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Waste plastic valorisation using acidic ionic liquids

Emma McCrea

Supervisors: Prof. Gosia Swadźba-Kwaśny
Prof. John Holbrey

QUILL meeting, 25-26th March 2024 – Confidential

Project overview

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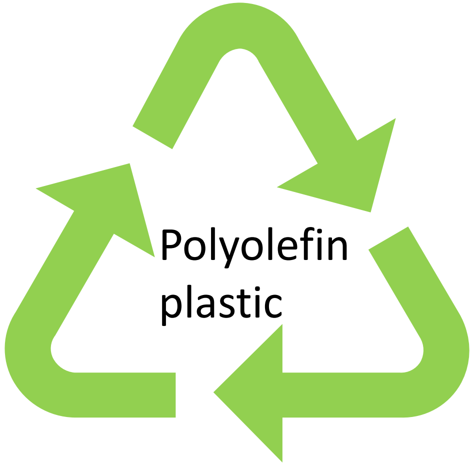
Low value plastic waste

Chemical recycling



Value added product

Motivation for this project

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- Industry standard to produce base oil from 1-decene and uses BF_3 as a catalyst which poses a significant safety risk

- Previous publications successfully used liquid coordination complexes and borenium ionic liquids with physical properties comparable with commercial grade base oil

- This work aims to replace 1-decene with waste polyolefin plastic

- \$576 million in 2020 to \$798 million by 2025[1]

Green Chemistry

PAPER

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Cite this: *Green Chem.*, 2015, **17**, 1831

Liquid coordination complexes: a new class of Lewis acids as safer alternatives to BF_3 in synthesis of polyalphaolefins

James M. Hogg, Fergal Coleman, Albert Ferrer-Ugalde, Martin P. Atkins and Małgorzata Swadźba-Kwaśny*

ACS Sustainable Chemistry & Engineering

Research Article

Cite This: *ACS Sustainable Chem. Eng.* 2019, 7, 15044−15052

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Borenium Ionic Liquids as Alternative to BF_3 in Polyalphaolefins (PAOs) Synthesis

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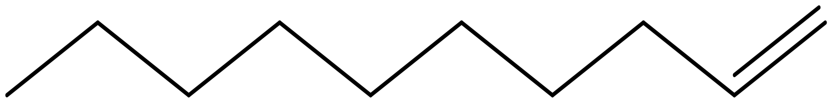

1-decene

1. 1-Decene Market by Derivative and Region - Global Forecast to 2025 - ResearchAndMarkets.com

Plastic

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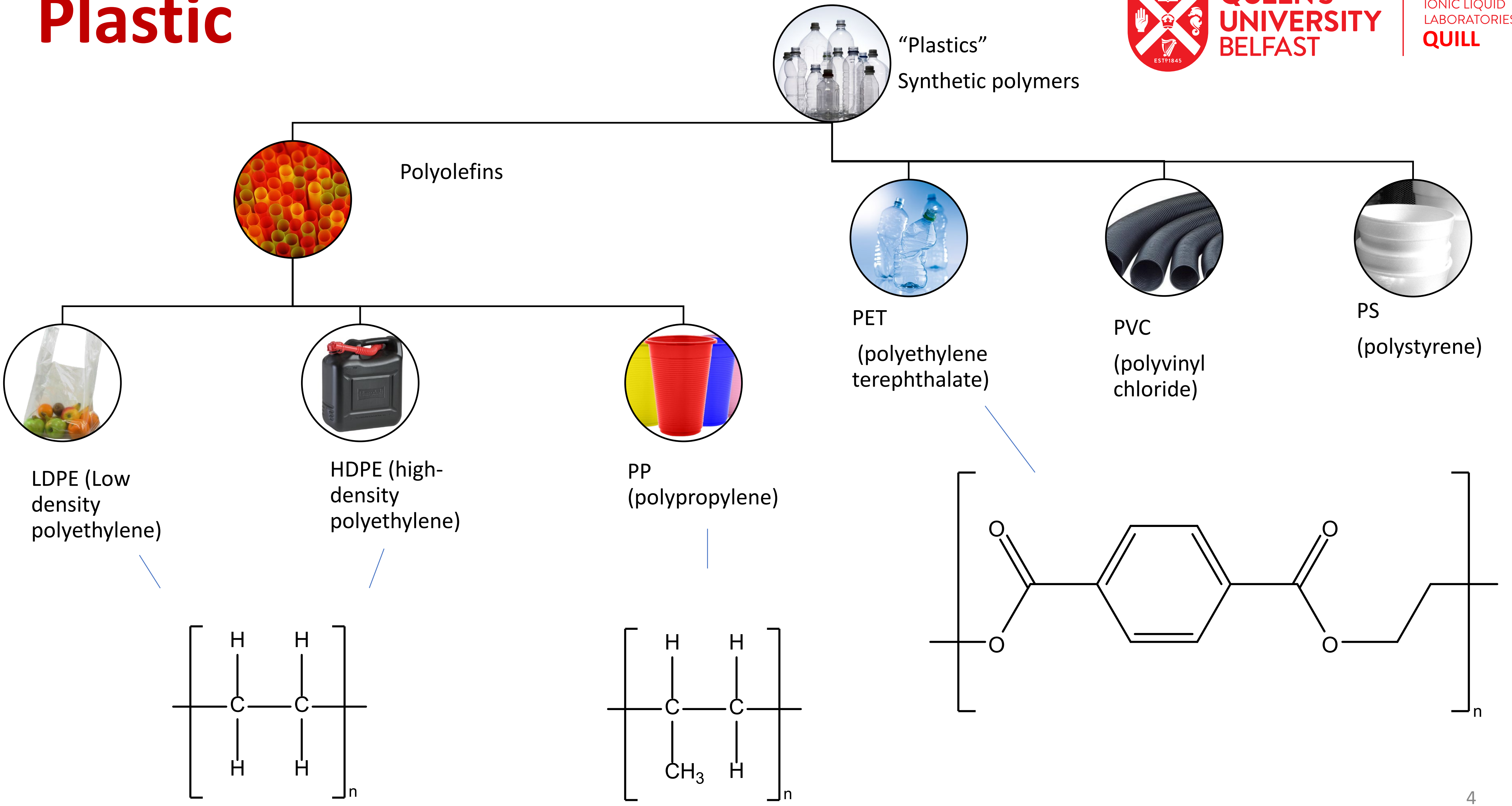

