Emerging Membrane Technologies in Biorefining

Bettina Muster-Slawitsch
Judith Buchmaier
Christoph Höfer
Sarah Meitz
Guideline

1. Emerging Membrane Technologies
2. Integration Examples
3. Long-Term Studies
4. Evaluating feasibility of membrane application in biorefining
5. Recommendations, future research needs

Contributing Authors:

Dr. Marlene Kienberger, Graz University of Technology
Dipl.-Ing. Paul Demmelmayer, Graz University of Technology
Elena Guillen, PHD, Universitat Politècnica de Catalunya (UPC)
Magdalena Cifuentes-Cabezas, PHD, Universitat Politècnica de València
Dr. Gianluca Di PROFIO, PHD, Consiglio Nazionale delle Ricerche (CNR), Istituto per la Tecnologia delle Membrane (ITM)
Soraya Sluijter, PHD, Sustainable Technologies for Industrial Processes, TNO
Emerging Membrane Technologies

Forward Osmosis – Membrane Distillation – Pervaporation – Liquid Membrane Permeation – Membrane assisted Crystallization
## Integration Examples

- Recover Ammonia from WWTP effluent
- MD as thermal separation process
- Driving force is vapour pressure difference
- 24 h continuous operation

### Integration Examples

<table>
<thead>
<tr>
<th>Objective</th>
<th>Feedstock stream</th>
<th>Highlights</th>
<th>Integration point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Remove/recover ammonia from WWTP effluent and produce a fertilizer in the form of an Ammonium Sulphate (AS) solution.</td>
<td>Digestate sludge supernatant (after dewatering of sludge)</td>
<td>Ammonia recovery up to 99%; Effluent &lt;10 mg TAN/l; CF of N-NH4+ concentration from feed to permeate up to 5; High purity of the product</td>
<td></td>
</tr>
</tbody>
</table>

### Selective recovery of ammonia/ water purification

<table>
<thead>
<tr>
<th>Production capacity</th>
<th>Challenges and development goals</th>
<th>TRL Application</th>
<th>TRL Membrane operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ 100 l ammonium sulfate at 6.4 g NH4+ l-1</td>
<td>Towards higher product (AS) concentration in the permeate and solid product.</td>
<td>4-5</td>
<td>4-5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>Membrane process</th>
<th>Module / Membrane</th>
<th>Treatment capacity</th>
<th>Membrane area deployed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtration of T5 and particles/cartridge filter (200 µm)</td>
<td>MD</td>
<td>Plate and frame / PP</td>
<td>~ 1 m³/day</td>
<td>Up to 14 m²</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Per day</td>
<td>Per membrane area</td>
</tr>
<tr>
<td>Membrane process inputs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Thermal energy</th>
<th>Electrical energy</th>
<th>Further potential applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>H₂SO₄</td>
<td>13.6 kWhₑ pro kg NH₃</td>
<td>Biogas plants, slaughterhouses, any ammonia-rich stream.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Further info sources: ThermaFlex project: <a href="https://thermaflex.greenenergylab.at/thermaflex/?lang=en">https://thermaflex.greenenergylab.at/thermaflex/?lang=en</a></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Contact: <a href="mailto:b.must@aeec.at">b.must@aeec.at</a></td>
</tr>
</tbody>
</table>

IEA IETS Task 17 | IETS Conference May 2023 Göteborg |
Integration Examples (2)

- Recovery of phenolic compounds from olive oil waste water
- Forward Osmosis
- No chemical requirements
- Challenges: fluctuation in water quality and seasonality; membrane availability

<table>
<thead>
<tr>
<th>Objective</th>
<th>Recovery of phenolic compounds and recovery of watercourses.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact</td>
<td>Research Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM), Universitat Politècnica de València, C/Camino de Vera s/n, 46022, Valencia, Spain. Magdalena Cifuentes-Cabezas (<a href="mailto:magnica@upv.es">magnica@upv.es</a>), Maria Cinta Viriast-Velia, and Antonio Mendoza-Roca, Silvia Alvarez-Blanco.</td>
</tr>
<tr>
<td>Feedstock stream</td>
<td>Olive Oil Washing Wastewater; Wastewater obtained at the outlet of the vertical centrifugation (olive oil washing) obtained from the olive oil production process by centrifugation in two phases. This olive oil production process is currently used in Spain. It uses less water than triphasic centrifugation (more widely used in other Mediterranean countries), so it is expected that more countries will opt for this more environmentally friendly option in the future.</td>
</tr>
<tr>
<td>Capacity</td>
<td>25 m³/day only from October to January/February (olive oil production)</td>
</tr>
<tr>
<td>Pre-treatment</td>
<td>A three-stage pre-treatment was planned. The first stage consisted of natural flotation, sedimentation, and cartridge filtration (60 µm)²⁰.</td>
</tr>
<tr>
<td>Membrane process</td>
<td>Ultrafiltration²¹,²², Nanofiltration²³, Forward osmosis</td>
</tr>
</tbody>
</table>

