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QUILL

Hydrophobic low melting mixtures for biogas upgrading

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Confidential 25/03/24

What is biogas?

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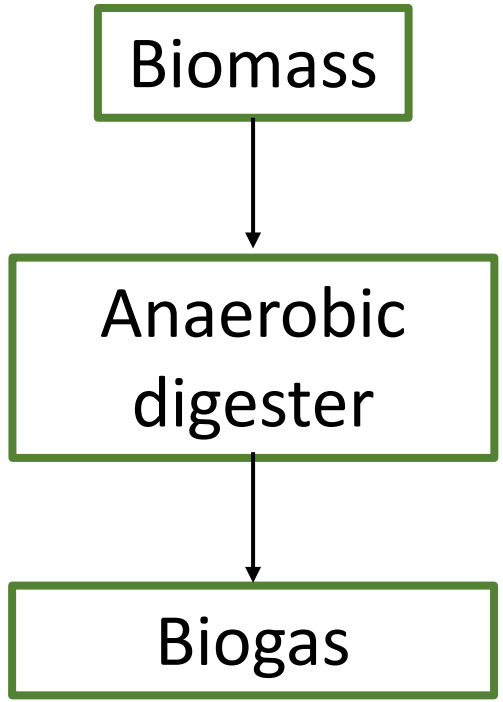
- Product of anaerobic digestion
- Carbon neutral energy source
- Under-utilised energy source
- No large industrial shift



Int. J. Green Energy, 2019, **16**, 401–412.

The problem

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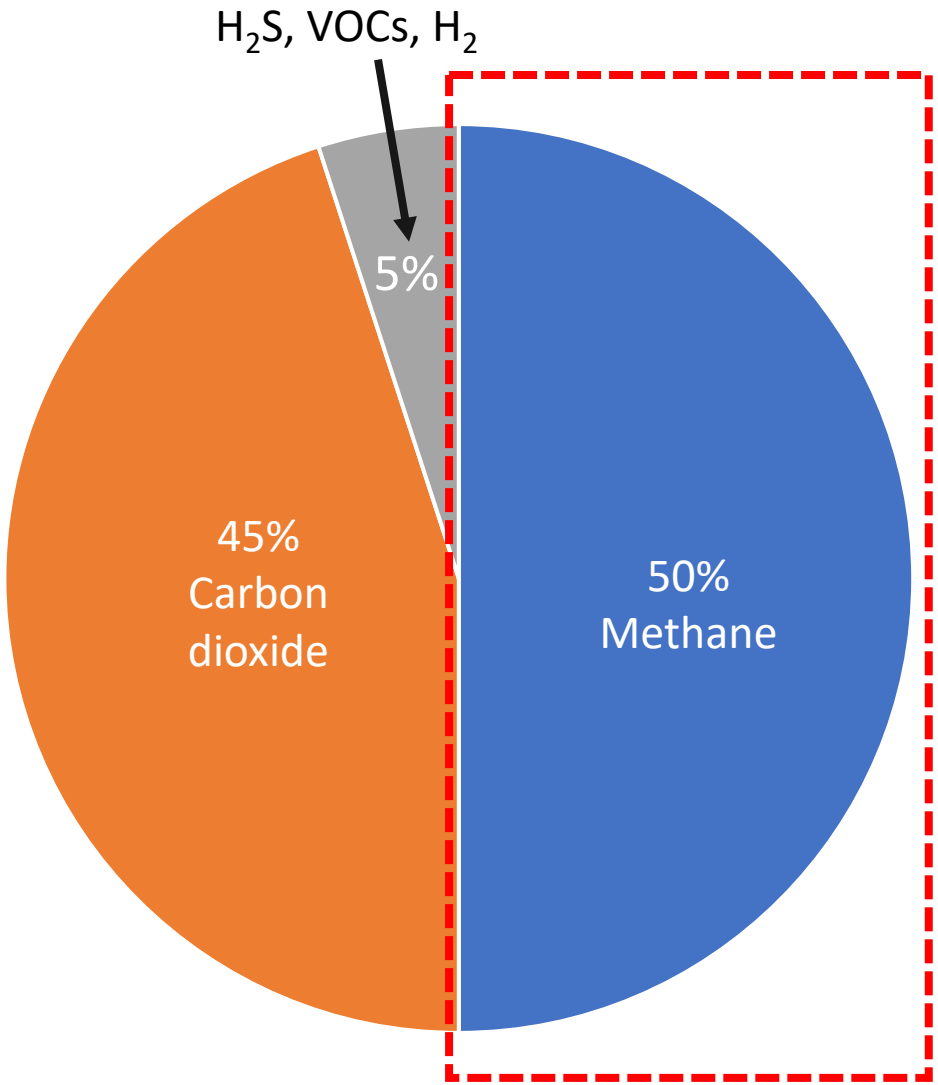
Methane needs to be separated from the contaminants

Around 50% of the gas volume is contaminants

Removal is currently costly and hazardous



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Current industrial technologies

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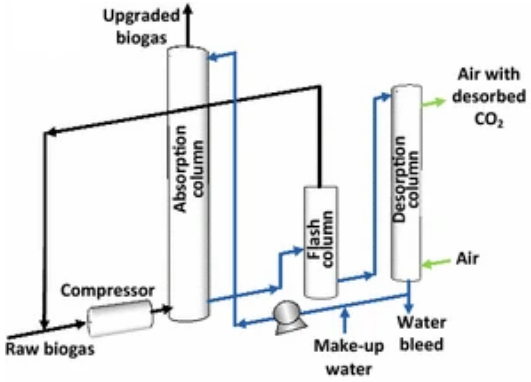
Liquid scrubbing – Chemical sorbents (alkanol amines)
– Physical scrubbing (Water, Selexol process)

PSA and TSA using porous solids – Zeolites, MOFs, COFs, PCPs

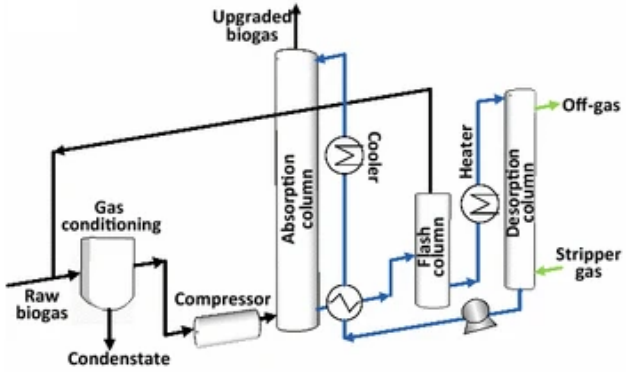
Membranes

Cryogenic methods

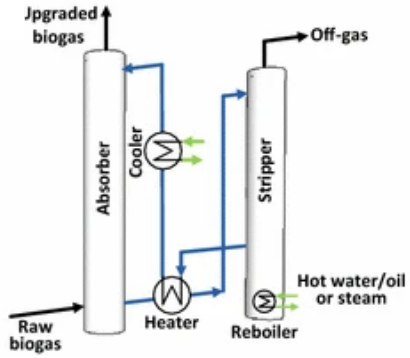
Biological methods – Algal, bacterial conversion of CO_2