Types of recycling

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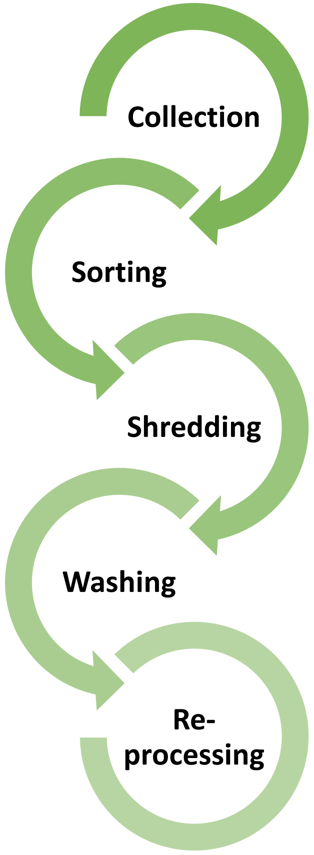
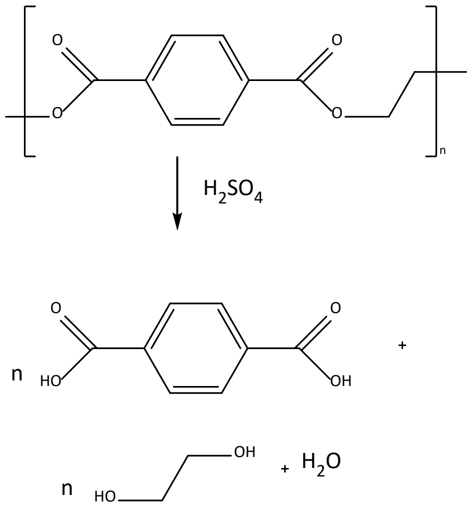
Chemical recycling

Mechanical recycling



Depolymerisation



Ionic liquids can be used as an alternative to H_2SO_4.

