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Recommended Citation
Patricia Gorgojo, Monica Alberto, Jose Miguel Luque-Alled, Lei Gao, Maria Illut, Aravind Vijayaraghavan, and Peter Budd, "PIM-1/graphene pervaporation membranes for bioalcohol recovery" in 'Advanced Membrane Technology VII', Isabel C. Escobar, Professor, University of Kentucky, USA Jamie Hestekin, Associate Professor, University of Arkansas, USA Eds, ECI Symposium Series, (2016). [http://dc.engconfintl.org/membrane_technology_vii/5](http://dc.engconfintl.org/membrane_technology_vii/5)
PIM-1/graphene pervaporation membranes for bioalcohol recovery

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The demand for energy requirement is increasingly growing.

It is difficult to reach the world energy demand only by using fossil fuel.

Alternative: BIOFUELS
A **biofuel** is any fuel source that is made from biological materials. The two most common kinds of biofuels are both gasoline alternatives: ethanol and biodiesel.

- Reduces greenhouse gas emissions as the release of CO\(_2\) from burning the biofuels is matched by the CO\(_2\) absorbed by the plants growing the biomass used to produce it.

- Using so-called second-generation technologies to convert material such as crop residues into bioenergy can avoid competition for land.
Bioethanol and biobutanol are produced via fermentation of biomass.

End-product inhibition is caused by the toxicity of the alcohol produced on the bacteria. A concentration of less than 2% of bioalcohol (ABE fermentation process for biobutanol production) is typically achieved.

The bioalcohol needs to be purified from the fermentation broth (contains mainly water) by a series of distillation columns → 60-80% of the total production costs.
Organophilic pervaporation membranes

Polymers of intrinsic microporosity (PIMs)

A continuous network of interconnected intermolecular voids, which forms as a direct consequence of the shape and rigidity of the component macromolecules.


- Inorganic membranes, zeolites: silicalite-1, ZSM-5
- Polymeric membranes, polydimethylsiloxane (PDMS), poly[1-(trimethylsilyl)-1-propyne] (PTMSP), PEBA, PTFE
- Hybrid membranes, polymer matrices containing selective fillers e.g. silicalite-silicon rubber

- Swelling in the presence of organic solvents → Reduction of the selectivity
- Ages over time → Increase in selectivity and reduction of flux
Bioethanol and biobutanol are produced via fermentation of biomass.

End-product inhibition is caused by the toxicity of the alcohol produced on the bacteria. A concentration of less than 2% of bioalcohol (ABE fermentation process for biobutanol production) is typically achieved.

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**Step 1:** Removal of alcohol from fermentation broth
Organophilic membranes

**Step 2:** Further purification of alcohol
Hydrophilic membranes
Hydrophilic graphene oxide (GO) membranes

PIM-1 membranes with graphene

**Simulations**


**Experimental work**

- PIM-1 is soluble just in few organic solvents, (CHCl₃, THF, DMAc)
- Direct mechanical exfoliation of graphite in these solvents is not good
- GO and rGO flakes prepared via oxidation of graphite cannot be dispersed

Functionalization of GO with alkylamines can lead to monolayer and few-layered graphene flakes that are easily dispersed in CHCl₃
Preparation of graphene-like flakes

Graphite → Oxidation (Hummers modified method) → Graphene Oxide (GO)

Octylamine (OA) → Functionalization → OCTadecylamine (ODA)

GO-OA → Chemical reduction (hydrazine) → rGO-OA

GO-ODA → rGO-ODA

Characterization of graphene-like flakes: FTIR

Peaks at 2850/2920 cm\(^{-1}\) $\rightarrow$ -CH\(_2\) of alkylamines

Decrease in intensity for reduced samples $\rightarrow$ loss of some alkylamine upon treatment with hydrazine

Peaks at 1470 cm\(^{-1}\) and 1580 cm\(^{-1}\) $\rightarrow$ covalent bonds (C-N-C) between alkylamines and GO
Characterization of graphene-like flakes: XPS

The higher C:O ratio corresponds to the sample functionalised with the alkylamine that has the longer chain.