Water scrubbing



Organic scrubbing



Chemical scrubbing

Bioresour. Technol., 2019, **279**, 43–49.
Chem. Soc. Rev., 2013, **42**, 9304–9332.
Angew. Chemie Int. Ed., 2017, **56**, 14246–14251.
Y. Xie, C. Ma, X. Lu and X. Ji, *Appl. Energy*, 2016, **175**, 69–81.
Rev. Environ. Sci. Bio., 2015, **14**, 727–759

What limits industrial application?

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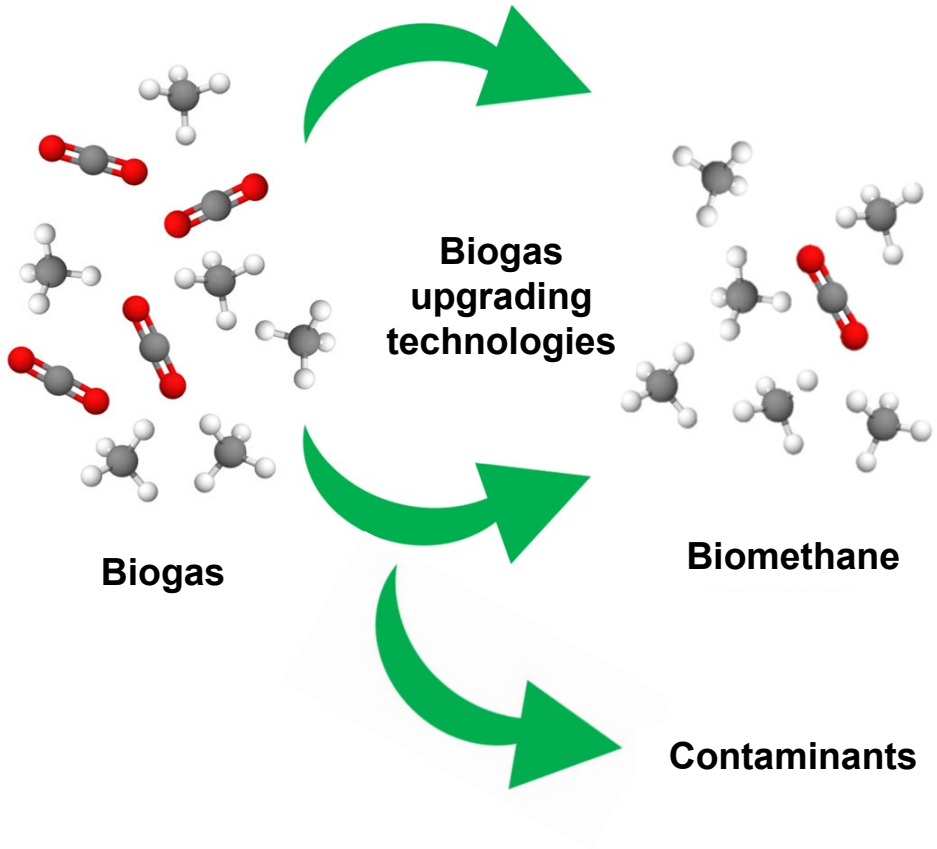
Costs:

Performance

Materials

Operational

Hazards



Why do I have a PhD project if we have all these options?

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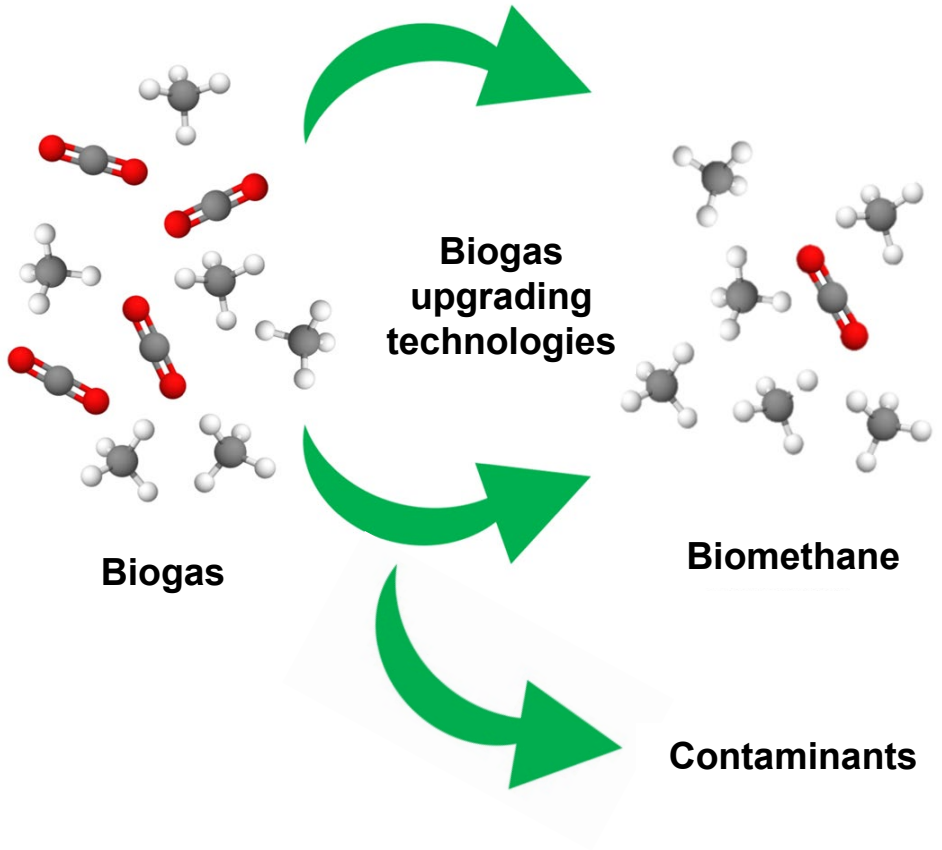
Upgrading processes are industrially mature

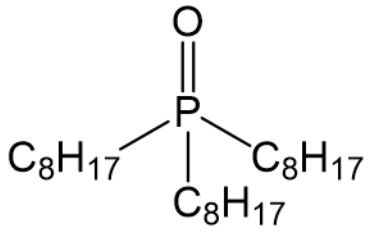
New materials are necessary for improved performance and sustainability

