Chemical Characterization and Thermodynamic Modeling of PET Recycling Streams

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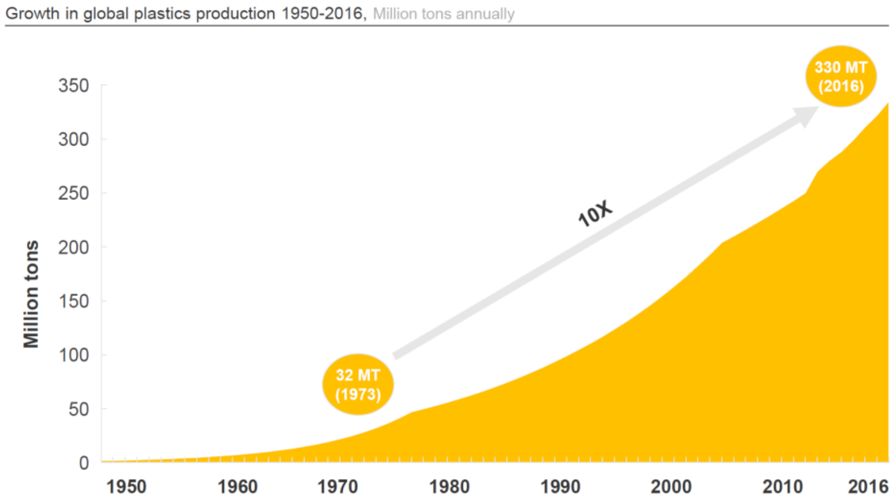
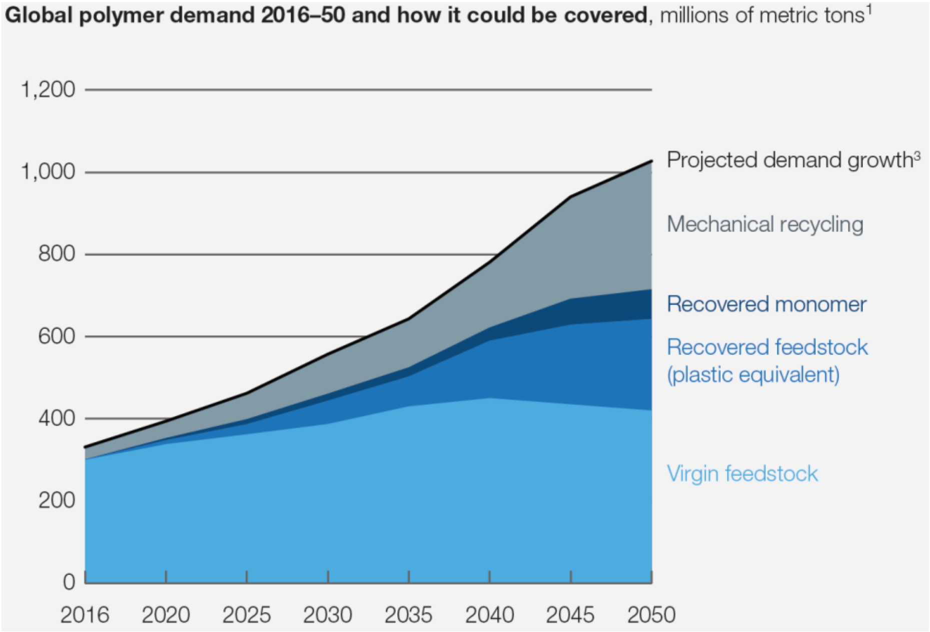
Today plastics issues:

- Human being throw away more than half their own weight in plastic every year – more than 330 million tons of it.

- The figure will probably reach 500 million tons by 2030.



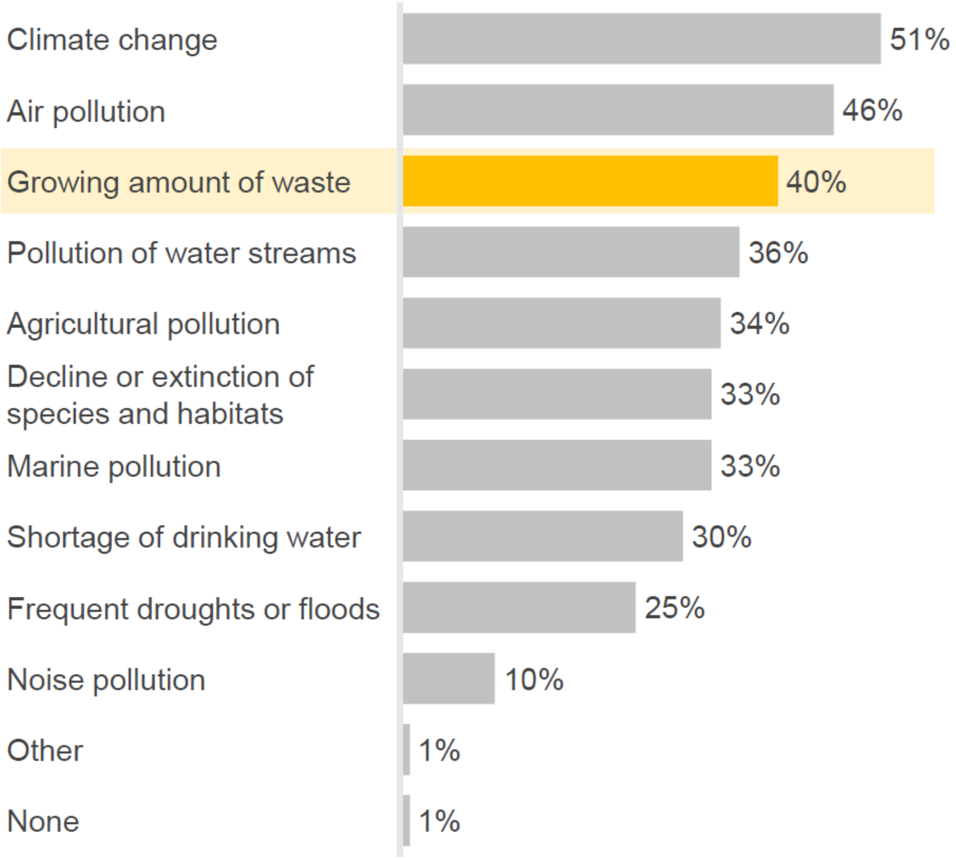
Ellen MacArthur Foundation and McKinsey & Company "New Plastics Economy" (2016); Plastics Europe "Plastics -The Facts 2013" (2013); Plastics Europe "Plastics -The Facts 2015" (2015); McKinsey plastic waste stream model



Thomas Hundertmark, Mirjam Mayer, Chris McNally, Theo Jan Simons, and Christof Witte, 2018, How plastics-waste recycling could transform the chemical industry, McKinsey on chemicals, McKinsey&Companey

Today plastics issues:

Most important environmental issues among Europeans
Share of respondents who chose the option (max 4 answers)



Addressing plastics waste is also high on the Danish agenda

99% find it important or very important to **do something about the amount of plastics in nature**

85% worry about the amount of **waste in the ocean**

52% think supermarkets should **focus on environmentally friendly plastic/packaging**

Eurobarometer poll, European Commission Special Eurobarometer 468 "Attitudes of European citizens towards the environment“ (2017); COOP “Forbrugerne til supermarkederne: Plastik og madspild er vigtigst” (2018); Ministry of Environment and Food of Denmark ”Danskerne går sammen om at rydde op på stranden” (2018); Plastic Change “Danskerne vil bekæmpe plastikspild i naturen” (Accessed 2018)

Today plastics issues:

- The arctic ocean became a sink for micro-plastics.
- About 8 million tons of plastics leak into the ocean annually
- Every year, Denmark collects 1,000 tons of waste on its western coastline

KIMO Denmark, Danish EPA press release, March 2018

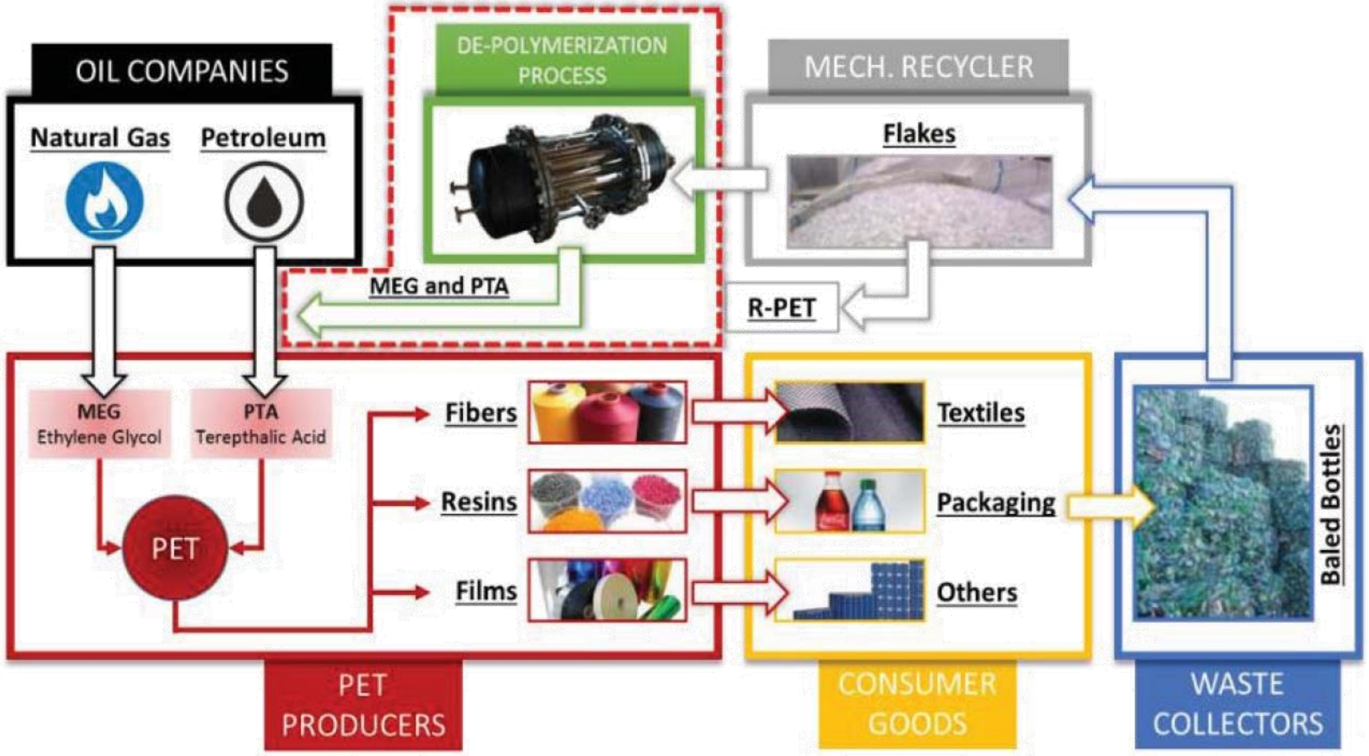
Cozar et al. “The Arctic Ocean as a dead end for floating plastics in the North Atlantic branch of the Thermohaline Circulation” in Science Advances vol. 3, no. 4 (2017); Nordic Council of Ministers “Marine Litter in Nordic Waters” (2015)

The DEMETO Project

- **Funding:** *European Union's Horizon 2020 research and innovation program*
- **Vision:** Eliminate the issue of PET waste on a global basis
- **Mission:** Profitable PET recycling and closing the life cycle of plastic

