ReSolve
SAFE AND EFFECTIVE BIO-BASED SOLVENTS

# Safe and high-performing bio-based alternatives to toluene

FERGAL BYRNE, UNIVERSITY OF YORK
ÁNGEL PUENTE, NOVA-INSTITUTE

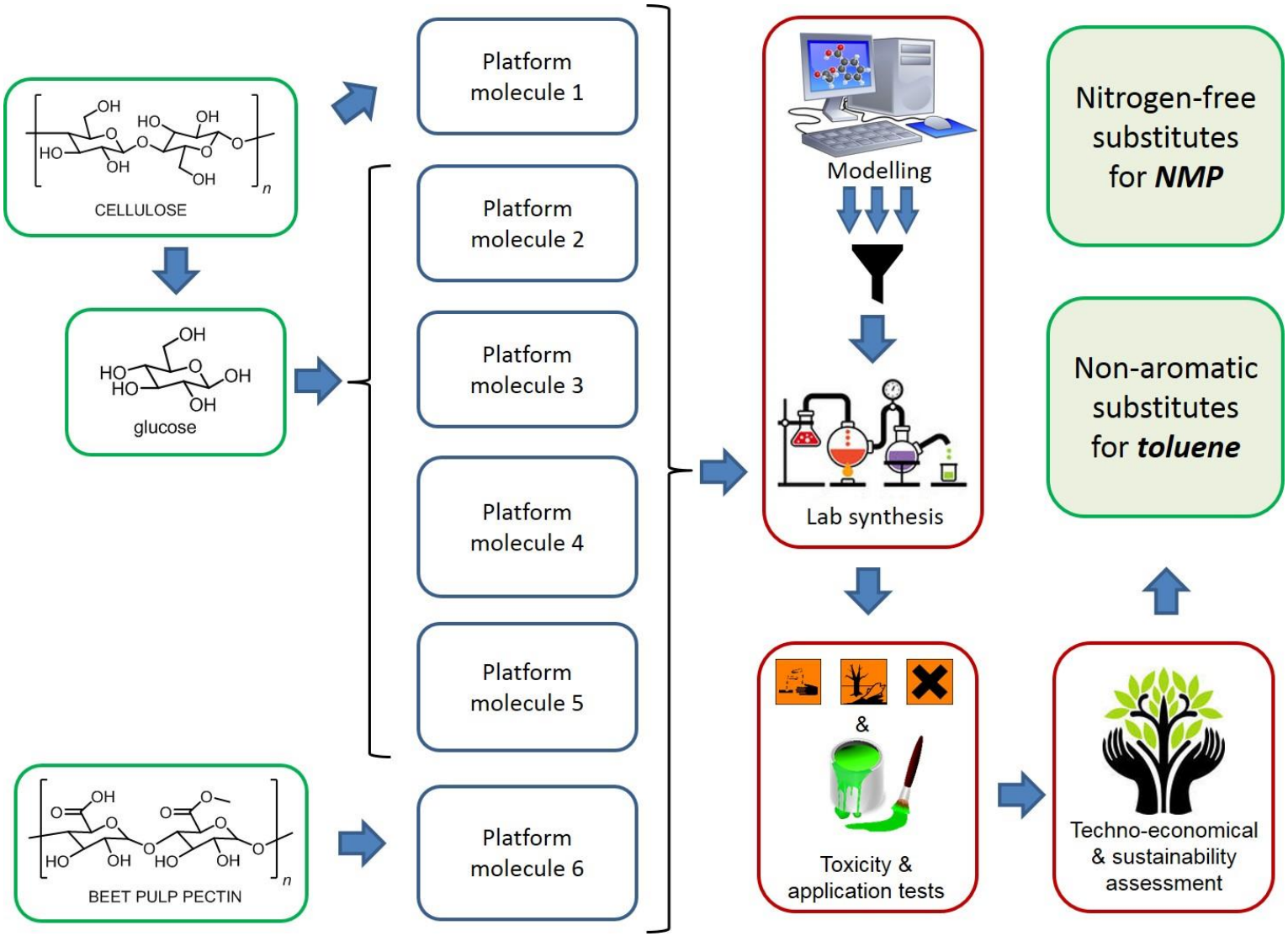
BBI JU

Bio-based Industries Consortium

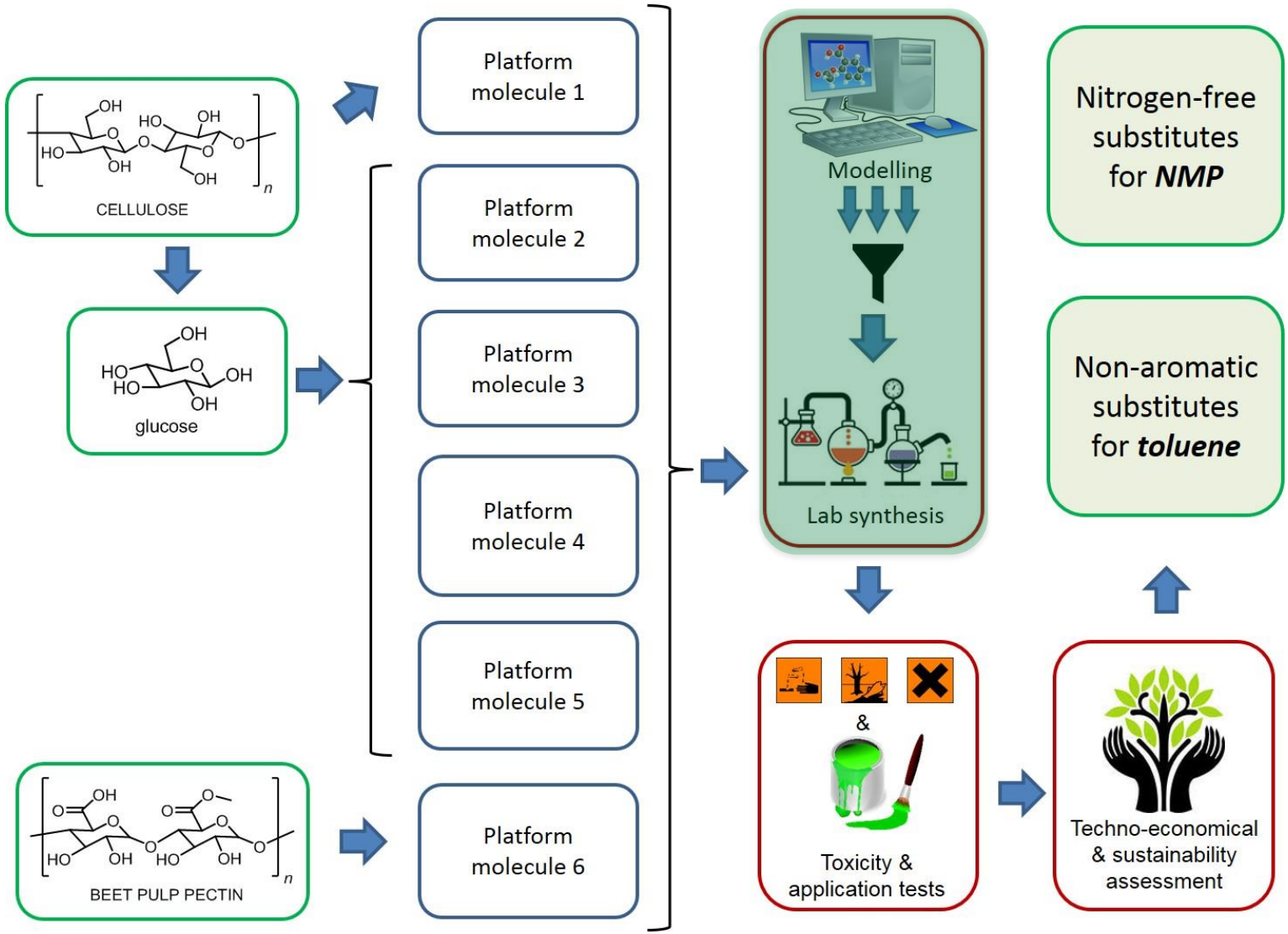
Horizon 2020
European Union Funding
for Research & Innovation

This project has received funding from the Bio Based Industries Joint Undertaking under the European Union‘s Horizon2020 research and innovation programme under agreement No 745450.

# The concept


CELLULOSE
glucose
BEET PULP PECTIN
Platform molecule 1
Platform molecule 2
Platform molecule 3
Platform molecule 4
Platform molecule 5
Platform molecule 6
Modelling
Lab synthesis
&
Toxicity & application tests
Techno-economical & sustainability assessment
Nitrogen-free substitutes for NMP
Non-aromatic substitutes for toluene

# The concept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# Hazardous Hydrocarbon Solvents

## Toluene

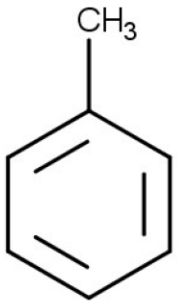
## Toluene another target for restriction?

### Substance identity

**EC / List no.:** 203-625-9

**CAS no.:** 108-88-3

**Mol. formula:** C7H8




### Hazard classification & labelling

*Danger!* According to the **harmonised classification and labelling** (CLP00) approved by the European Union, this substance may be fatal if swallowed and enters airways, is a highly flammable liquid and vapour, is suspected of damaging the unborn child, may cause damage to organs through prolonged or repeated exposure, causes skin irritation and may cause drowsiness or dizziness.

**Additionally**, the classification provided by companies to ECHA in **REACH registrations** identifies that this substance is suspected of damaging fertility or the unborn child, is harmful to aquatic life with long lasting effects and causes serious eye irritation.

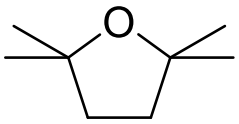
At least one company has indicated that the substance classification is affected by impurities or additives.