Project goal – create high performance physisorbant materials at low cost with a low environmental footprint

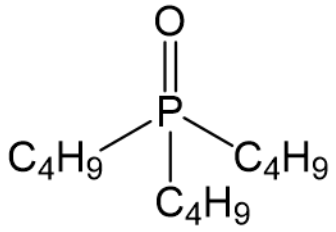


Phosphine oxide based low melting mixtures (LMMs)

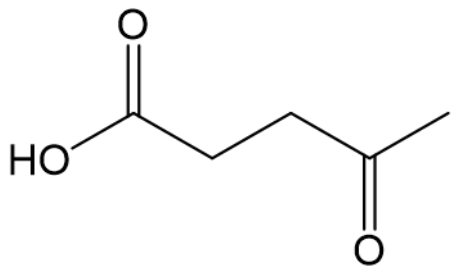
- TOPO is an industrial extractant for various process
  - TOPO based DES previously reported
  - Never been applied to gas separation
- Low vapour pressure and low viscosity materials
- Possibility to have strong interactions with CO_2 without chemisorption



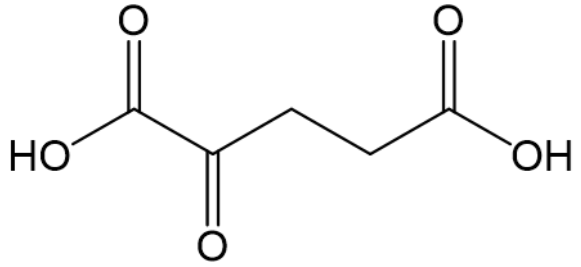
Trioctyl phosphine oxide (TOPO)



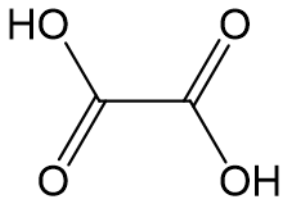
Tributyl phosphine oxide (TBPO)



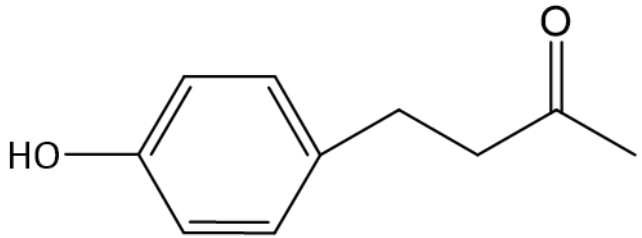
Levulinic acid (Lev)



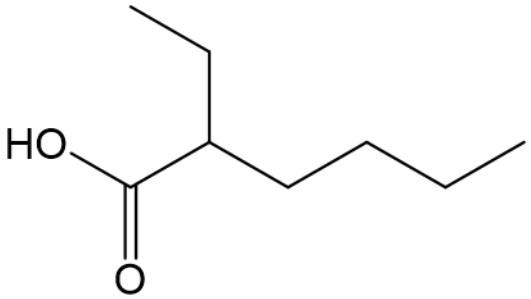
α-ketoglutaric acid (α-keto)



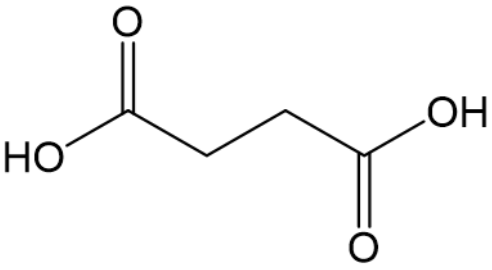
Oxalic acid (Ox)



Raspberry ketone (Rasp)



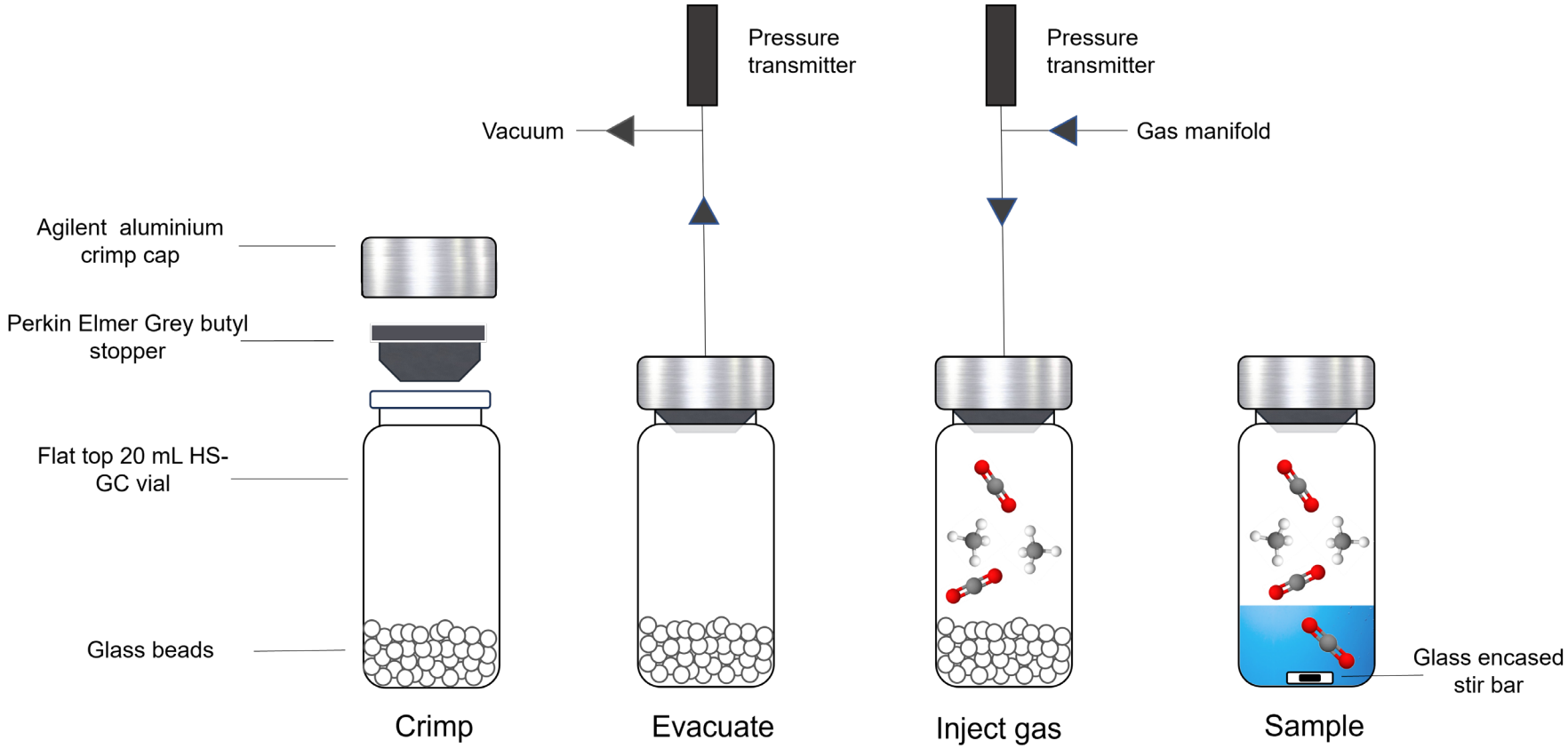
2-ethyl hexanoic acid (EHA)