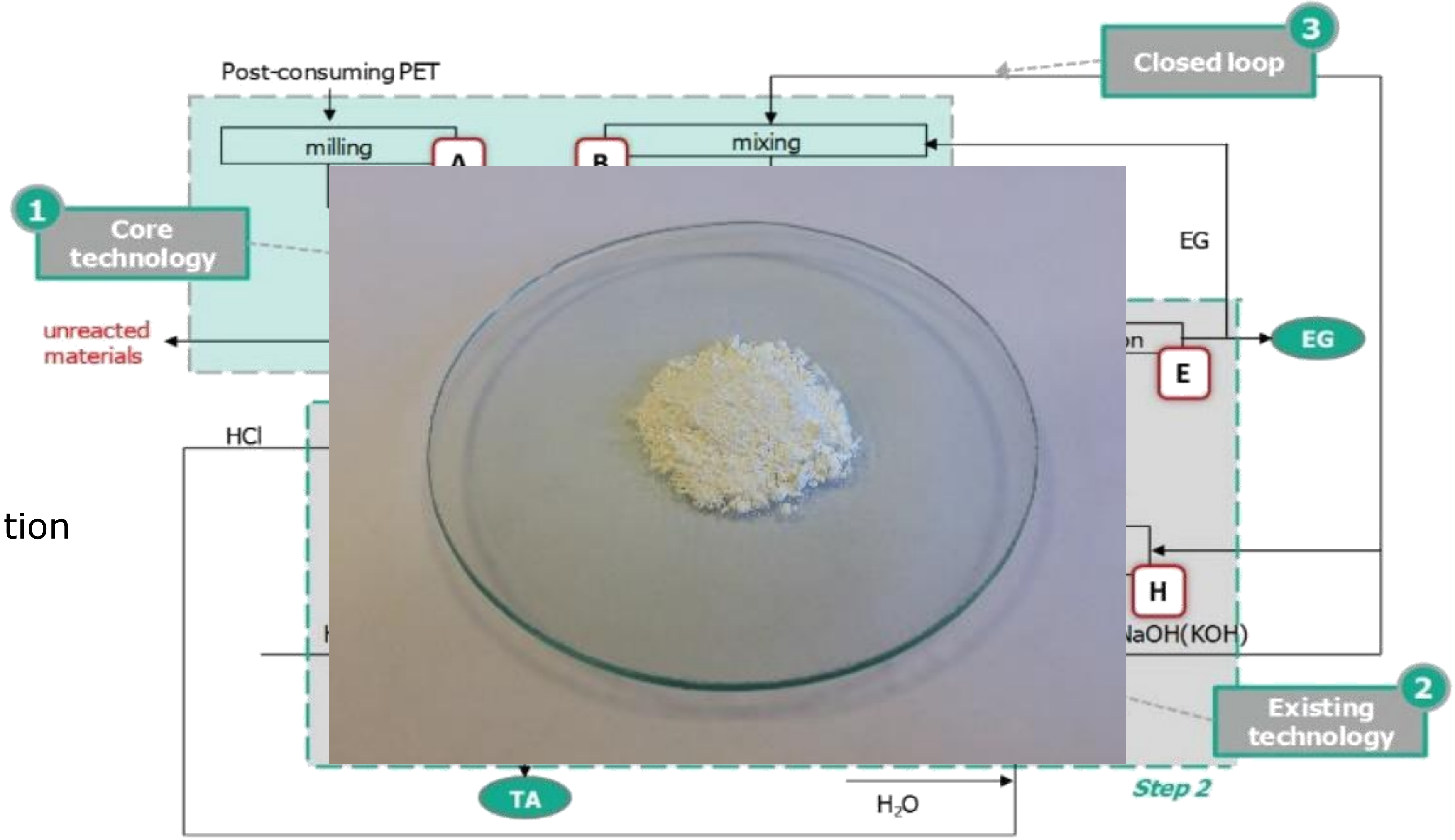
The DEMETO technology

- Hydrolysis for **PET** plastics
- Microwave reactor
- De-polymerize PET to:
  - Terephthalic Acid (H_2TP)
  - Ethylene Glycol (MEG)
- Resource recycling



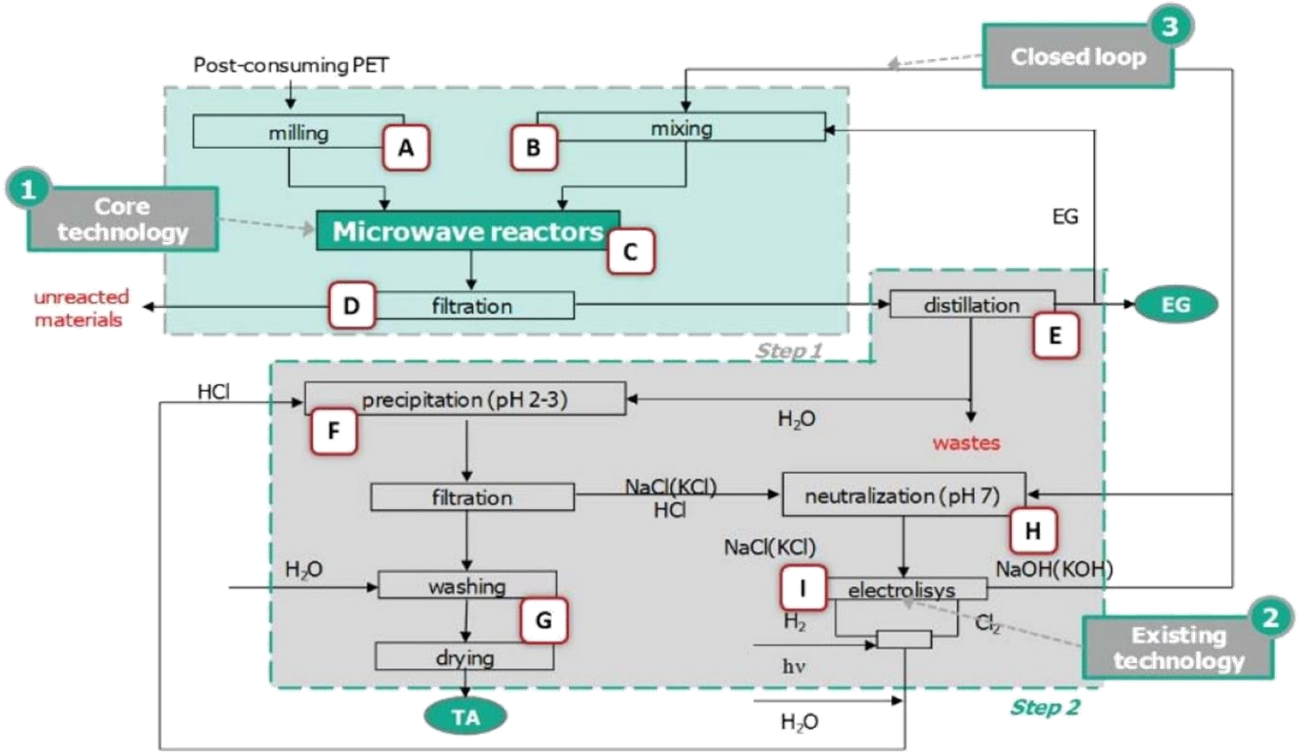
The DEMETO Project process

- Two main functional units:
  - Core: De-polymerization
  - Closed chemical process
- DTU contribution
  - Thermodynamics
  - Process development
    - Experimental evaluation
    - Modelling
    - Design
    - Simulation
    - Optimization