ACS Sustain. Chem. Eng., 2021, **9**, 15157–15165

Gasification

Plastic waste

↓

Oxygen and steam

↓

Syngas

A reaction with a gasifying agent (steam) at high temperatures

Pyrolysis

Plastic waste

↓

Oxygen deficient

↓

Hydrocarbon fractions

Thermal degradation in an oxygen deficient environment at high temperatures

Recycled feedstock reaction

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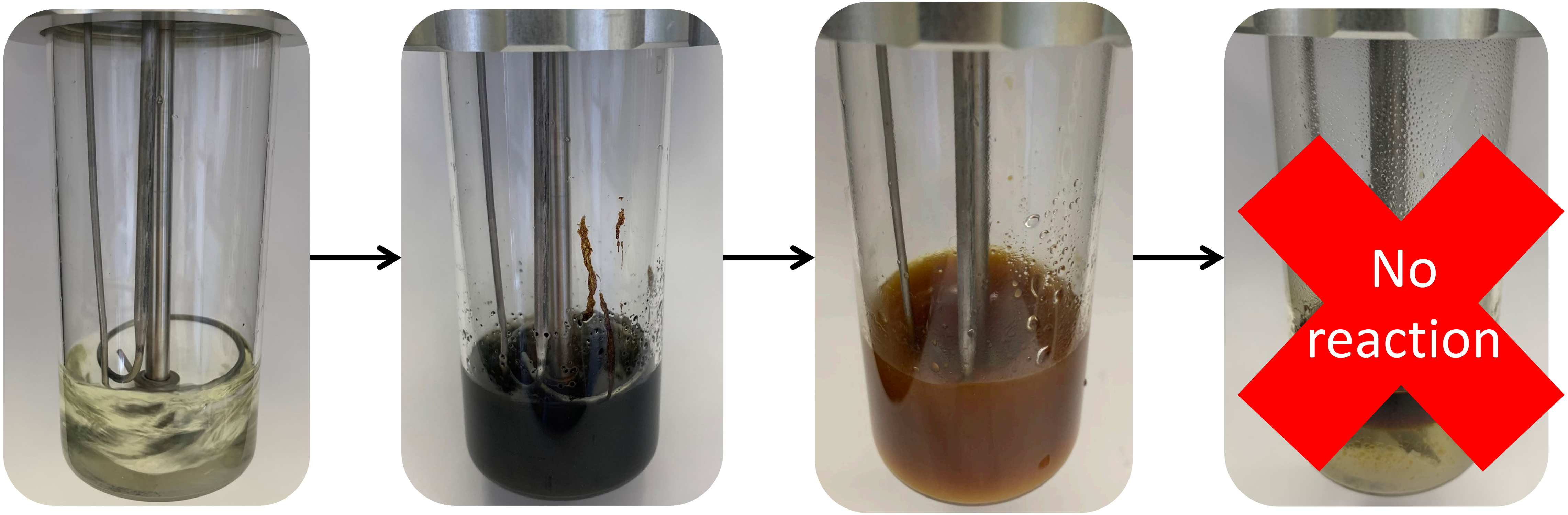

Recycled feedstock

Ur-$AlCl_3$: 0.28 mmol/ml

Quenched with water to remove catalyst

Removal of aqueous layer

Optimised catalyst loading for 1-decene reaction
Ur-$AlCl_3$: 0.028 mmol/ml

Method

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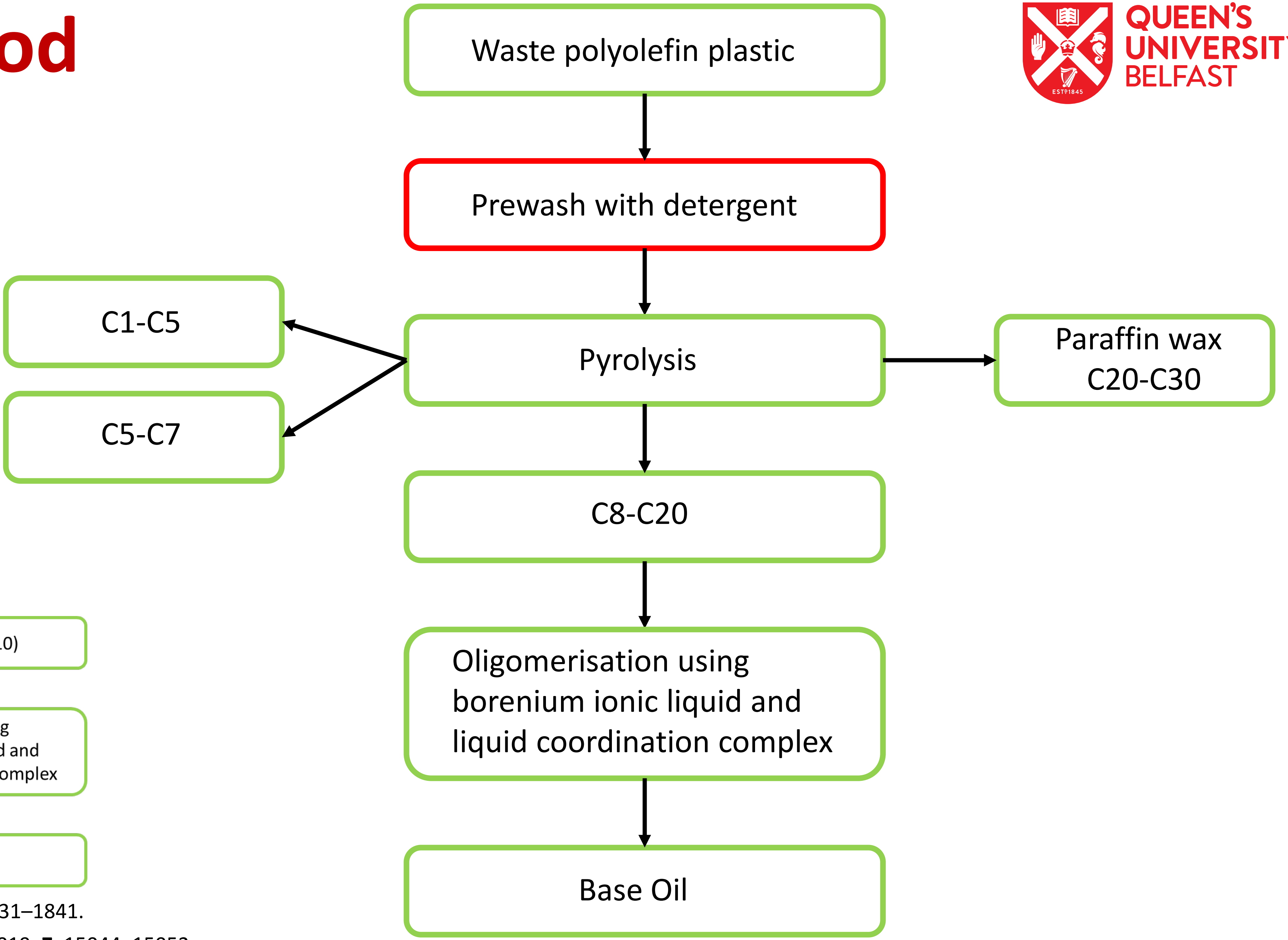