Succinic acid (Succ)

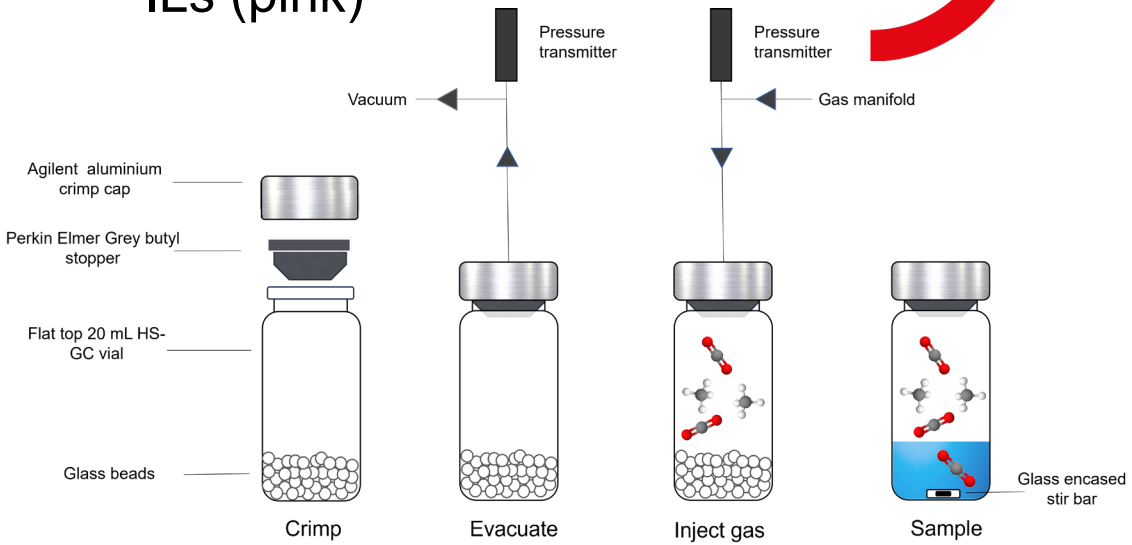
Headspace GC screening method

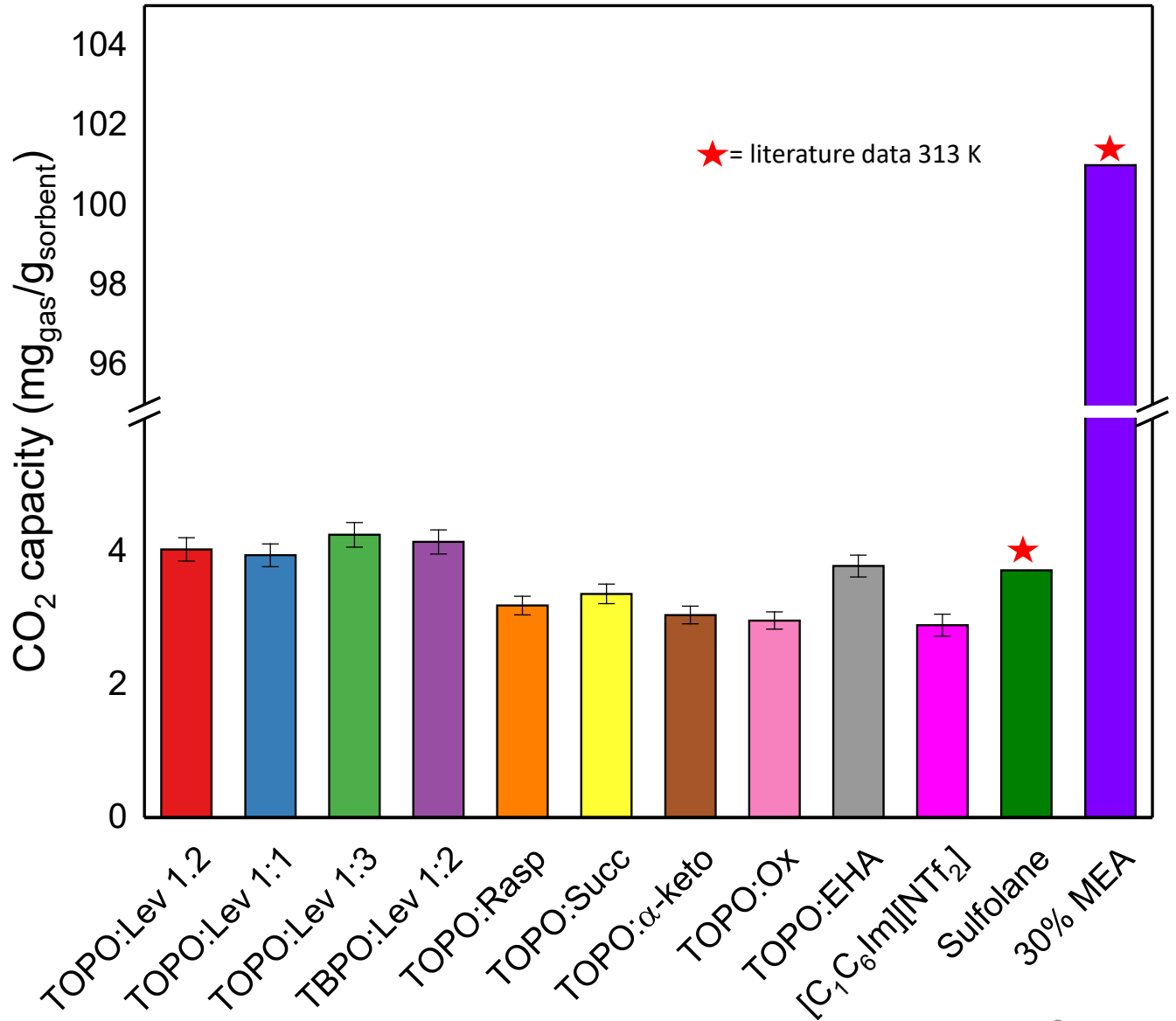
- Bulk screening of wide range of materials
- Reactors for less than a pound