### Regulatory activities

- Substance included in the Community Rolling Action Plan (CoRAP).
- Some uses of this substance are restricted under Annex XVII of REACH.

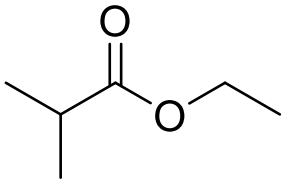
Data taken from ECHA – Information on Chemicals

# Top toluene replacement candidates



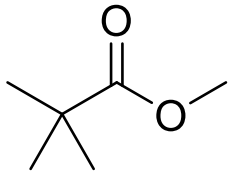
**AK1**

TMO



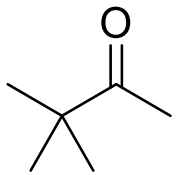
**AK4**

Ethyl isobutyrate



**AK6**

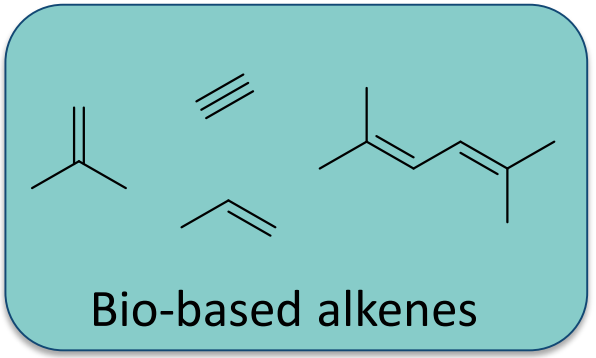
Methyl pivalate



**AK7**

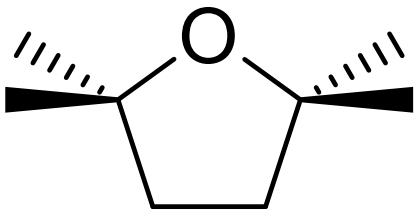
Pinacolone

- All from bio-based alkenes platform
- Other platforms were O containing
  - Adds polarity to molecules



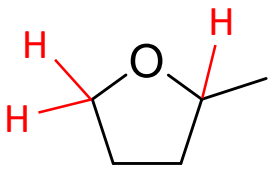
# Flagship toluene replacement: TMO

Non-peroxide forming ether

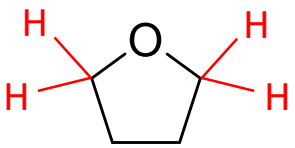


## Traditional ethers

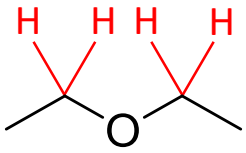
- Abstractable *alpha* hydrogens
- Removed radically is ambient conditions



2-MeTHF



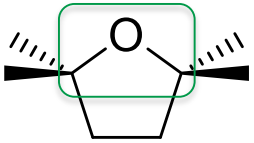
THF



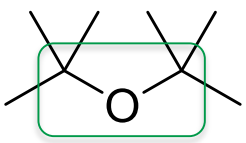
Diethyl ether

## Quaternary ethers

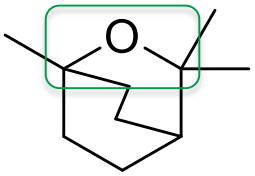
- Unabstractable *alpha* methyl groups
- Very difficult to remove



TMO



DTBE



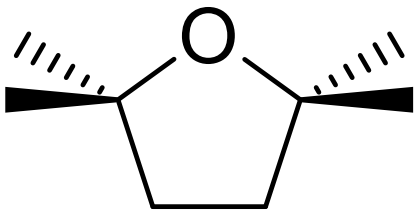
Eucalyptol

F. Byrne, B. Forier, G. Bossaert, C. Hoebers, T. J. Farmer, J. H. Clark, and A. J. Hunt. "2,2,5,5-Tetramethyltetrahydrofuran (TMTHF): A Non-Polar, Non-Peroxide Forming Ether Replacement for Hazardous Hydrocarbon Solvents." *Green Chemistry* 19, 3671–78. https://doi.org/10.1039/C7GC01392B.