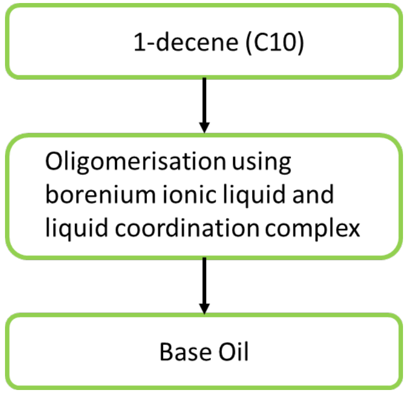

Green Chem., 2015, **17**, 1831–1841.
ACS Sustain. Chem. Eng., 2019, **7**, 15044–15052.

Results

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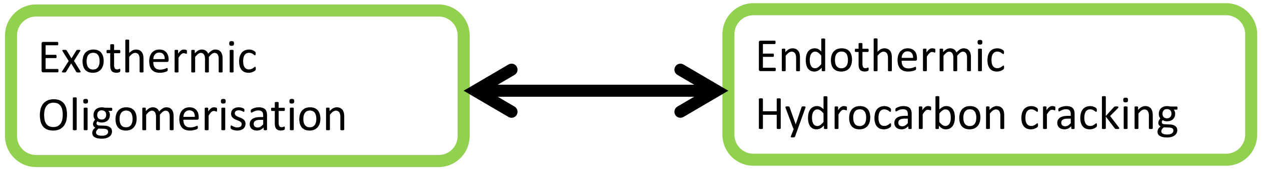
- Based on previous work on 1-decene using liquid coordination complexes and borenium ionic liquids the expectation was that **oligomerisation** would occur increasing the product distribution of **heavier** oligomers.