Screened CO_2 capacities

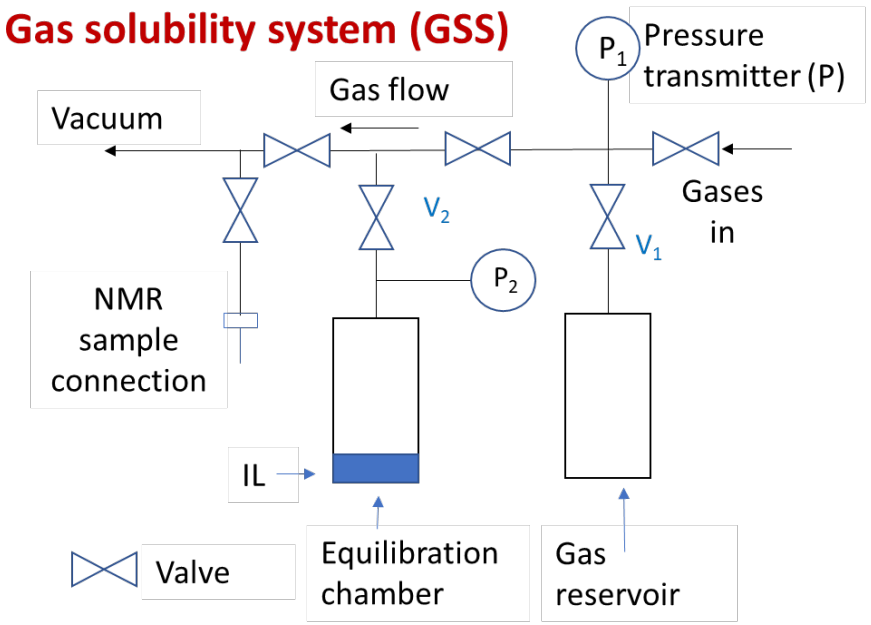
- Capacities for CO_2 calculated at 1 bar and 35°C
- All phosphine oxide based LMMs have high capacities for CO_2
- Many phosphine oxide based LMMs have higher capacities than one of the best physisorbent ILs (pink)

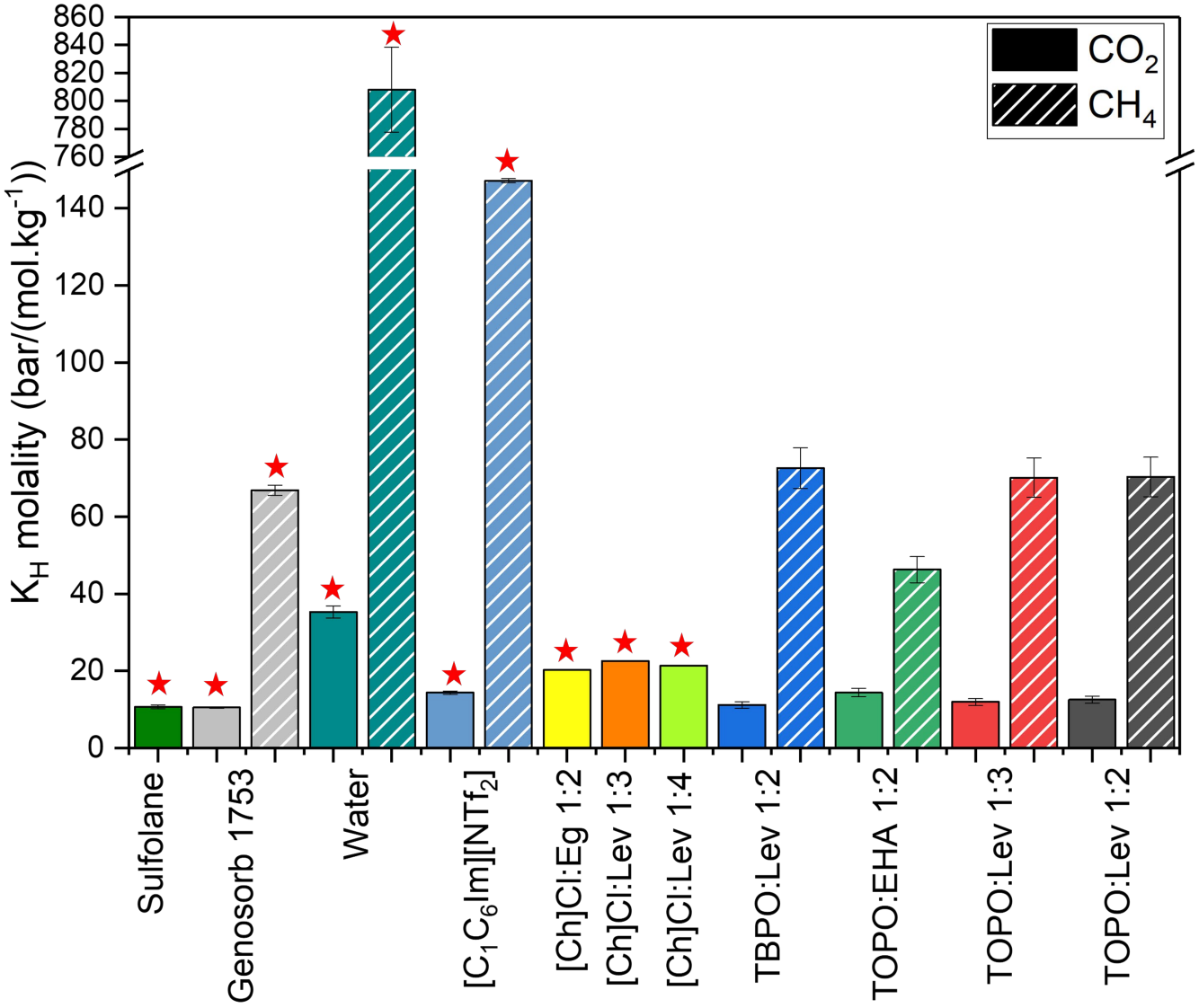




Accurate gas measurements

- Good agreement with previous screening method (both trends and values)
- Comparable capacities to genosorb 1753
- Higher capacity than IL, DES and water