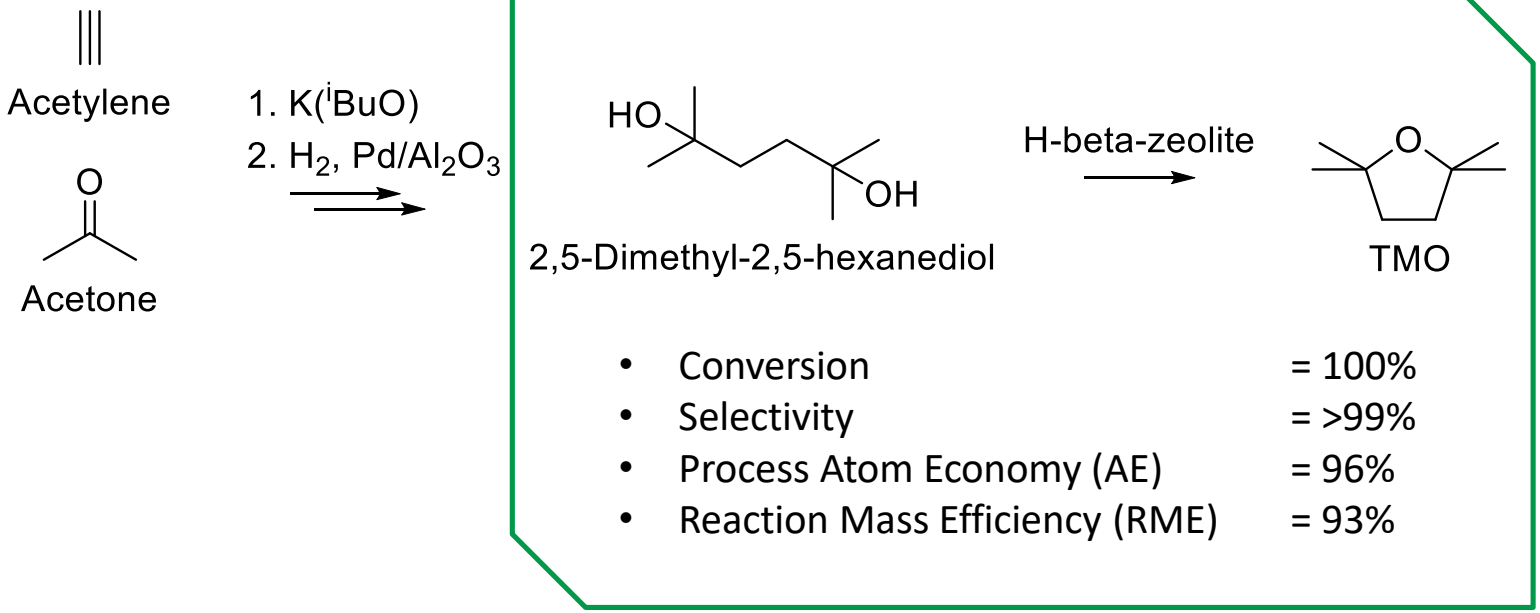
# Flagship toluene replacement: TMO

## (2,2,5,5-Tetramethyloxolane)

Synthesis



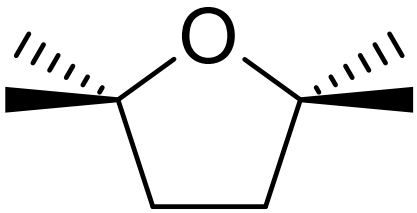
Patented by Nitto (as TMTHF)
WO2018033635 (A1)




- Conversion = 100%
- Selectivity = >99%
- Process Atom Economy (AE) = 96%
- Reaction Mass Efficiency (RME) = 93%

