Tunable Graphene Oxide Membranes for Energy-Efficient Black Liquor Concentration

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**Background and Motivation**

- Kraft process widely used in paper making; black liquor (BL) is a byproduct
- Around 500 million tons/yr BL produced worldwide in kraft mills
- BL concentration by evaporators is highly energy intensive (~0.2 Quad/yr in the US alone)
- BL is at pH~13 and has ~15 wt% solids: lignin, organics, inorganic salts

By developing membrane-based processes, one can:

- Save up to 50% energy by avoiding phase change
- Separate lignin from the inorganics for use elsewhere
- Separate the organic chemicals (hydroxy acids) and valorize BL
- Separate the inorganic salts and recycle to kraft chemical loop
- Main challenge: developing membranes stable in BL and with high lignin and salts rejections

**Graphene Oxide (GO) Membranes**

**Scalable fabrication routes**

- 2-D GO sheets will self-assemble on the porous support membrane in a layer-by-layer manner
- Interlayer porous space between GO sheets acts as molecular sieve
- Tuning the interlayer space in the subnanometer range can allow a range of membranes to separate different BL components

**Tunable effective pore size**

- Example: Reduced GO produced by alkali treatment of GO
- XPS C1s of GO and rGO

**References**

- Mi, B., Science 2014, 343 (6172), 740.

**Nanofiltration (NF) Membranes:**

**GO-1, GO-2, GO-3**

- GO-1 membrane permeate flux and lignin rejection for BL at different concentrations and temperatures
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**Scale-up and long-term operation of GO-3 membranes**

- GO-3 membrane supported on a PES sheet (400 cm² area).
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- GO-3 sheet membranes deliver excellent performance and stability over more than 1,500 hours of continuous operation
- Lignin rejection > 99%

**Acknowledgements**

- Schematic and photographs of production and permeation testing of scaled-up GO-3 membranes on PES sheets.

- Photograph of crossflow membrane permeation test bed.
- Permeate flux behavior during long-term pressure cycling (from 10 bar to 50 bar TMP) of a scaled-up GO-3 membrane supported on a PES sheet (400 cm² area).
- Salt rejections of GO membrane coupons from a BL (15 wt% TS) feed: (a) Na\textsubscript{2}SO\textsubscript{4}, (b) Na\textsubscript{2}SO\textsubscript{3}, (c) Na\textsubscript{2}S, and (d) Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}
- Rejections of the GO-1, GO-2, and GO-3 coupon membranes: (a) Total solids (TS), (b) Lignin, (c) Total organic carbon (TOC), and (d) Total Inorganic salts
- Membrane Cost Delta NPU ($) $20/m² 36,332,543 $55/m² 36,256,805 $100/m² 36,130,574
- Technoeconomic analysis summary for a membrane system processing 500 gal/min BL feed

**Permeate flux behavior during long-term pressure cycling (from 10 bar to 50 bar TMP) of a scaled-up GO-3 membrane supported on a PES sheet (400 cm² area).**

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