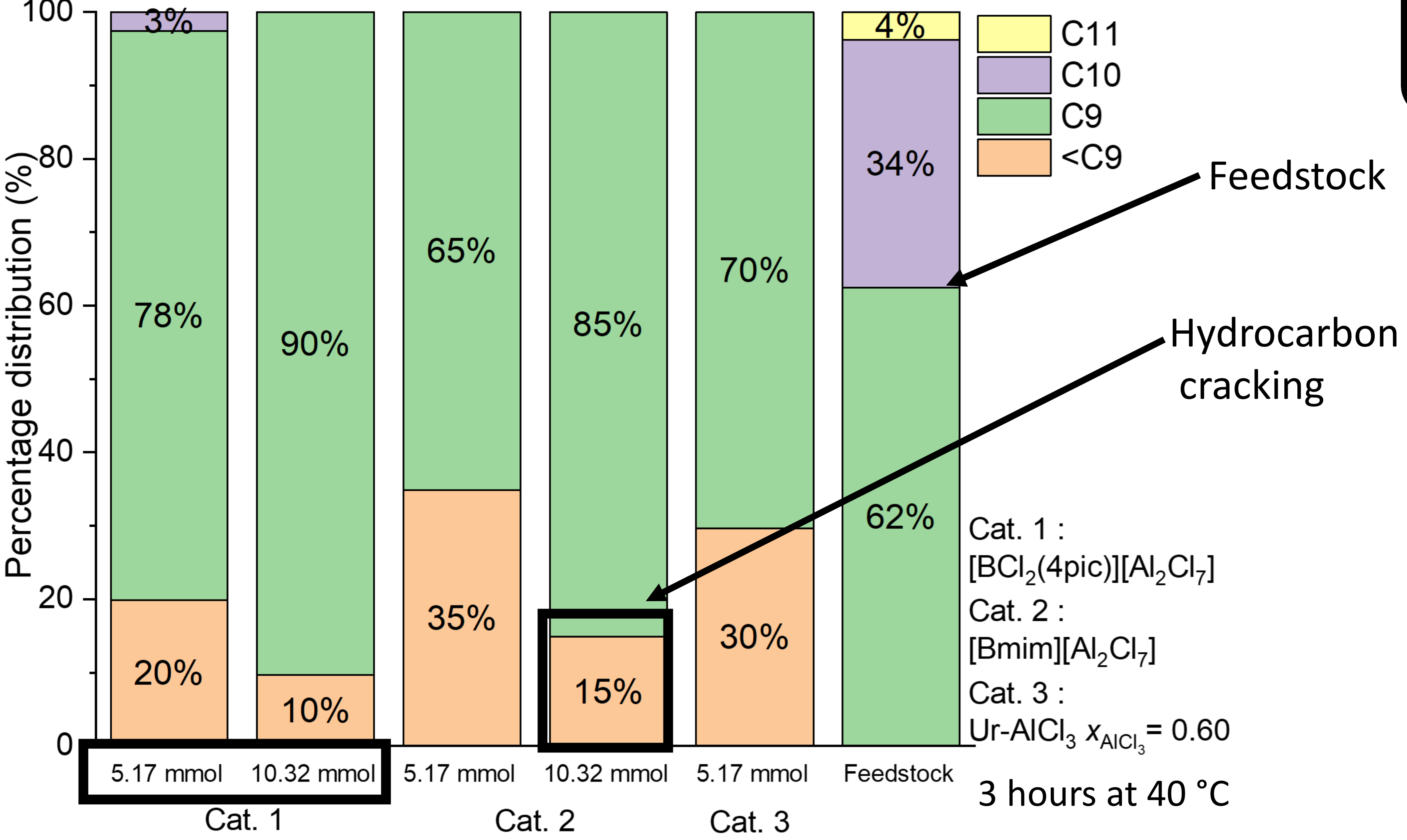
- However, this was not the case and hydrocarbon cracking, and oligomerisation was observed.

- This can be explained from the balance between the exothermic reaction (oligomerisation) and endothermic reaction (hydrocarbon cracking)