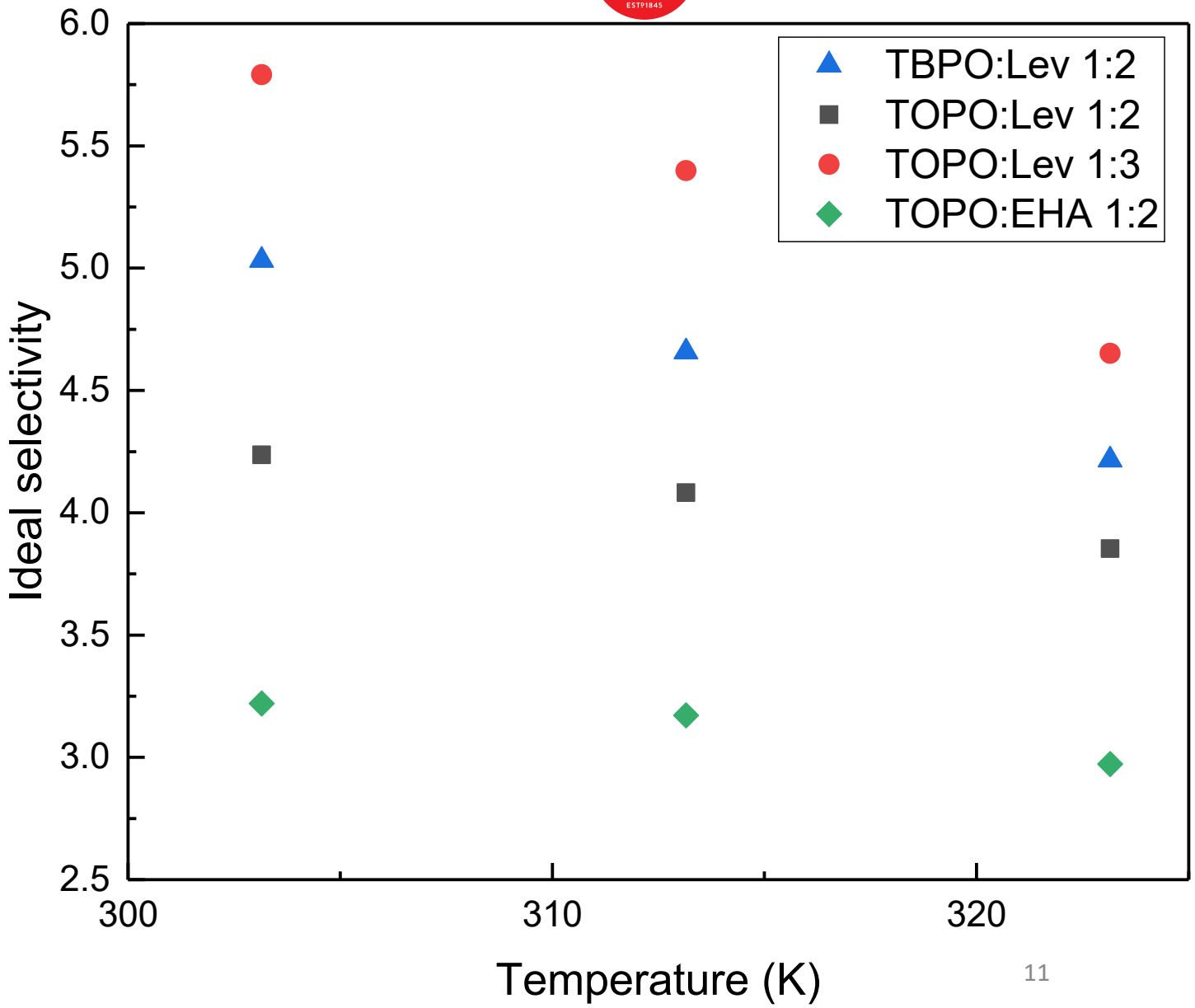




Ideal selectivity

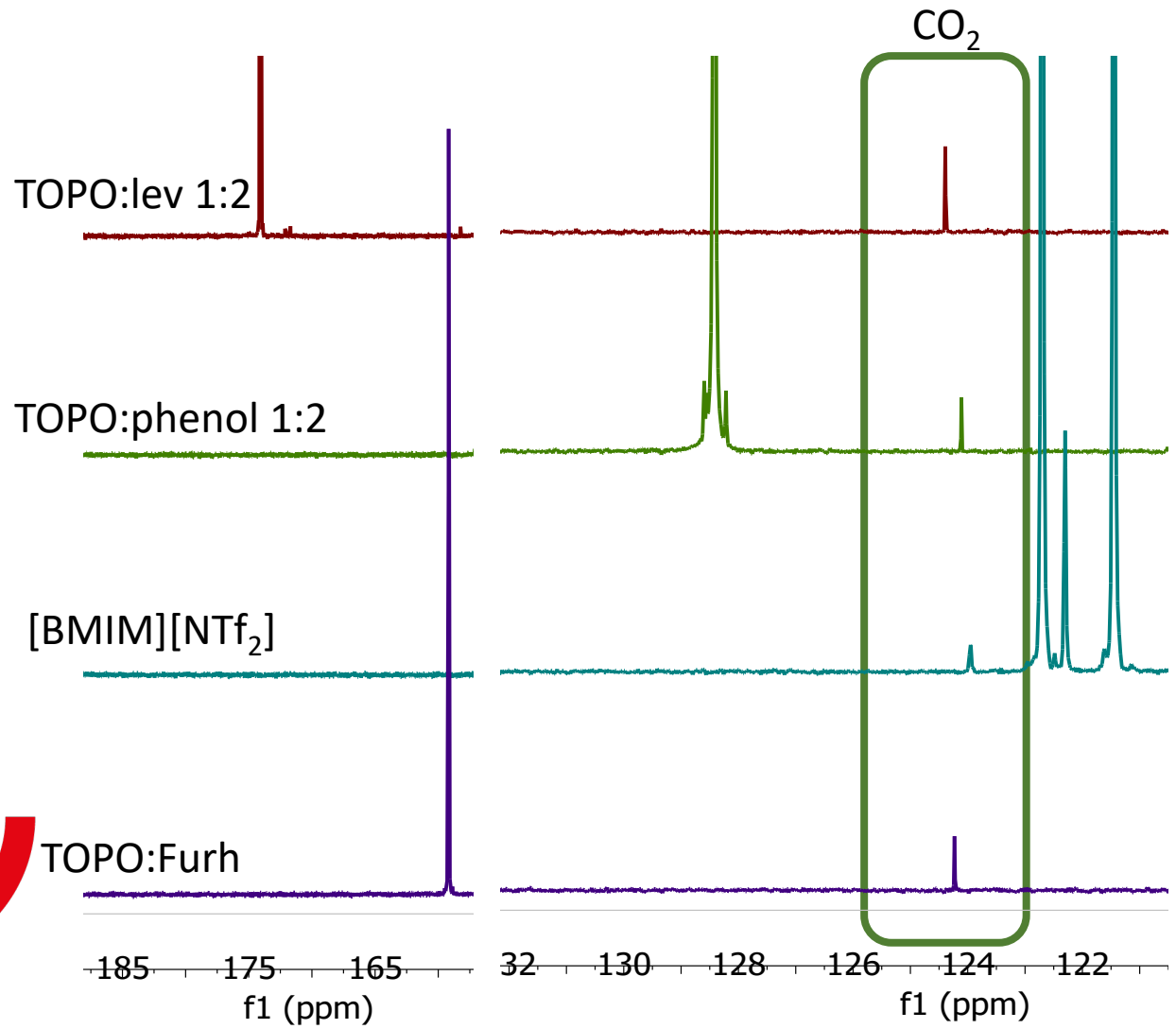
- Ideal selectivities were based on a ratio of K_H (molality)
- Higher selectivities are observed at lower temperatures
- Information could be utilised for regeneration