C:O ratio decreases upon chemical reduction as a result of a small portion of the grafted alkyl chains being removed.
Characterization of graphene-like flakes: TGA

- Enhancement in the hydrophobicity degree of starting material GO in this order: rGO-ODA > GO-ODA > rGO-OA
- Presence of both physically adsorbed and chemically bonded ODA to the GO flakes
- Weight loss for rGO-ODA > rGO-OA as ODA chains having larger mass
Characterization of graphene-like flakes: AFM

lateral dimensions of GO sheets are in the expected range with flakes of sizes ranging from few tens of nanometers to few micrometers

monolayer and few-layered structures are observed
Membrane fabrication

1. Preparation of casting solutions

<table>
<thead>
<tr>
<th>wt.%</th>
<th>Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>rGO-ODA</td>
</tr>
<tr>
<td>0.05</td>
<td>GO-ODA</td>
</tr>
<tr>
<td>0.1</td>
<td>rGO-OA</td>
</tr>
<tr>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Filler in CHCl$_3$ + 5 wt.% PIM-1 in CHCl$_3$ → Casting solution

2. Casting-evaporation on flat petri dishes

Dope solution

Drying ~3 days

PIM-1

PIM-1 + rGO-ODA
Membrane fabrication

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>Filler</th>
<th>wt% of filler Values from the preparation of casting solutions</th>
<th>wt% of filler Values from UV of re-dissolved membranes *</th>
<th>Membrane Thickness (µm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIM-1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>60 ± 9.1</td>
</tr>
<tr>
<td>0.01GO-ODA</td>
<td>GO-ODA</td>
<td>0.01</td>
<td>0.040 ± 0.008</td>
<td>54 ± 6.5</td>
</tr>
<tr>
<td>0.1GO-ODA</td>
<td>GO-ODA</td>
<td>0.1</td>
<td>0.197 ± 0.024</td>
<td>65 ± 4.2</td>
</tr>
<tr>
<td>0.5GO-ODA</td>
<td>GO-ODA</td>
<td>0.5</td>
<td>0.601 ± 0.045</td>
<td>57 ± 2.2</td>
</tr>
<tr>
<td>1GO-ODA</td>
<td>GO-ODA</td>
<td>1</td>
<td>1.340 ± 0.316</td>
<td>51 ± 8.8</td>
</tr>
<tr>
<td>0.01rGO-ODA</td>
<td>rGO-ODA</td>
<td>0.01</td>
<td>0.018 ± 0.003</td>
<td>59 ± 6.2</td>
</tr>
<tr>
<td>0.1 rGO-ODA</td>
<td>rGO-ODA</td>
<td>0.1</td>
<td>0.065 ± 0.012</td>
<td>56 ± 2.4</td>
</tr>
<tr>
<td>0.5rGO-ODA</td>
<td>rGO-ODA</td>
<td>0.5</td>
<td>0.316 ± 0.078</td>
<td>68 ± 7.6</td>
</tr>
<tr>
<td>1rGO-ODA</td>
<td>rGO-ODA</td>
<td>1</td>
<td>0.704 ± 0.207</td>
<td>52 ± 6.9</td>
</tr>
<tr>
<td>0.01rGO-OA</td>
<td>rGO-OA</td>
<td>0.01</td>
<td>0.031 ± 0.006</td>
<td>48 ± 3.9</td>
</tr>
<tr>
<td>0.1rGO-OA</td>
<td>rGO-OA</td>
<td>0.1</td>
<td>0.125 ± 0.094</td>
<td>51 ± 2.1</td>
</tr>
<tr>
<td>0.5rGO-OA</td>
<td>rGO-OA</td>
<td>0.5</td>
<td>0.487 ± 0.085</td>
<td>54 ± 6.3</td>
</tr>
<tr>
<td>1rGO-OA</td>
<td>rGO-OA</td>
<td>1</td>
<td>0.972 ± 0.097</td>
<td>59 ± 6.1</td>
</tr>
</tbody>
</table>

(*) Average of 10 measurements with a screw gauge in different areas of the membrane.
Membrane characterization: SEM

a) PIM-1

b) 0.01 rGO-ODA

c) 0.1 rGO-ODA

d) 1 rGO-ODA

e) 1 GO-ODA

f) 1 rGO-OA
Membrane characterization: STEM

- Presence of single-layer flakes of GO-ODA and rGO-OA in the polymeric matrices
- O:C ratio mapping → features correspond to alkylamine-functionalized GO flakes
Membrane characterization