[Diagram showing the process of olive oil washing wastewater treatment with membranes and recovery of phenolic compounds]
Separation of monomeric sugars and lignin after organosolv process
Separate monomeric sugars from salts to enable/improve fermentation
**Integration Example (5)**

- Novel L-Malic acid enzymatic production route
- Fumaric acid recovery via membrane assisted crystallization

Please send us your integration examples to enrich the document!
long-term performance of ammonia recovery from centrate water

- Stable and robust operation
- AS conc. ~ 25 g/l
- Energy demand in low T
- Citric acid cleaning worked well
- Removal and diffusion coefficient reduced with water rinsing
Module and membrane inspection

PTFE membrane with PP backing, 0.45 μm pore size, 130–230 μm thickness, 70-85% porosity
Module and membrane inspection

Cleaning done with 3 cleaning agents and various times @ 50°C
Ammonia removal tests for 1 h @38°C 1g/l N-NH4, pH 4
no clear visible effect on ammonia transfer, slight flux degradation → to short experimental time?
Elemental analysis

Virgin  Fouled  Fouled & Cleaned

BSE
Elemental analysis

Virgin

Fouled

Fouled & Cleaned

BSE
Elemental analysis

Virgin  Fouled  Fouled & Cleaned

The IR-spectrum from the “membrane cleaned” (black) show additionally to the PTFE peaks (~1300 cm\(^{-1}\) – 600 cm\(^{-1}\)) additional peaks of a protein (here called “marin protein concentrate”, red line).
Feasibility approach

Pre-treatment strategies - decision trees

Feasibility evaluation criteria

Cleaning considerations
Feasibility

Criteria:

- Criteria per emerging technology:
  - Driving force suitability
  - Flux feasibility
  - ....
- Membrane suitability
- Feedwater Suitability
Feasibility

Pretreatment strategies

Flowchart:
- Feed stream
  - Remove TSS
  - Remove Oxidizers
  - Prevent precipitation
  - Membrane

Processes:
- Pretreatment
- Feasibility
- TSS contact
- Degreasing
- Coagulation + centrifuge/deslaver
- Oil/grease remaining?
- Fats/grease removed?
- Posttreatment / Aeration
- Hydrolysis
- TSS reduced?
- > 1%
- < 1%
- UF/ coarse filters
Feasibility approach
Future research

• Studies on tailored and cost-effective protocols for respective selection of pre-treatment agents preferably of high performance, low cost and reduced hemicellulose degradation

• New membrane developments (configuration and fabrication). Advanced membranes – e-beam irradiation; 3D printing of membranes, membranes without halogenated elements (PP instead of PTFE)
  • Membrane surface engineering, e.g., membrane modification via E-beam or cold plasma modification to tailor the polymeric structure (crosslinking, pore size) and to functionalize surfaces.
  • Development of more sustainable materials (non-halogenated polymers, such as PP or PE instead of PTFE/PVDF or biopolymers) with suitable thermal and mechanical properties
  • Development of novel membrane structures via 3D printing
  • Model-based membrane design based on transport and fouling models to overcome existing bottlenecks

• Mechanisms to enhance selectivity via decoupling valuable transport driving force from others.

• Integrated membrane process designs, that allow coupling of various membrane processes.
Future research

• More elaborated effective combined physical and chemical membrane cleaning protocols, where the costs of the required chemicals don’t affect the economic feasibility of the overall membrane technologies that much and where environmental issues are also regarded.

• Further data is required on the identification of major foulants by advanced membrane autopsy and characterisation techniques, for addressing the complexity and the high fouling propensity of P&P effluents.

• Identification of optimal operating conditions, in terms of hydrodynamics, feed and membrane characteristics.

• Long-term pilot studies in 24h operation to evaluate stable operating scenarios and determine maintenance requirements.

• Establishment of research on membrane reactors, for in-situ removal of valuable substances from reaction processes in biorefineries.
Know-How Technologies

- (polymeric) membrane fabrication
- MF, UF, NF
- Crystallization
- Membrane Emulsification
Know-How Feedstock

- By-product streams from food industry, agricultural waste, nutraceuticals, pigments, whey protein
- Drinking water, waste water treatment
- Organic waste streams, grass
- Other plant and marine sources, namely microalgae

- Cellulose
- Hemicellulose
- Lignin
- Others (please add)