$$\text{Ideal selectivity} = \frac{\text{Kh}_{\text{CO2}}}{\text{Kh}_{\text{CH4}}}$$



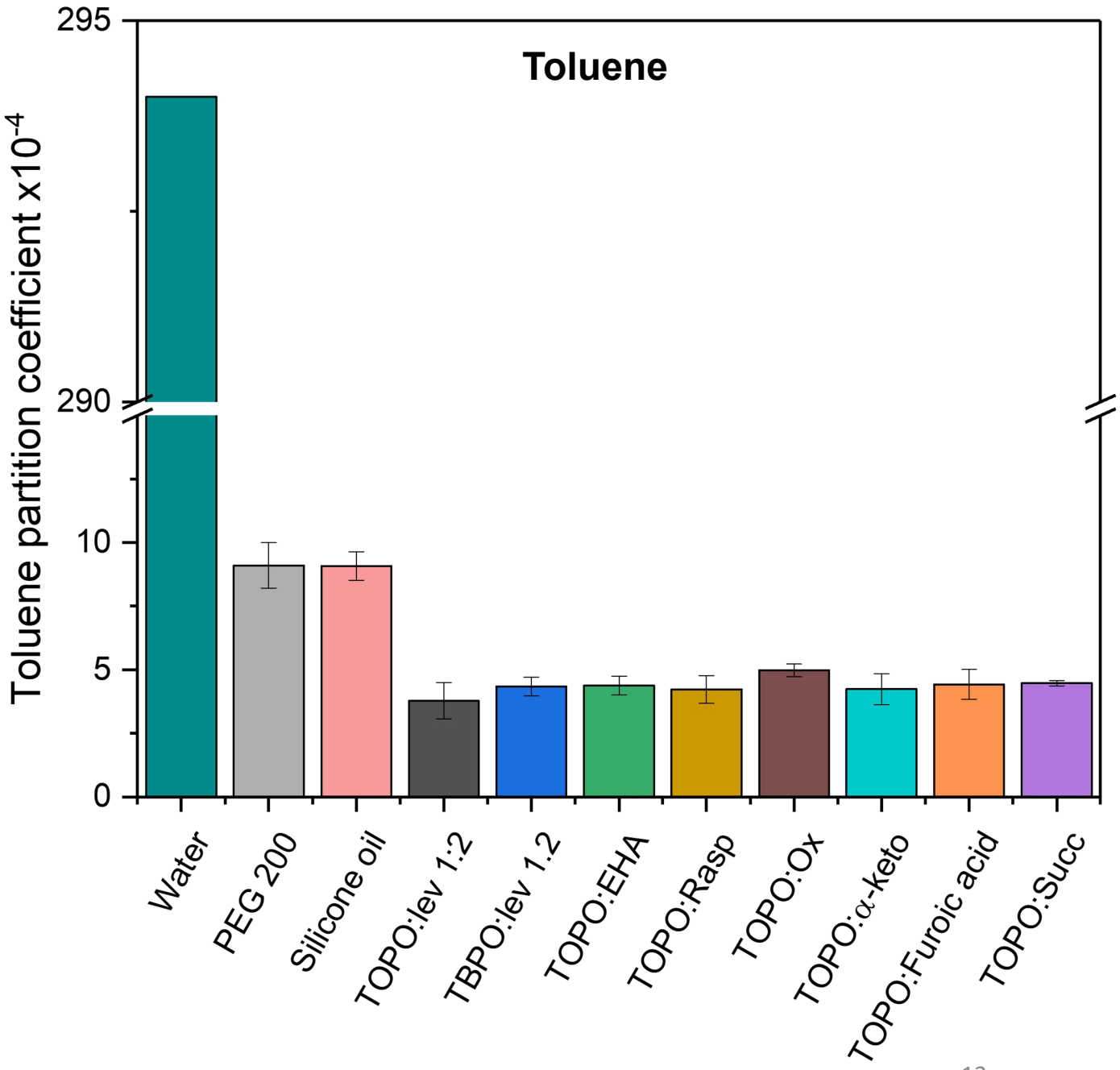
Gas sorption mechanism

- Results achieved by bubbling CO_2 through liquids in an NMR tube
- ^{13}C NMR peak at ~124 ppm represents physiosorbed CO_2
- No sign of carbonate, carbamate or carboxylate peak appearing in ^{13}C NMR 160-185 ppm
- Indicates possible low energy of regeneration for these materials



