
<tr>
<td>Moorella thermoacetica</td>
</tr>
<tr>
<td>Sporomusa sphaeroides</td>
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<tr>
<td>Sporomusa silvacetica</td>
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<tr>
<td>Clostridium formicaceticum</td>
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<td>Clostridium magnum 2767</td>
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<td>Clostridium magnum 13760</td>
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<td>Moorella thermoautotrophica</td>
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<td>Clostridium ljungdahlii</td>
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<tr>
<td>Acetitomaculum ruminitis</td>
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<tr>
<td>Acetobacterium beki</td>
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<td>Acetobacterium tundrae</td>
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<tr>
<td>Acetohalobium aralaticum</td>
</tr>
<tr>
<td>Clostridium scatologenes</td>
</tr>
<tr>
<td>Holophaga foetida</td>
</tr>
<tr>
<td>Ruminococcus productus (U-1)</td>
</tr>
<tr>
<td>Ruminococcus productus (Marburg)</td>
</tr>
<tr>
<td>Sporomusa termitida</td>
</tr>
</tbody>
</table>

Figure 2 – Adapted tolerance of a selected acetogen strain.
Presentations

Results from this project were presented at:

1) S.W. Snyder “Production and Separation of Fermentation-Derived Acetic Acid” AIChE Spring Meeting, April 2007, Houston TX

2) Snyder, SW “Advancing Process Technologies towards Commercialization”, Texas Technology Showcase, December 2006, Galveston TX

3) S.W. Snyder, et al., “Production and Separation of Fermentation-Derived Acetic Acid”, AIChE Spring Meeting, 2005, Atlanta, GA

Figure 3 – Membrane format for vapor-assisted permeation to separate ammonia from ammonium acetate