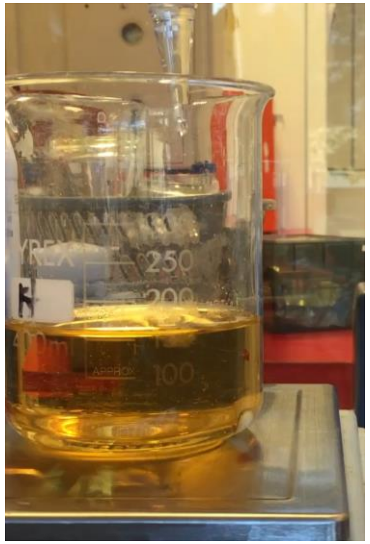


Experimental work

Experimental evaluation of downstream process

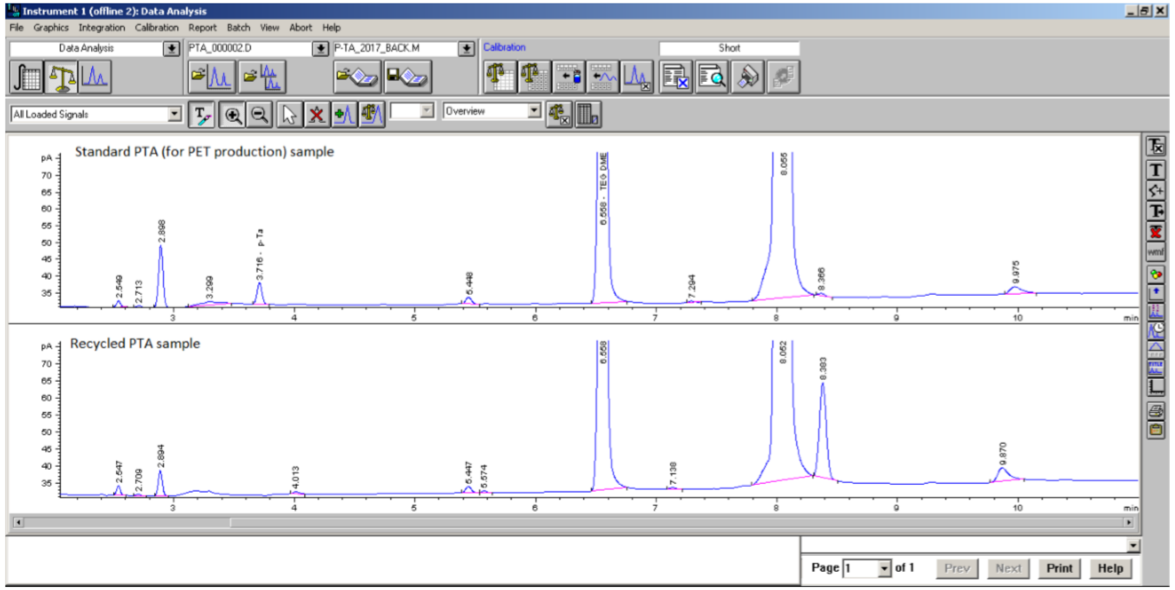


- Filtration
- Distillation
- Dissolution
- Decolorization with Activated Carbon
- Acidification
- Recovery of pure H2TP and MEG



Characterization of streams

- **Composition** of MW reactor's effluent
- **Density** & **Viscosity** of process streams at different T
- **Particle size distribution** of Na2TP
- **Solubility** of Na2TP in H2O
- **Quality** of produced H2TP & MEG
  - ✓ In-spec products, **virgin grade** quality
- **TOC** & identification of **impurities** in brine stream
  - ✓ Brine to be treated in chloroalkali unit, for recovery of NaOH and NaCl **– closed process loop**
- **Purification** of brine stream to meet specifications of the chloroalkali unit



No.	Parameter	Standard method	Specification	Result
1.	Acid number, mg KOH\g	WN-B010-1046D	≤ 0.03	≤ 0.03
2.	Chlorides, ppm	WN-B010-1011D	≤ 2	< 2
3.	Sulfates, ppm	WN-B010-1017D	≤ 20	< 20
4	Moisture, wt. %	WN-B010-1065D	≤ 0.1	**0.26***
5.	UV transmittance at 220 nm, %	ASTM E-2193	≥ 70	**33***
	250 nm, %		≥ 90	**61***
	275 nm, %		≥ 95	**83***
6.	Diethylene glycol, wt. %	WN-B010-1020D	≤ 0.05	≤ 0.05
7.	Acetaldehyde, ppm	WN-B010-1089D	≤ 10	≤ 10
8.	Colour, APHA	WN-B010-1052D	≤ 5	≤ 5
9.	APHA color after 4 hours boiling		≤ 20	≤ 20

* - quality parameter is out of the specification range

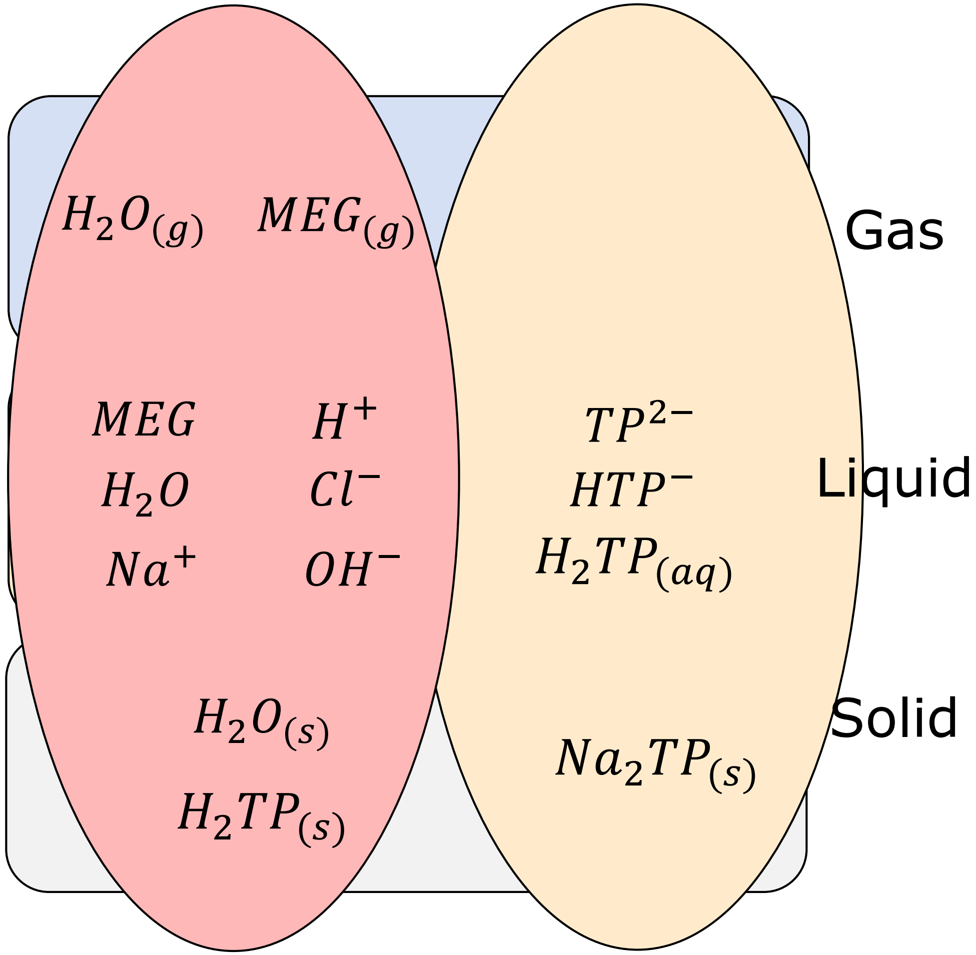
Lab scale experimental work resulted in:

- Experimental evaluation of downstream process
- Measurements of the properties of the different streams
- Identification of impurities and purification of brine
- Production of virgin-grade monomers (ethylene glycol and terephthalic acid)