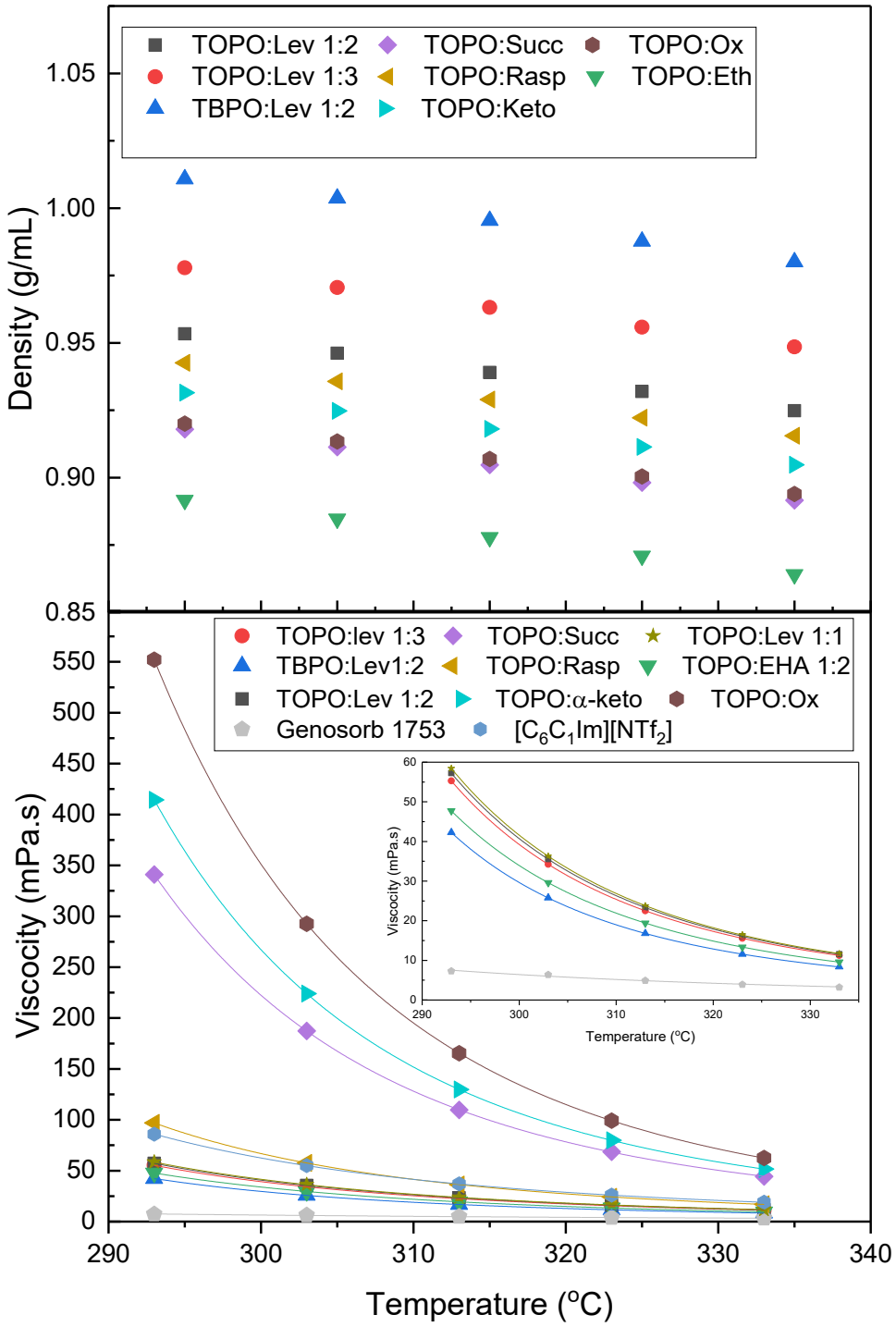
VOC removal

- Volatile organics are an important type of contaminant found in biogas
- Lower partition coefficients indicate better VOC absorption by a liquid
- Toluene used as a standard
- Several other VOC classes were tested showing similar trends

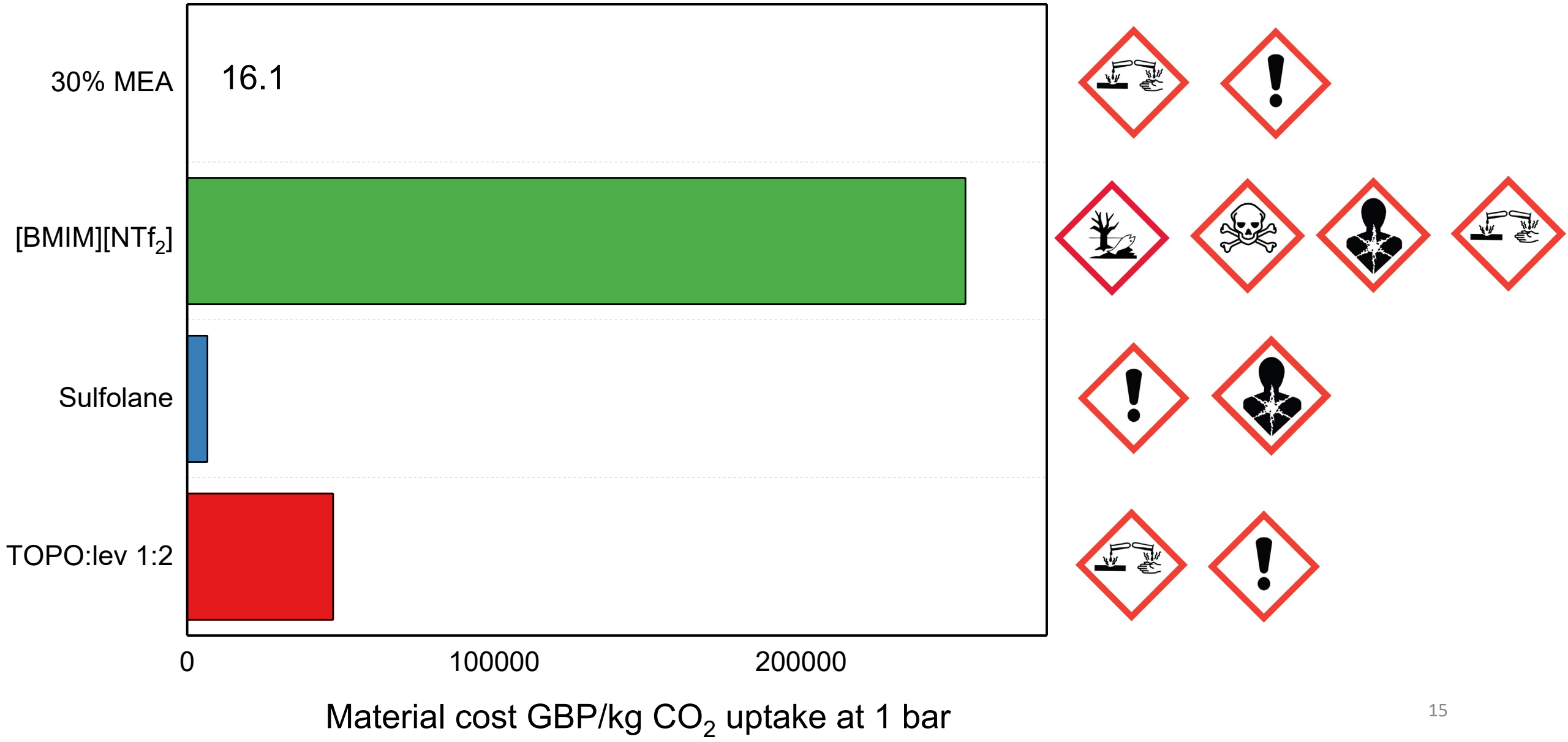


Physico-chemical properties

- While capacity and selectivity are important there are other factors
- PO based LMMs have variable viscosity dependant on HBD
- PO based materials also have low densities when compared with many other liquids



Cost and hazards of liquid sorbents



Future work

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Publish findings

Write thesis

Finish PhD

Acknowledgements

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