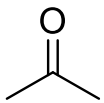
# Flagship toluene replacement: TMO

## Synthesis



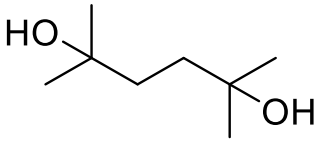

>300 L synthesis carried out at BBEPP in Belgium


Acetylene



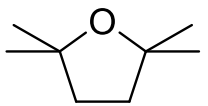

Acetone

1. K($^{i}$BuO)
2. $H_2$, $Pd/Al_2O_3$




2,5-Dimethyl-2,5-hexanediol

H-beta-zeolite




TMO

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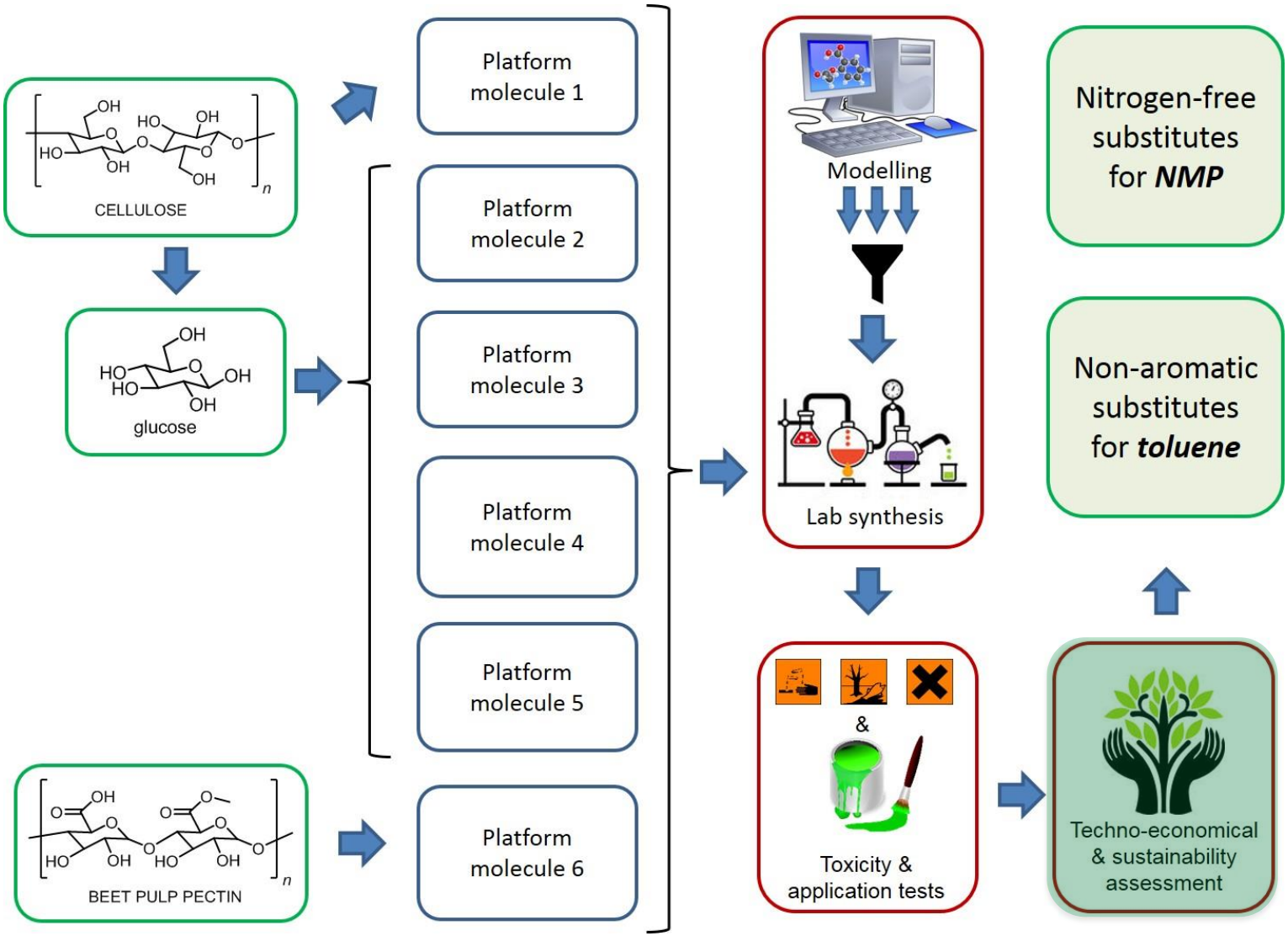
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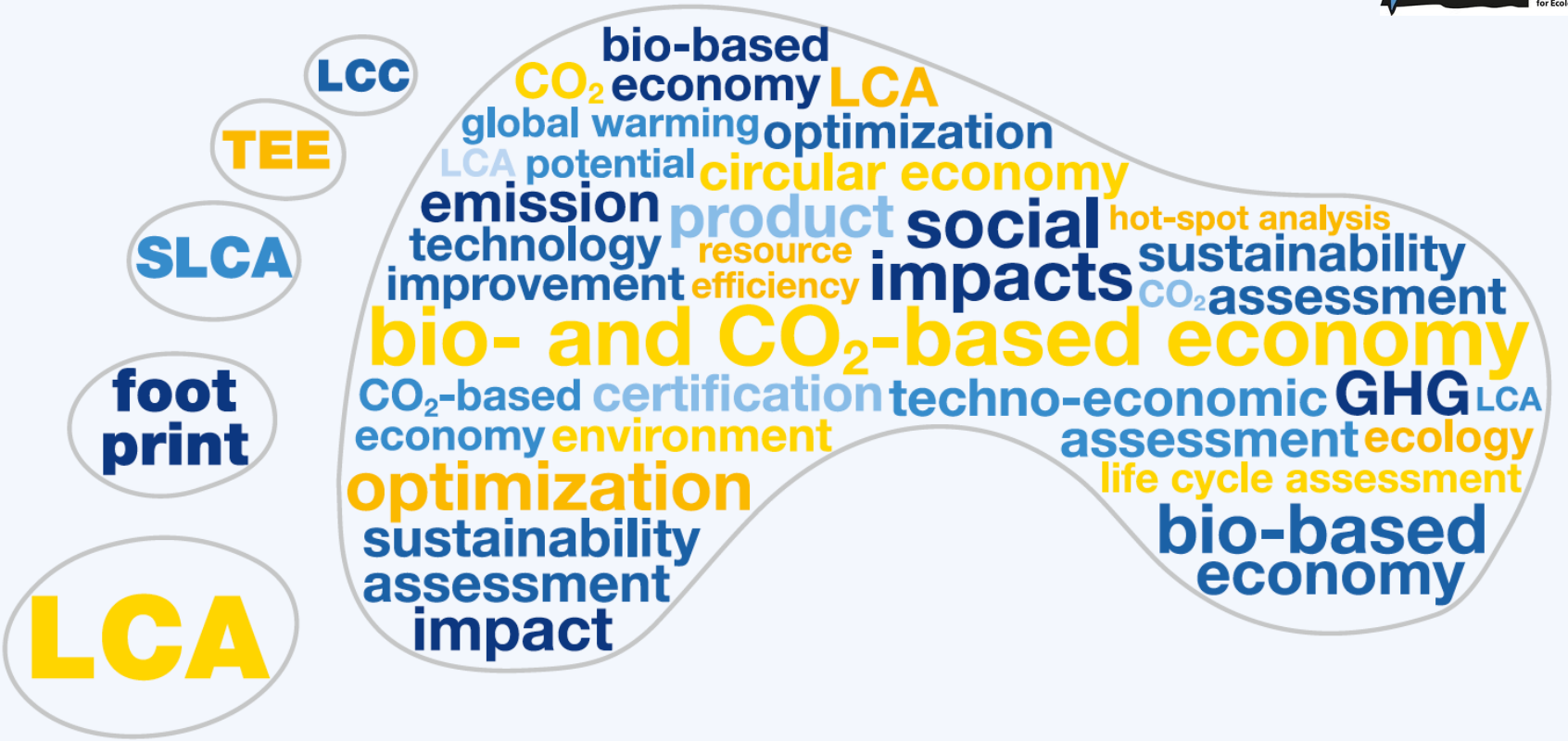
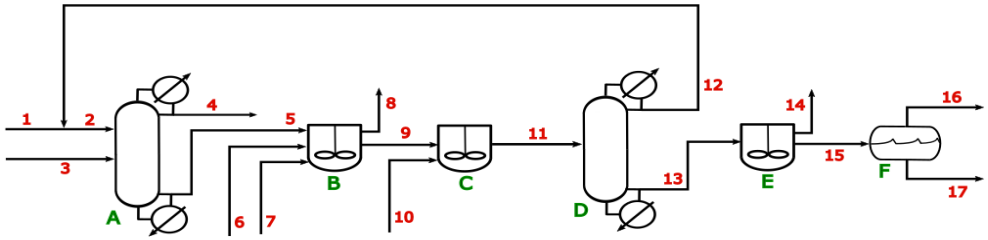
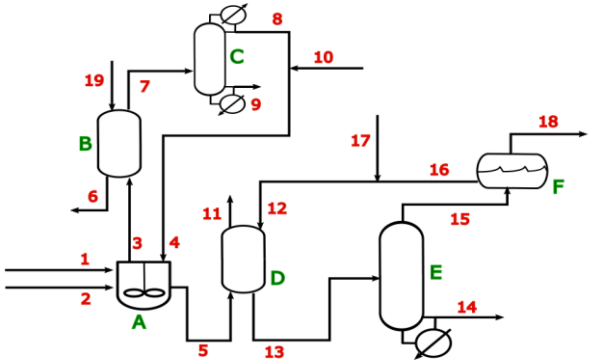
# Economic and environmental performance

