ORGANOPHILIC PERVAPORATION FOR ABE RECOVERY FROM LAB TO PILOT

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VITO IN NUMBERS

» 784 employees
» 34 nationalities

» HQ in Mol, Belgium
» Subsidiary in China and Qatar

» 1000 research projects

» More than 500 research partners

» 230 scientific articles in 2016

» More than 400 patents worldwide

» 170 mio € turnover in 2016

Biomass for sustainable biofuels and biobased products: from lab to pilot plant, 17th October 2017, CENER Pamplona (Spain)
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From lab to pilot to plant

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OUTLINE OF A TRADITIONAL ABE PLANT

Kagi plant (Taiwan) in 1939; batch process on sweet potato; 5500 tons of butanol produced in 1945.


Biobutanol plant in Jilin province (China, 2011); Continuous operation with annual capacity of 65,000 tons biobutanol

Dokshukino plant (currently Nartkala, Russia, 1963)

**CHALLENGES IN TRADITIONAL FERMENTATION**

**Challenges in traditional fermentation**

- Cost of substrate
- Product toxicity:
  - Low product titers
  - Low productivity
  - High purification costs
  - High waste water volumes
  - Energy-intensive separation

\[
EROI = \frac{\sum \text{of the } E \text{ content of fuels delivered}}{\sum \text{of all the } E \text{ costs of getting those fuels}}
\]

**EROI traditional process:**

\[
EROI_{n-\text{butanol}} = 0.37 - 0.71^* \quad \text{and} \quad EROI_{n-\text{butanol}} = 0.5^{**}
\]

**Waste water volumes traditional process:**

- Maximal solvent titers \(\sim 20 \text{ g.L}^{-1}\) solvents
- \(\sim 50\text{L effluent per kg solvent}\)


Challenges in traditional fermentation

- Cost of substrate
- Product toxicity:
  - Low product titers
  - Low productivity
  → High purification costs
  → High waste water volumes
  → Energy-intensive separation

Integration with pervaporation

Integration of
- Organophilic pervaporation and clostridial fermentation
- using a membrane-based in situ product recovery technique (ISPR)
  → Selective product withdrawal from reaction medium

Benefits

- Higher productivity
- Decreased water consumption
- Lower steam consumption
- Applicable to (fed)-batch & continuous processes
- Lower production price
### INTEGRATION WITH PERVAPORATION

<table>
<thead>
<tr>
<th>Pervaporation</th>
<th>Fermentation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Flux (kg.m(^{-2}).h(^{-1}))</strong></td>
<td><strong>Yield (g.g(^{-1}))</strong></td>
</tr>
<tr>
<td>Determines capital costs</td>
<td>Determines feedstock costs</td>
</tr>
<tr>
<td>~ Temperature</td>
<td></td>
</tr>
<tr>
<td>~ Solvent concentration</td>
<td><strong>Titer (g.L(^{-1}))</strong></td>
</tr>
<tr>
<td>~ Applied permeate pressure</td>
<td>Determines downstream processing costs</td>
</tr>
<tr>
<td><strong>Separation factor α</strong></td>
<td><strong>Productivity (g.L(^{-1}.h(^{-1}))</strong></td>
</tr>
<tr>
<td>Determines solvent composition in permeate</td>
<td>Determines capital costs</td>
</tr>
</tbody>
</table>

Interdependency of critical parameters  
Integration requires compromises  
Trade-offs need to be properly understood
ISPR CONFIGURATIONS IN WHOLE CELL FERMENTATION

Lowest complexity preferred when presence of microorganisms adversely affects performance ISPR technology.

Direct contact:
- Internal
- External

Indirect contact:
- Easy access to separation unit
- Separate sterilization
- Highest complexity
- Operation at high cell density possible
- Independent optimization possible

EXPERIMENTAL CONFIGURATIONS AND CONDITIONS

- External, direct contact configuration was always used:
  - Chemical sterilization of PV unit
  - Autoclavation of fermentor

- Cells were never retained prior to pervaporation operation

- Pervaporation performed at similar temperature as fermentation

- Fed-batch, one-stage continuous and two-stage continuous configurations tested

- *C. acetobutylicum* ATC824 & GBL proprietary clostridial strains were used

- PDMS, POMS, PTMSP based organophilic pervaporation membranes were tested.

- Feedstocks:
  - Up to 100 g.L\(^{-1}\) glucose and 50 g.L\(^{-1}\) xylose in feed
  - Wheat straw hydrolyzate and Miscanthus hydrolyzate

- Effect of permeate pressure was investigated
EXPERIMENTAL CONFIGURATIONS

Laboratory-scale conversions

Lab-scale demonstration unit @ VITO
Batch/fed-batch/continuous fermentations up to ~1000h

From lab to pilot...

