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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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Argonne Funding: $1,350,000

Argonne PI: Seth W. Snyder
Section Leader
Process Technology Research
Energy Systems Division
630-252-7939
seth@anl.gov

Industrial Partner:
BP Amoco Chemicals
Acetyls and Aromatics
Robert Niedzielski
Global Methanol Business Manager
150 W. Warrenville Road
Naperville, IL 60563-8460
630-961-7834
robert.niedzielski@BP.com

DOE Program Manager:
Dickson Ozokwelu
US DOE - EERE – Industrial Technologies Program
1000 Independence SW
Washington DC 20585
dickson.ozokwelu@ee.doe.gov
202-586-8501

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

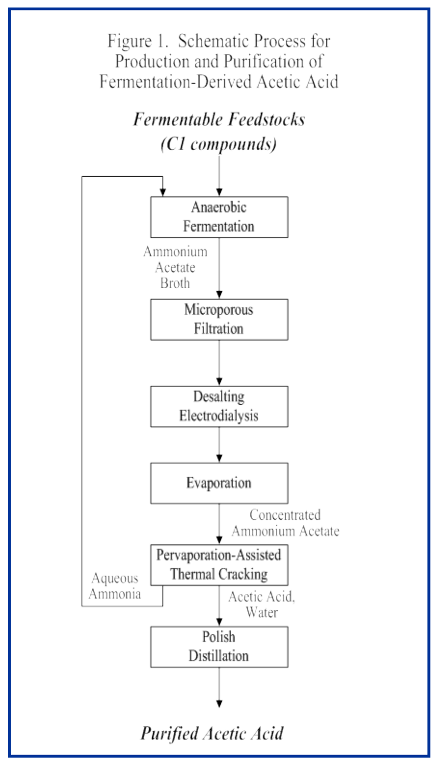

Figure 1: Schematic to produce fermentation-derived acetic acid.

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.

Table 1: Example Acetogens
Acetobacterium woodii
Acetobacterium wieringa
Thermoanaerobacter kivui
Clostridium aceticum
Moorella thermoacetica
Sporomusa sphaeroides
Sporomusa silvacetica
Clostridium formicaceticum
Clostridium magnum 2767
Clostridium magnum 13760
Moorella thermoautotrophica
Clostridium ljungdahlii
Acetitomaculum ruminis
Acetobacterium bakii
Acetobacterium tundrae
Acetohalobium arabaticum
Clostridium scatologenes
Holophaga foetida
Ruminococcus productus (U-1)
Ruminococcus productus (Marburg)
Sporomusa termitida

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)

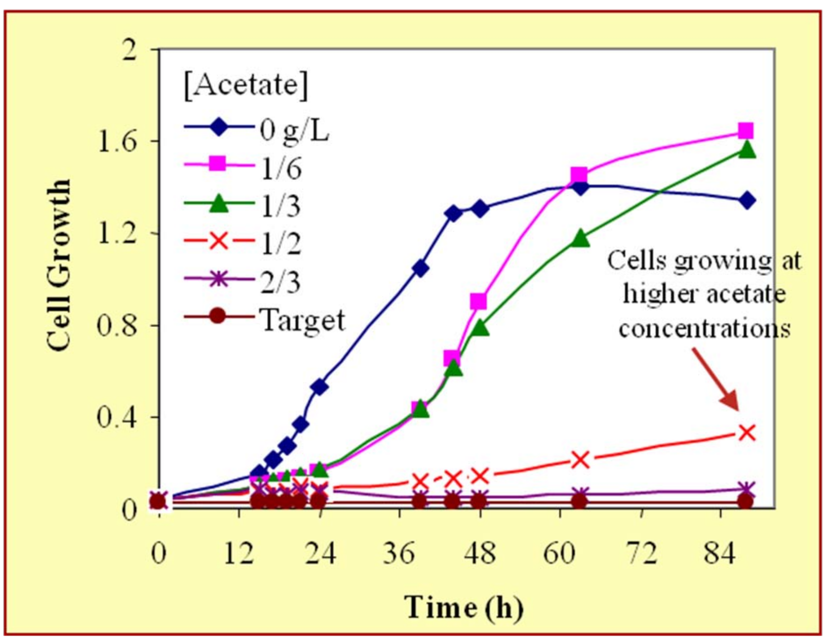

Figure 2 – Adapted tolerance of a selected acetogen strain.

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

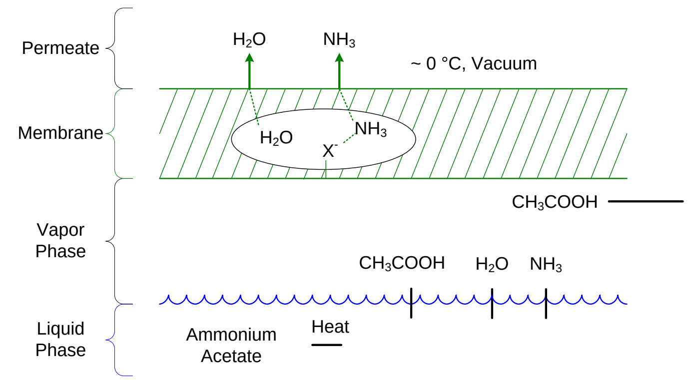

Figure 3 – Membrane format for vapor-assisted permeation to separate ammonia from ammonium acetate

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