Contact angle

- All values for water ranged from 80 to 90° → addition of graphene-like fillers do not change significantly the surface properties
- Ethanol contact angles 9.8° - 15.4° (13° for PIM-1)
- Butanol contact angles 7.6° - 9.8° (9° for PIM-1)

Solvent uptake

\[ SU = \frac{m_f - m_i}{m_i} \times 100\% \] 3 days

- All the membranes show preferential sorption butanol > ethanol > water,
- Graphene-based fillers improve in all cases the sorption towards alcohols
- Chemically reduced samples hinder the sorption of water
Pervaporation set-up

Liquid samples are analysed with a GC equipped with FID.
PV performance of MMMs

**Experiment conditions**

- Feed composition: ~5wt% EtOH/BtOH in H₂O
- Feed temperature: 65 °C
- Downstream pressure: 10 mbar
- Effective membrane area: 2.5 x 10⁻⁴ m²

**Flux, J**

\[ J = \frac{m}{A t} \]

- m: weight of the permeate (kg)
- A: effective area of the membrane (m²)
- t: permeate collection time (h)

**Separation factor, β**

\[ \beta = \frac{Y}{(1 - Y)} \frac{X}{(1 - X)} \]

- Y: mole fraction of the alcohol in the permeate
- X: mole fraction of the alcohol in the feed side

---

**Graphs**

- **GO-ODA**
  - Normalized flux (µm kg m⁻² h⁻¹)
  - Separation factor, β

- **rGO-ODA**
  - Normalized flux (µm kg m⁻² h⁻¹)
  - Separation factor, β

- **rGO-OA**
  - Normalized flux (µm kg m⁻² h⁻¹)
  - Separation factor, β
**PV performance of MMMs**

**Experiment conditions**
- Feed composition: ~5wt% EtOH/BtOH in H₂O
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- Downstream pressure: 10 mbar
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**Separation factor, β**

\[ \beta = \frac{Y/(1-Y)}{X/(1-X)} \]

Y: mole fraction of the alcohol in the permeate
X: mole fraction of the alcohol in the feed side

---

**Graphical representation**

- **Water flux**
  - **1/\(\beta_{\text{BtOH/H₂O}}\)**
  - **Water flux**

- **1/\(\beta_{\text{BtOH/H₂O}}\)** vs. **rGO-OA**

---

**PV performance of MMMs**

The University of Manchester
Comparison with reported values

- PDMS/CNT (10wt%) [5]
- PDMS [8]
- PDMS/60 wt% silicalite-1 [8]
- PDMS/PE [43]
- PEBA/25 wt% ZIF-71 [13]
- PEBA 2533 [10]
- PEBA/10 wt% CNT [44]
- PTFE [11]
- PIM-1 this work
- 0.1rGO-OA this work
- 0.1rGO-ODA this work

**Separation factor, \( \beta \)**

- \( \beta_{BtOH/H_2O} \)
- \( \beta_{EtOH/H_2O} \)

**Total flux (g m\(^{-2}\) h\(^{-1}\))**

**Normalized flux, \( \mu m \ Kg m^{-2} h^{-1} \)**

**Flux**

**PDMS/CNT (10wt%) [5]**
**PDMS [8]**
**PDMS/60 wt% silicalite-1 [8]**
**PDMS/PE [43]**
**PEBA/25 wt% ZIF-71 [13]**
**PEBA 2533 [10]**
**PEBA/10 wt% CNT [44]**
**PTFE [11]**
**PIM-1 this work**
**0.1rGO-OA this work**
**0.1rGO-ODA this work**

![Graph showing comparison with reported values](image-url)
Conclusions

i. Alkylamine-functionalized GO and rGO (GO-ODA, rGO-ODA, rGO-OA that could be dispersed in chloroform was prepared.

ii. Free-standing MMMs were prepared with PIM-1 and these graphene-like materials.

iii. The MMMs were tested for ethanol and butanol recovery from water via pervaporation.

iv. 0.1 wt% of filler showed the highest improvement in selectivity towards butanol.
Acknowledgments

Molecular separations
(School of Chem. Eng.)
&
Nano-functional materials
(School of Materials)

Prof Budd’s group
School of Chemistry

Dr Haigh and Dr Prestat
TEM experts