Waste polyolefin feedstock results: Light fraction

Results obtained by SimDist GC and mass balance as light hydrocarbons evaporated



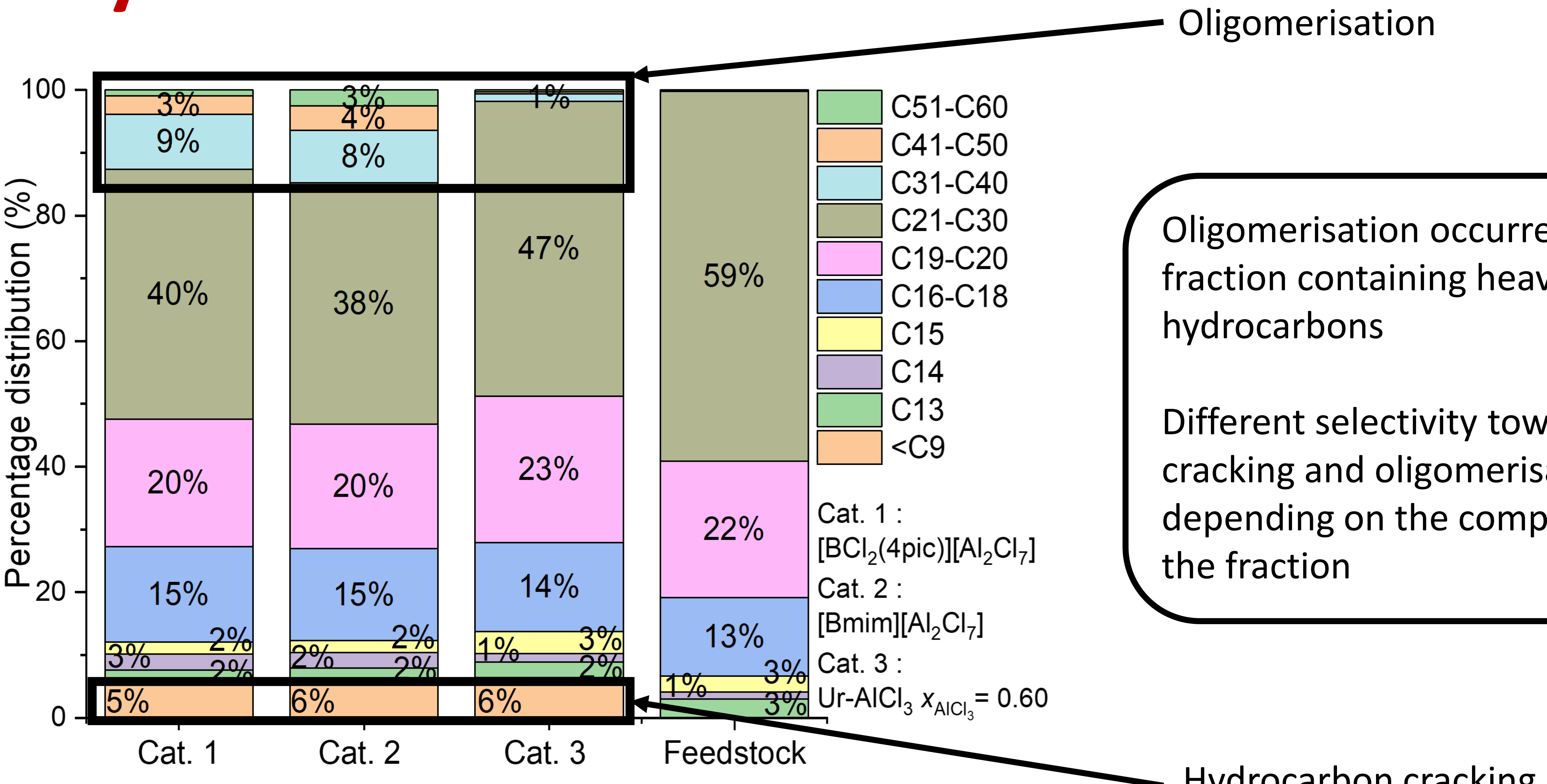
Cat. 1 : $[BCl_2(4pic)][Al_2Cl_7]$

Cat. 2 : $[Bmim][Al_2Cl_7]$

Cat. 3 : Ur-$AlCl_3$ x_{AlCl_3}= 0.60

3 hours at 40 °C

Waste polyolefin feedstock results: Heavy fraction

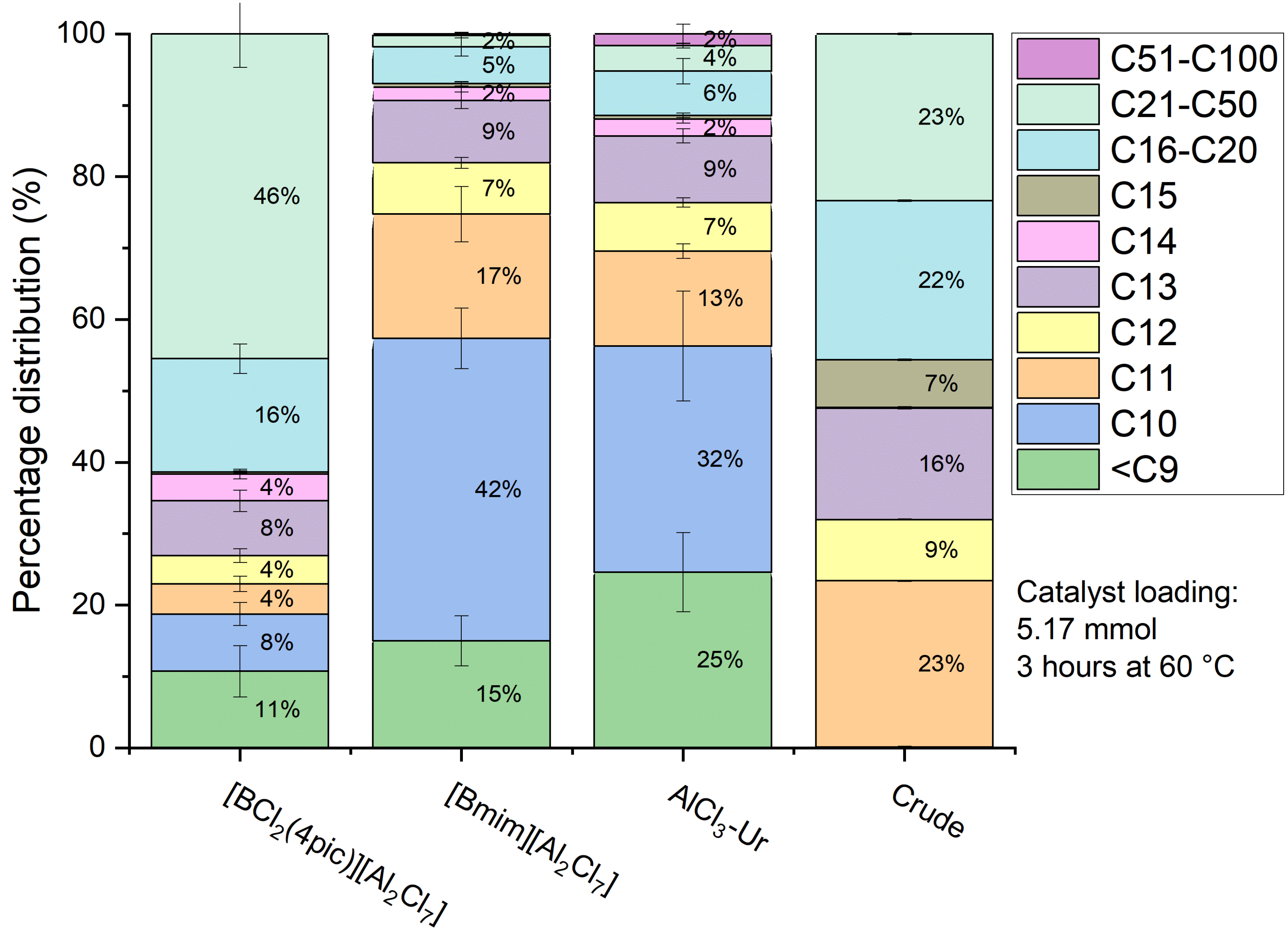


3 hours at 40 °C Catalyst loading: 5.17 mmol

Oligomerisation occurred with the fraction containing heavier hydrocarbons

Different selectivity towards cracking and oligomerisation depending on the composition of the fraction

Waste polyolefin feedstock results : crude feedstock



Catalyst loading:
5.17 mmol