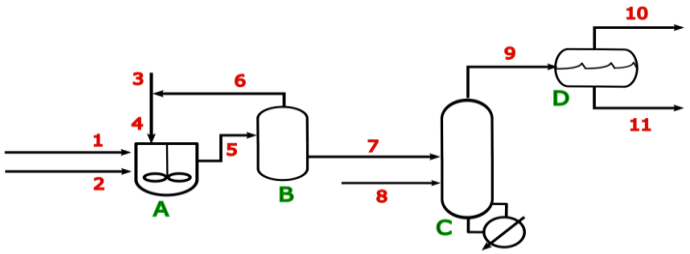


# Conceptual Process Designs

- Processes were designed for most promising candidates.
- Production of process flow diagrams with corresponding energy and stream tables and equipment design

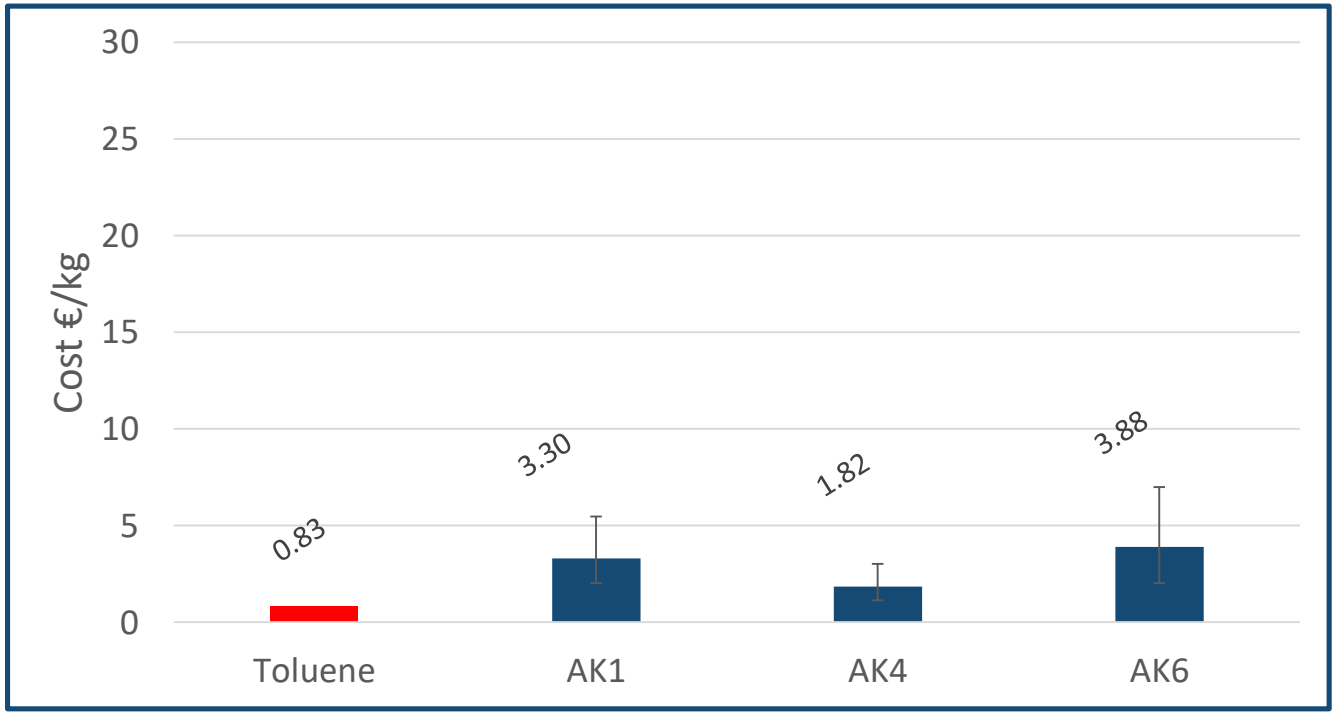


# Cost assessment

Together with market analysis CAPEX and OPEX were estimated to give insight on production costs for selected candidates