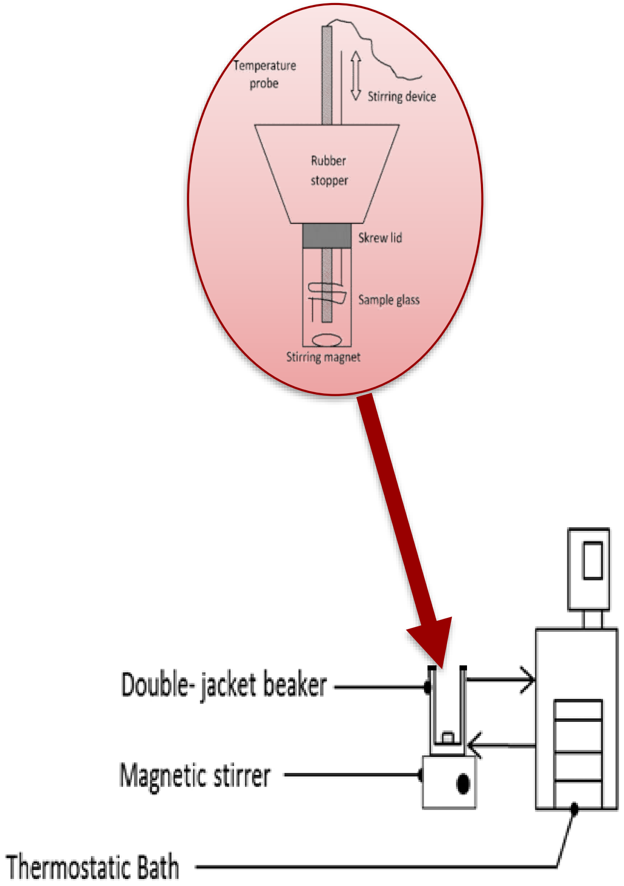
Chemical system:

$$H_2O + H_2TP + Na_2TP + MEG + NaCl + NaOH$$

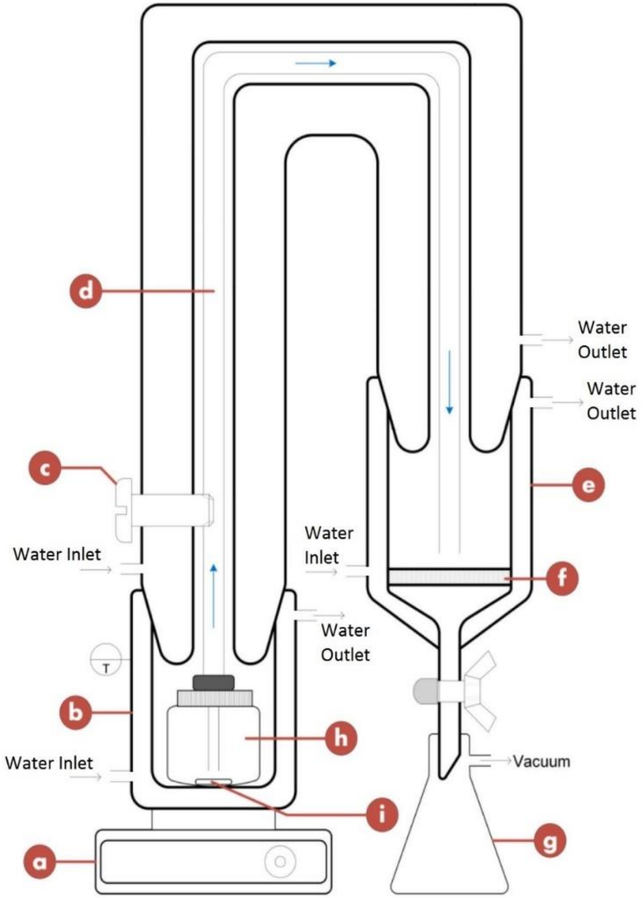
Outlet of the reactor



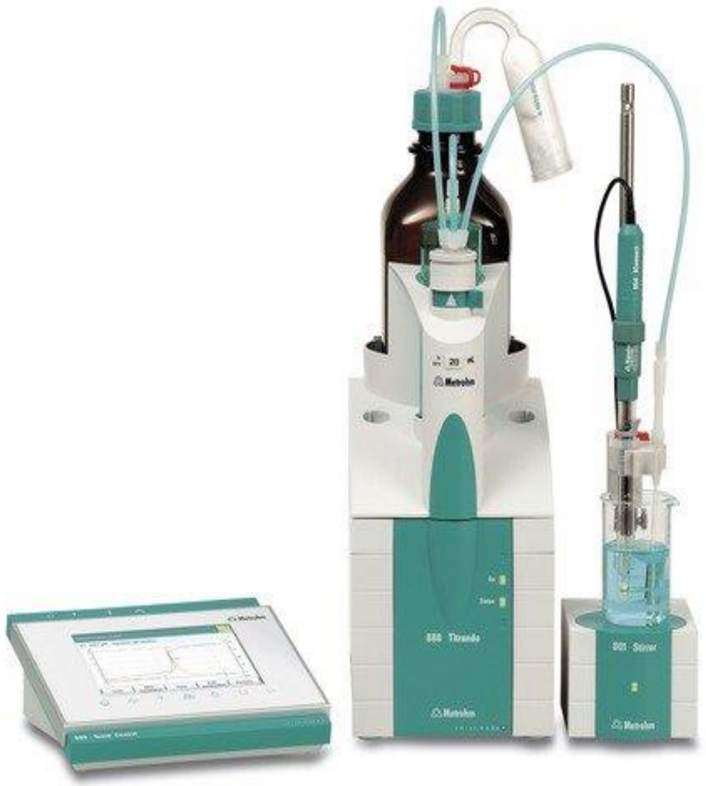
Solid Liquid Equilibrium (SLE) experiments:



Freezing Point Depression experiments

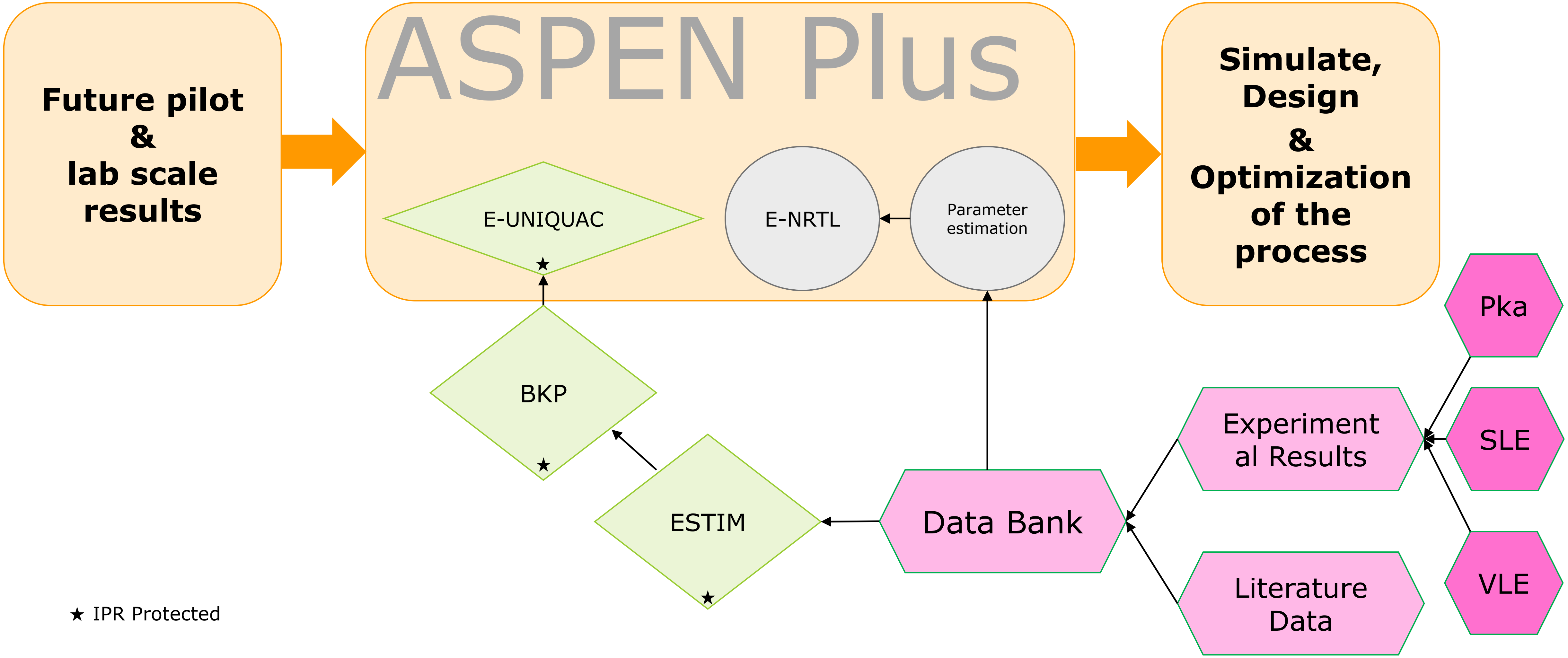


Gravimetry experiments



Titration experiments

Modelling:



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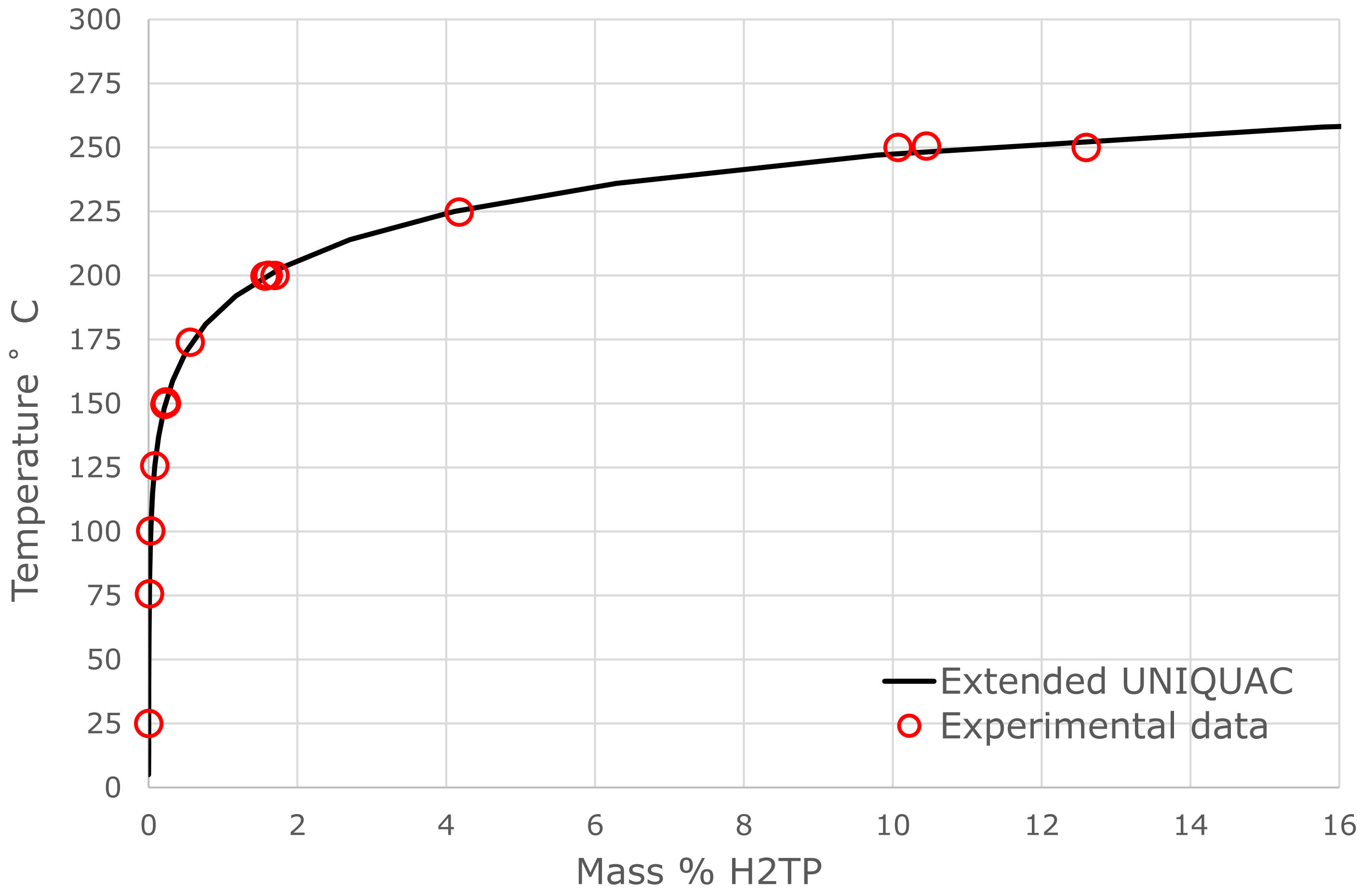
Modelling Results