3 hours at 60 °C

Increase 20 °C to ensure the feedstock slurry was liquid on addition of the catalyst

Strength of Lewis acid impact product distribution

Conclusions: Polyolefin recycling

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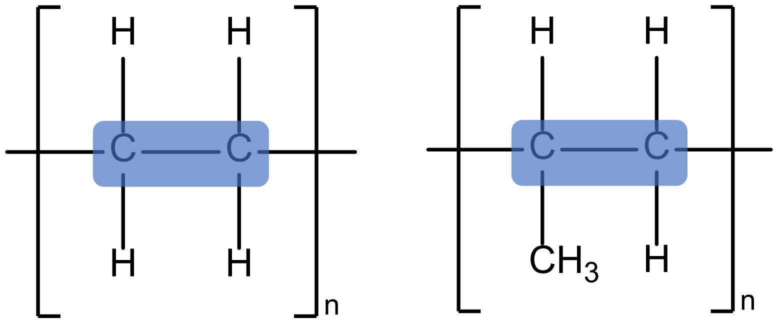
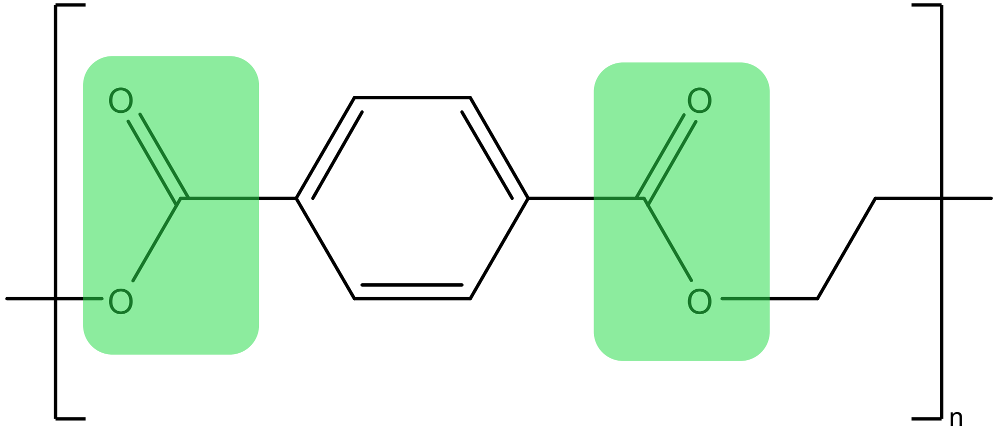
- Competition between cracking and oligomerisation reaction
- Endothermic C-C cleavage vs exothermic reaction
- Heavy feedstock: oligomerisation of feedstock to lubricant base oil range
- Light feedstock: cracking feedstock toward fuel range
- High sensitivity towards feedstock, Lewis acidity, catalyst loading and reaction parameters

Moving on: Polyethylene terephthalate (PET)