DEMONSTRATION AT PILOT-SCALE

In collaboration with:

CENER
Fouling was not observed during 654h of operation
Solvent fluxes depend on solvent concentration in feed
Water flux remains fairly stable

Component and total fluxes in function of solvent titers in the fermentor. (□) fluxes of PDMS membranes using artificial lignocellulosic hydrolyzates as feedstock. Tests were performed at 9-14 mbar and 37°C.
PERVAPORATION MEMBRANES USED: PTMSP – PDMS – POMS

Composite PTMSP membrane made in VITO (◊), composite PDMS membrane from Pervatech (△), composite POMS membrane from Pervatech (▽). T=37°C and permeate pressure was 9-14 mbar for PDMS and PTMSP experiments; T=32°C and permeate pressure was 20 mbar for POMS membrane.
Lignocellulosic biomass is the largest potential feedstock. Offers potential for cost reduction on the longer term. Lignocellulose consists of lignin, hemicellulose and cellulose and needs special pretreatment before obtaining fermentable C5 and C6 carbohydrates (wheat straw and miscanthus hydrolyzate provided by CENER, Aoiz, Navarra). Proprietary strains of Green Biologics were used in fed-batch and continuous mode.
Solvent productivity in function of xylose utilization. GBL-A (△); ATCC824 (◇) from Van Hecke et al. [2]; GBL-B (▽); GBL-C (□); GBL-B (▼) with wheat straw hydrolyzate as feedstocks; GBL-B (▽) with Miscanthus hydrolyzate as feedstocks. In all experiments, glucose was fully utilized.
Non-condensable gases CO\(_2\) and H\(_2\) are generated:
- 2.6 mole of CO\(_2\) and 1.59 mole of H\(_2\) per mole of solvent (Jones & Woods, 1986)
- Impact frequently ignored
- Borisov et al (2017) mention that vacuum pervaporation is unsuitable for recovery of butanol due to the high power consumption
- However, the power consumption of vacuum pumps heavily depend on the applied permeate:

Non-condensables related power consumption of vacuum pumps expressed as MJ electricity consumed expressed per kg butanol produced (left axis), operating costs of vacuum pumps expressed per kg butanol produced (right axis). A. Estimated for reciprocating vacuum pumps; B. Estimated for rotary piston vacuum pumps. ● evacuation of 15% non-condensables; ◆ evacuation of 30% non-condensables; ▲ evacuation of 60% non-condensables; ■ evacuation of 100% non-condensables.

Characterization of (novel) pervaporation membranes for ABE recovery conducted at permeate pressures < 3.9 mbar (Kießlich et al., 2017; Li et al., 2011; Liu et al. 2011; Cai et al., 2017; Cai et al. 2016) B

This is far below the industrially relevant 10-100 mbar range, the performance parameters do not allow trustworthy techno-economic evaluations.

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**Assumptions**

- 100 ktons/year biobutanol plants
- Multiple stage waste water evaporators

**BENEFITS**

- Productivity x 2.5 by removal product inhibition
- Fermentor volume ↓
- Water footprint -50%
- Steam consumption -50%
- Applicable to (fed)-batch & continuous processes
- Lower production price

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$EROI_{n\text{-butanol}} = 0.50$

Base case

Acetone Ethanol

Decanter

acetone

ethanol

butanol

water

$EROI_{n-butanol} = 1.08$
50% lower steam costs due to savings in steam stripper and evaporators
2,5 times lower waste water / kg

Estimation of PV module prices:

<table>
<thead>
<tr>
<th>Membrane production volume (m²/y)</th>
<th>20</th>
<th>200</th>
<th>2.000</th>
<th>20.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated cost (€/m²)</td>
<td>PDMS/POMS</td>
<td>210</td>
<td>130</td>
<td>52</td>
</tr>
<tr>
<td>commercial price (€/m²)</td>
<td>PDMS – supplier A</td>
<td>500 - 250</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Estimation of PV module allowing an interesting business case:

<table>
<thead>
<tr>
<th>Bare cost of pervaporation module</th>
<th>Change in butanol production price for flux of 0,62 kg/m²/h</th>
<th>Change in butanol production price for flux of 1 kg/m²/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 €.m²</td>
<td>-23%</td>
<td>-26%</td>
</tr>
<tr>
<td>200 €.m²</td>
<td>-15%</td>
<td>-22%</td>
</tr>
<tr>
<td>300 €.m²</td>
<td>-6%</td>
<td>-17%</td>
</tr>
<tr>
<td>400 €.m²</td>
<td>+2%</td>
<td>-12%</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Pervaporation
- No fouling observed in the entire course of the experiment for POMS and PDMS
- Room for improvement in design of industrial membrane modules for integration with fermentation processes

Fermentation
- Productivity increase / improved water footprint
- Further use of lignocellulosic hydrolyzates as feedstock ongoing

Integrated tests
- Potential of technology clearly demonstrated
- 2-fold lower energy costs using patent pending technology
- Pilot scale: further improvements towards fluxes/productivities needed
The ButaNexT project has received funding from the European Union Horizon 2020 Research and innovation Programme under grant agreement n° 640462