- Phase diagrams

$$H_2TP + H_2O$$

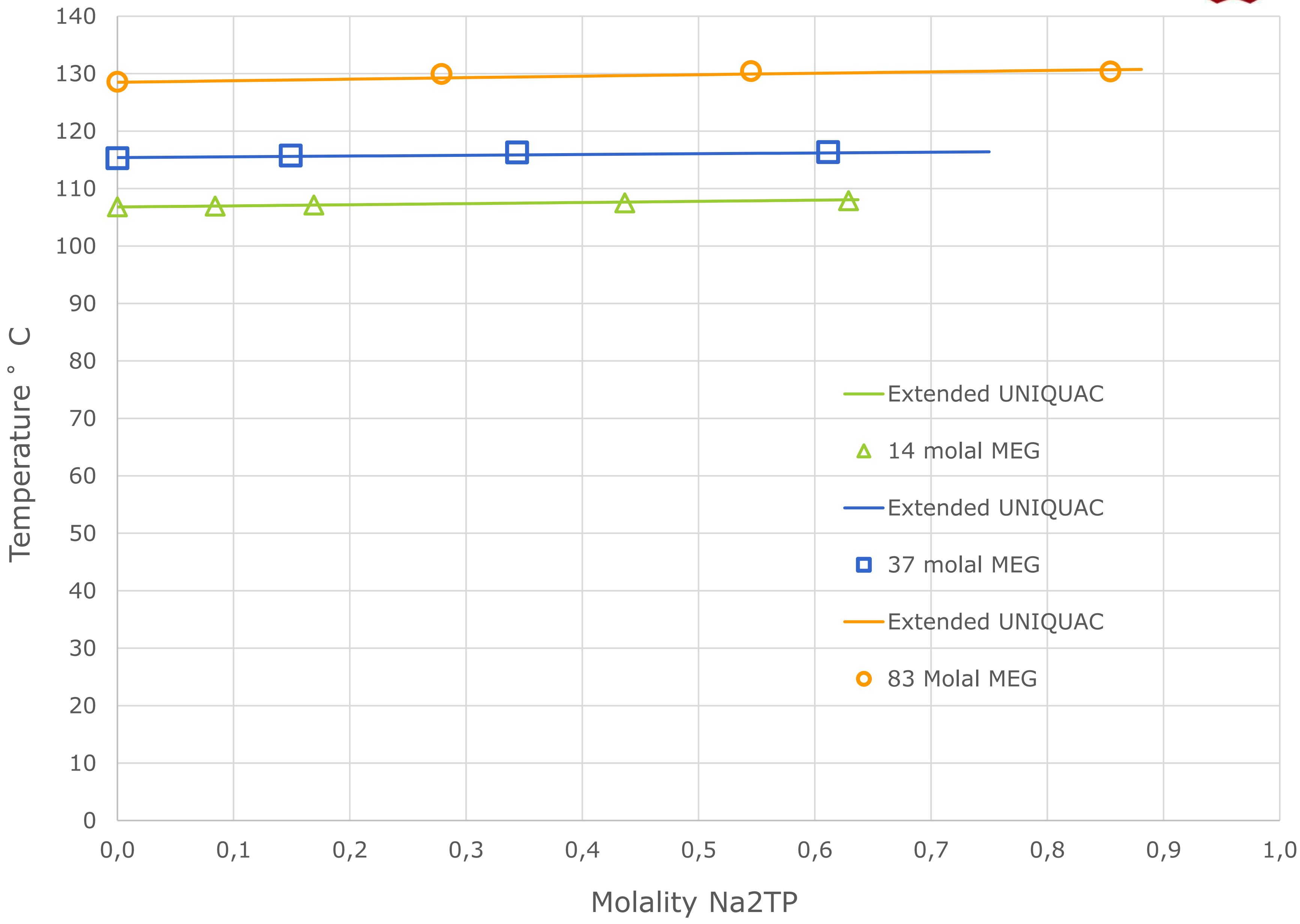


References:
- Takebayashi et al. 2012
- Sheehan et al. 2012

Modelling Results

- Vapor Liquid Phase diagram
  Boiling points

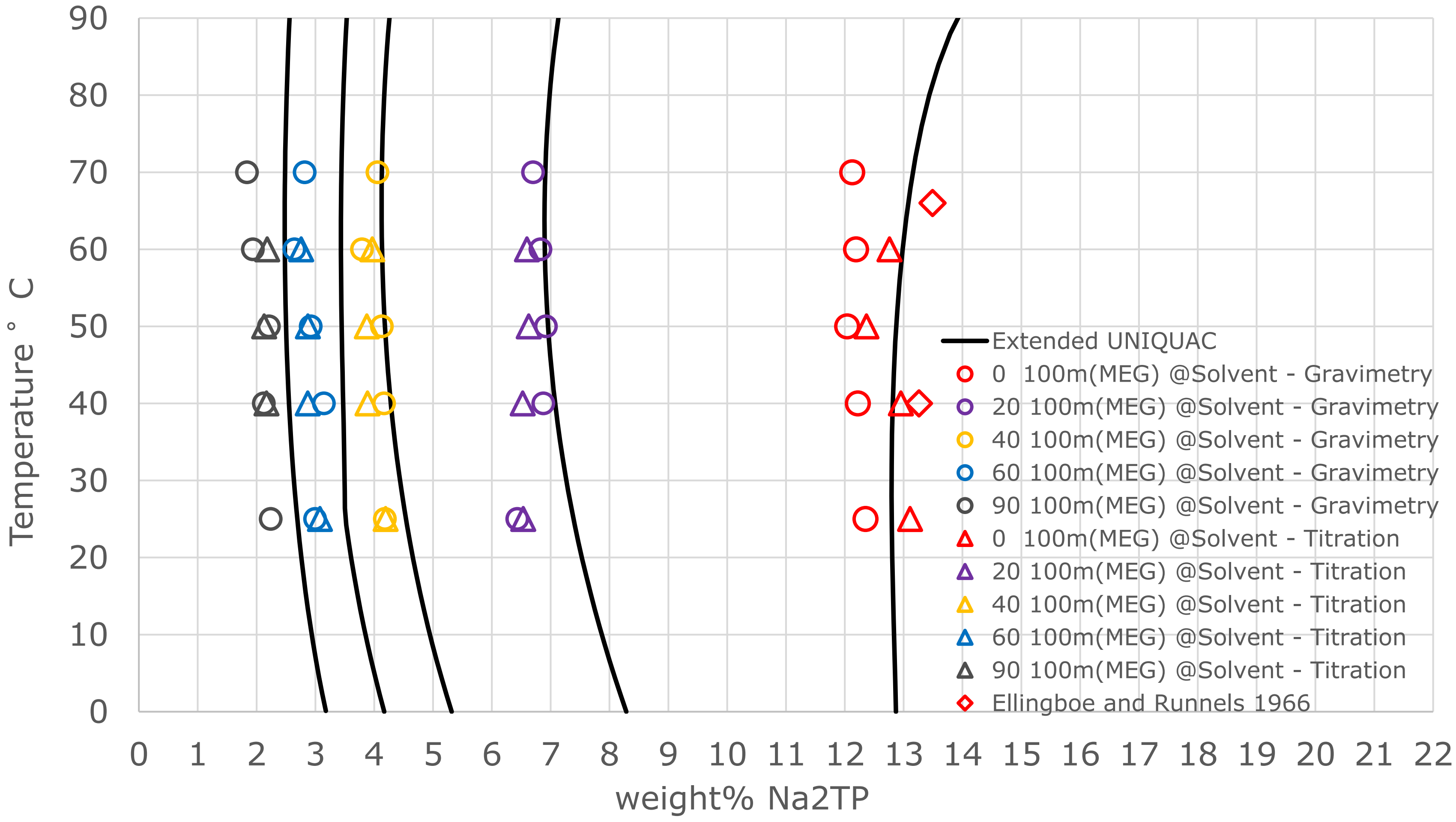
$$Na_2TP + H_2O + NaOH + MEG$$



Modelling Results

- Solid Liquid Phase diagram
  solubility points

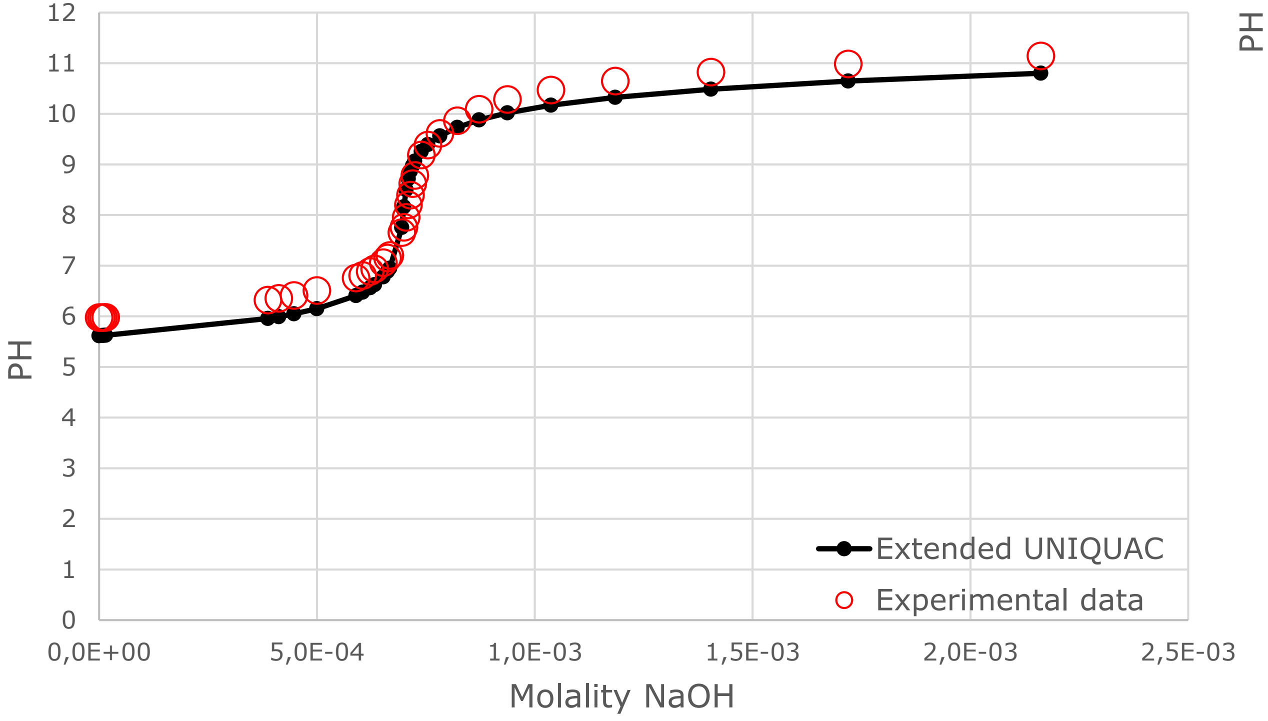
$$Na_2TP + H_2O + NaOH + MEG$$

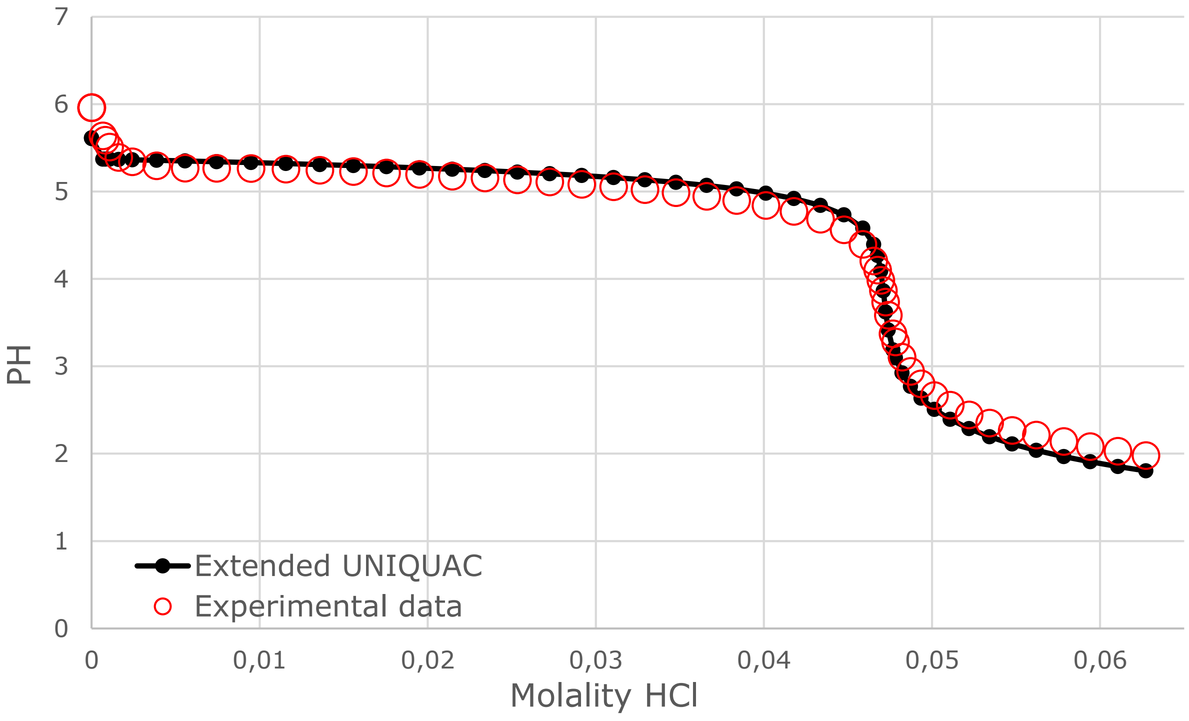


Modelling Results

- Titration curves

$Na_2TP + H_2O + NaOH$





$Na_2TP + H_2O + HCL$

Conclusion

- Downstream processing of depolymerized PET stream was successfully tested in lab scale to produce pure ethylene glycol and terephthalic acid.
- Thermodynamic properties of complex downstream mixtures have been defined and successfully modeled.
- The modeling is almost ready to design and simulate a closed downstream process for chemical recycling of Poly Ethylene Terephthalate (PET) by ASPEN Plus.

Thank you for your attention!