Acetone-butanol-ethanol (ABE) Production from Cassava by a Fermentation-pervaporation Coupled Process

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Butanol — An Important Platform Chemicals

In 2007, annual consumption
> 400,000 tons in China

Dibutyl phthalate
Aliphatic dibutyl diester
(Plasticizer)

In 2007, annual consumption
> 900,000 tons in China

Polybutadiene rubber,
Styrene-Butadiene rubber

In 2007, annual consumption
> 1,300,000 tons in China

Butyl acetate
(solvent)

Butyl amine

In 2007, annual consumption
> 800,000 tons in China

Butyl aldehyde,
Butanic acid

Butadiene

Butanol

In 2007, annual consumption
> 900,000 tons in China

Butyl acrylate
(solvent)
Butanol — A Promising Biofuel with Huge Market

- weak hydrophility, low corrosion, easy to pipe
- mixing with gasoline at random proportion
- oxygen content similar to MTBE

**Calorific value**

<table>
<thead>
<tr>
<th></th>
<th>Gasoline</th>
<th>Butanol</th>
<th>Ethanol</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Btu/gallon</td>
<td>114,000</td>
<td>110,000</td>
<td>84,000</td>
<td>64,000</td>
</tr>
</tbody>
</table>

**Octane number**

<table>
<thead>
<tr>
<th></th>
<th>Gasoline</th>
<th>Butanol</th>
<th>Ethanol</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>96</td>
<td>94</td>
<td>92</td>
<td>91</td>
</tr>
</tbody>
</table>

Butanol-fuelled car driving 10,000 miles, DOE, 2005
Bottleneck in Industrial Fermentation—Products Toxicity and Inhibition

- Low productivity
  
  Titer: normally <20 g/L
  
  Volume productivity:
  
  ~0.35 g/Lh

- High energy consumption
  
  Steam: 13 tons/ton ABE

- Large amount of wastewater
  
  50 tons wastewater / ton ABE
Engineering Strategy: Developing Fermentation-\textit{in situ} Separation Coupled Process

Comparison of in-situ Product Recovery Technologies

<table>
<thead>
<tr>
<th></th>
<th>Stripping</th>
<th>Adsorption</th>
<th>Extraction</th>
<th>Pervaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>Moderate</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Selectivity</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Fouling</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
<td>Low</td>
</tr>
<tr>
<td>Energy required (MJ/kg ABE)</td>
<td>21</td>
<td>33</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>Operational simplicity</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

Groot et al., Process Biochemistry 27 (1992) 61-75
Fermentation-pervaporation Coupled Process

Schematic of fermentation-pervaporation process

Advantages:
- Low product inhibition
- High fermentation productivity
- Low separation energy consumption
- Low wastewater production

Key techniques:
- Development of PV membrane with high performance
- Optimization of the coupled process
- Module development & fouling control
**Membrane Materials and Membrane Performance**

<table>
<thead>
<tr>
<th>Pervaporation membrane materials</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymeric materials</strong></td>
<td>PDMS (α=30-45)、PTMSP(α=52-75)</td>
</tr>
<tr>
<td><strong>Inorganic materials</strong></td>
<td>Silicalite-1 (α=80-125)</td>
</tr>
<tr>
<td><strong>Hybrid materials</strong></td>
<td>Silicalite-1 filled PDMS (α=50-111)</td>
</tr>
</tbody>
</table>
Problem and Solution in Preparation of Hybrid Membrane

Problem

- Silicalite flocculation in membrane
  - Decreasing the membrane selectivity
  - Decreasing the membrane strength when the silicalite loading was over 60%.