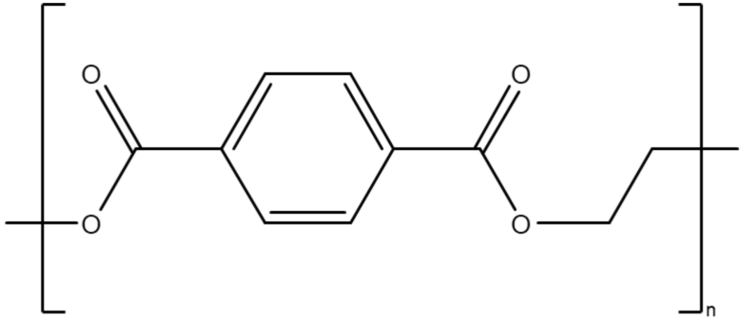


Polyolefins

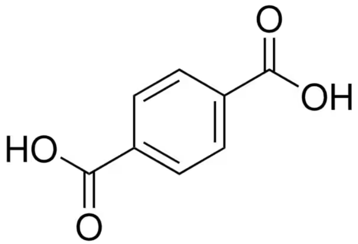
Polyethene terephthalate



PET recycling

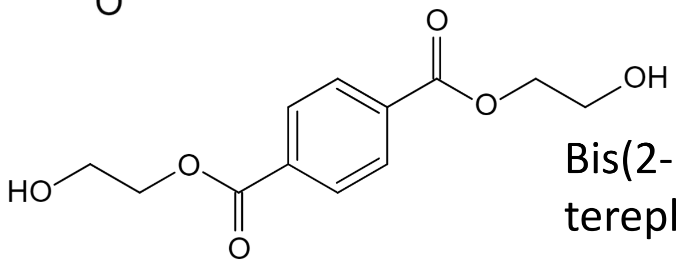


Hydrolysis



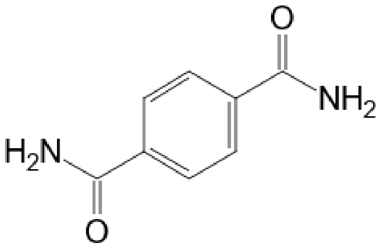
Terephthalic acid (TPA)

Glycolysis



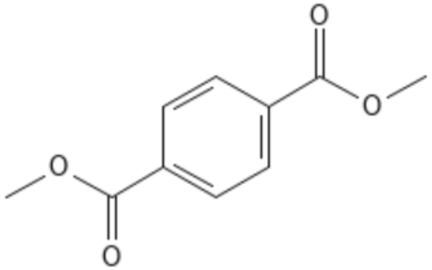
Bis(2-Hydroxyethyl) terephthalate (BHET)

Aminolysis



Terephthalamide

Methanolysis



Dimethyl Terephthalate (DMT)

Reasoning and industry standard

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- Industrial standard is mechanical recycling which leads to continuous degradation of the plastic.
- Garbo – Chempet©: producing 55-65 ton per day of BHET production
- Eastman methanolysis technology producing DMT using temperatures over 200 °C
- Depolymerisation of PET with Brønsted acidic ionic liquids: high reaction temperatures between 200 – 400 °C
- Can we develop a method that utilises ionic liquids to produce an energy efficient process?

Sorting and mechanical recycling

Method

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PET water bottle purchased from local supermarket

Washed, dried and cut into 1 cm^3 x 1 cm^3 squares

Mesh sieve to achieve uniform power

Add Brønsted acidic ionic liquid and methanol

Formulated from tributylamine (N_{444}) and sulfuric acid from earlier published work [1]

[1] Green Chem., 2021,23, 4421-4429

Microwave depolymerisation

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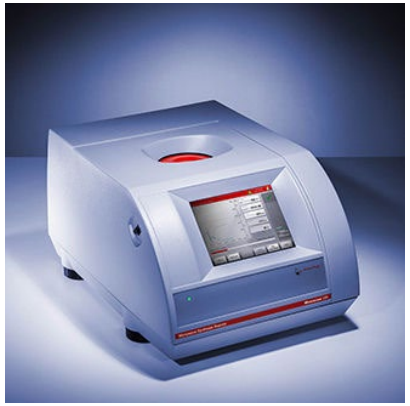
- Ionic liquids efficiently absorb microwaves through an ionic conduction mechanism, rapidly reaching high temperatures.

- This combination enables an energy-efficient method to achieve higher temperatures at lower energy costs.

- $[N_{444}H][HSO_4].H_2SO_4$ $\chi_{H2SO4} = 0.67$



Chemical processing

ÈVA BOROS
KENNETH R. SEDDON
CHRISTOPHER R. STRAUSS

Chemical processing with microwaves and ionic liquids

Èva Boros, Kenneth R. Seddon, Christopher R. Strauss, Chemistry today, 2008, **6**, 26

Future work

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- Optimise PET reactions conditions using Brønsted ionic liquid catalyst
- Measure percentage conversion of PET using a mass balance
- Access the purity of DMT by GC-MS and NMR spectroscopy
- Investigate the reusability of the Brønsted ionic liquid catalyst

Acknowledgements

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- Prof. John Holbrey
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