Our solution

- Modify the outer surface of the silicalite to improve the affinity between silicalite and polymer matrix
Surface Modification of Silicalite-1 Particles

1. Hydrolysis of the ethoxy groups
2. Condensation
   a. with the silanol groups of silicalite
   b. between adjacent silane molecules

Contact angles:
- 38.1° (unmodified)
- 143.7° (modified)

Unmodified silicalite-1

VTES (vinyltriethoxysilane)

Silane modified silicalite-1
Cross-linking Reaction of PDMS and Modified Silicalite-1

Prepolymer (RTV615A) + Crosslinker (RTV615B) → Silane-modified silicalite-1 → Crosslinked polymer network
Effect of butanol concentration on flux and separation factor using butanol/water model solutions at 37°C. (a) flux and (b) separation factor.
Experimental Setup for the Coupled Process

Membrane module

Fermentation-Pervaporation System
## Batch ABE Fermentation from Cassava by *C. Acetobutylicum* ATCC 824 and DP217

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Strains</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ATCC 824</td>
</tr>
<tr>
<td>Fermentation time (h)</td>
<td>72</td>
</tr>
<tr>
<td>Acetone (g/L)</td>
<td>3.04±0.18</td>
</tr>
<tr>
<td>Butanol (g/L)</td>
<td>5.67±0.05</td>
</tr>
<tr>
<td>Ethanol (g/L)</td>
<td>0.55±0.14</td>
</tr>
<tr>
<td>Total solvent (g/L)</td>
<td>9.26±0.35</td>
</tr>
</tbody>
</table>
Inhibition of Butanol

The butanol inhibition concentration: >5g/L

7 g/L-13 g/L Butanol results in a 50 % inhibition of growth.

Effect of butanol on ABE production by C. acetobutylicum
ABE Batch Culture with Optimized Medium

(a) OD$_{620}$, glucose concentrations and pH, (b) solvent and acid concentrations.

- Medium: 70 g/L cassava power + 2.17 g/L CSP + 0.01 g/L FeSO$_4$•7H$_2$O
- Initial pH: 6.81
- The culture produced 20.14 g/L total solvent
- Acid concentration was above 1 g/L
ABE Production in Batch Fermentations using Cassava with PV

- PV operation started at the 16th hour when butanol concentration was 4.3 g/L
- More ABE was produced (21.78 g/L ABE, i.e., 7.36 g/L acetone + 12.95 g/L butanol + 1.47 g/L ethanol)
- Acid concentration was less than 1.0 g/L
- Higher productivity, higher yield, shorter fermentation time (42 h)
Performance of the Membrane in Batch Fermentation-PV Coupled Process

The performance of the membrane was very stable in terms of the flux and separation factor.
Continuous ABE Production by Fermentations-PV Coupled Process

- Glucose: 20-30 g/L
- ABE: ~ 7.5 g/L
- Butanol: ~ 4.5 g/L
- Acetone: ~ 1.8 g/L
- Ethanol: ~ 1.2 g/L

Legend:
- Glucose: □
- Total solvent concentration: ■
- Acetone: ▲
- Ethanol: ▼
- Butanol: ●
- Acetic acid: ▶
- Butyric acid: ◀
Permeate Concentration in Continuous ABE Fermentations-PV Coupled Process

- Total solvent
- Acetone
- Ethanol
- Butanol
Membrane Performance in Continuous ABE Production by the Coupled Process

Average flux:
557 g/m²•h

Separation factor:
39.4 for acetone
31.2 for butanol
8.4 for ethanol

- Total flux; Separation factor for △ Acetone ▽ Ethanol and ○ Butanol
## Summary of Solvent Production by Fermentation with and without Pervaporation

<table>
<thead>
<tr>
<th>Process</th>
<th>Solvent Productivity (g/Lh)</th>
<th>Solvent Yield (g/g)</th>
<th>Glucose utilization rate (g/Lh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch-PV</td>
<td>0.49</td>
<td>0.35</td>
<td>1.26</td>
</tr>
<tr>
<td>Continuous Coupling</td>
<td>0.76</td>
<td>0.38</td>
<td>2.02</td>
</tr>
<tr>
<td>Batch</td>
<td>0.42</td>
<td>0.33</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Summary

◆ In ABE fermentation from cassava, it is technically feasible to eliminate the product inhibition by the fermentation-pervaporation coupled process. ABE could be effectively concentrated in the permeate.

◆ With the coupled process, the ABE yield could be increased, therefore, substrate can be utilized more efficiently.

◆ Developing PV membranes with higher selectivity and higher flux and optimizing the integrated process would further promote the economic and technical feasibility of the process.
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Thank You!