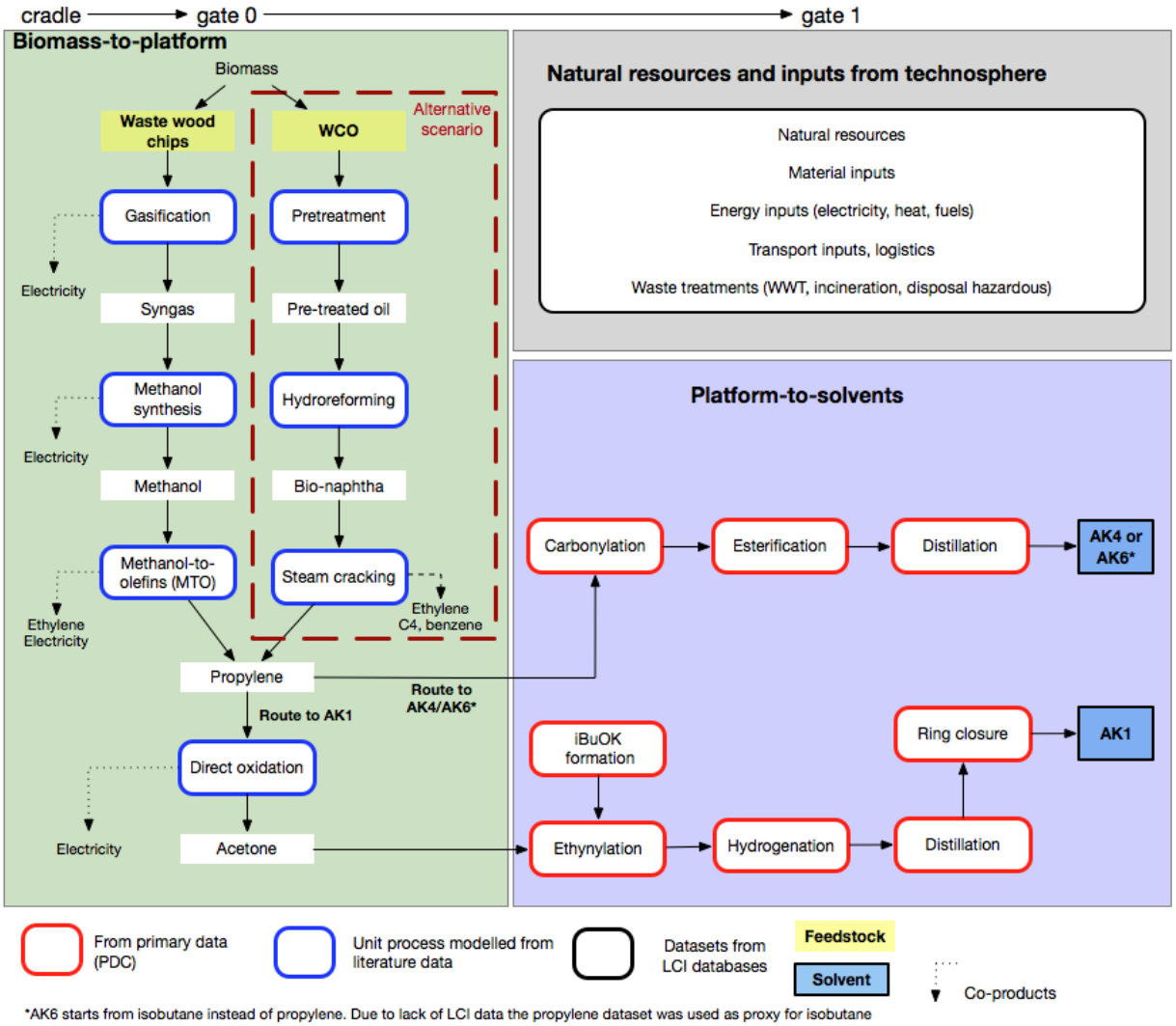


# Bio-based content & BUE

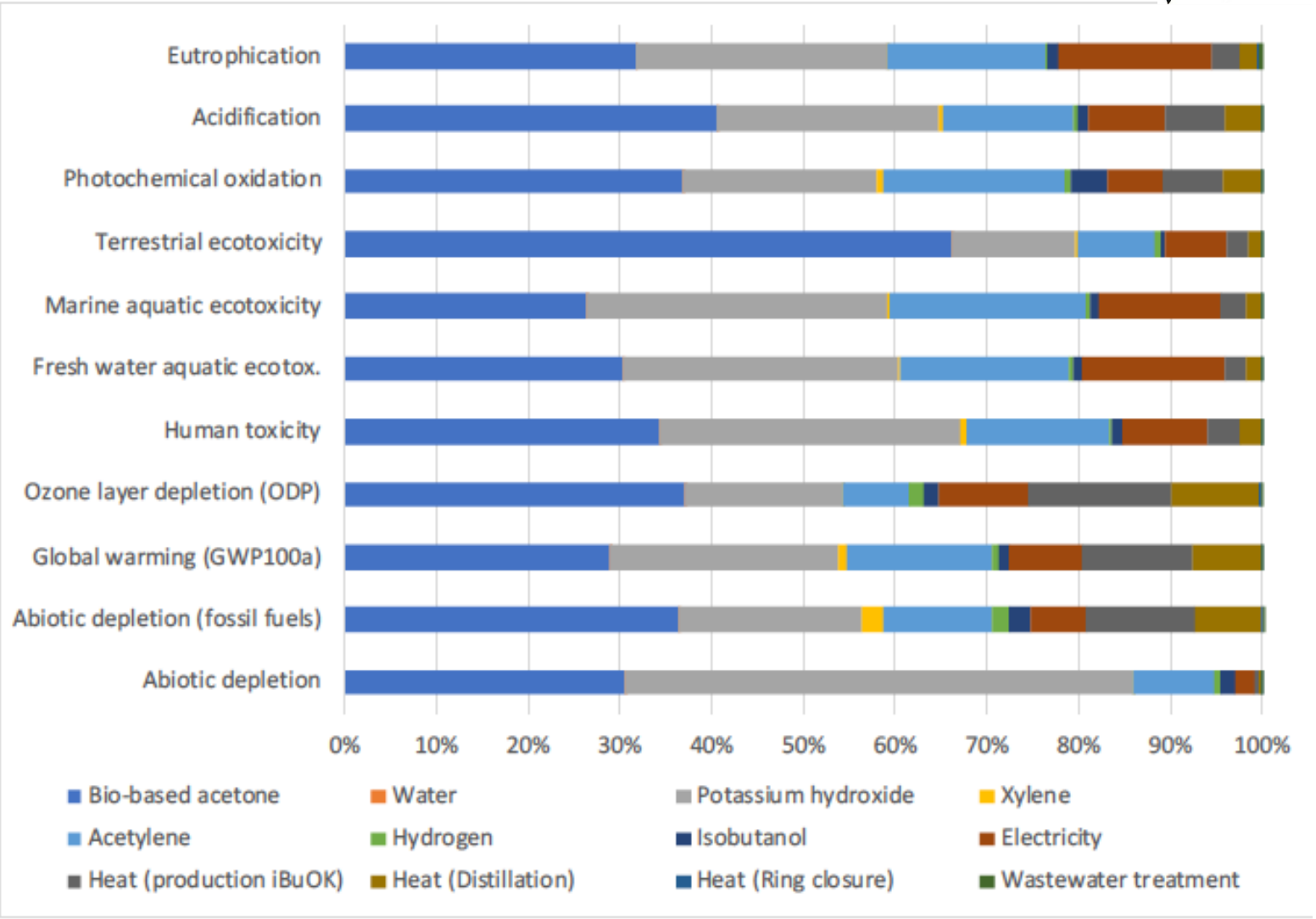
| Toluene replacements | Bio-based content, % | BUE, % |
|---|---|---|
| AK1 | 66% | 47% |
| AK4 | 36% | 23% |
| AK6 | 48% | 31% |

# AK platform

## System boundaries

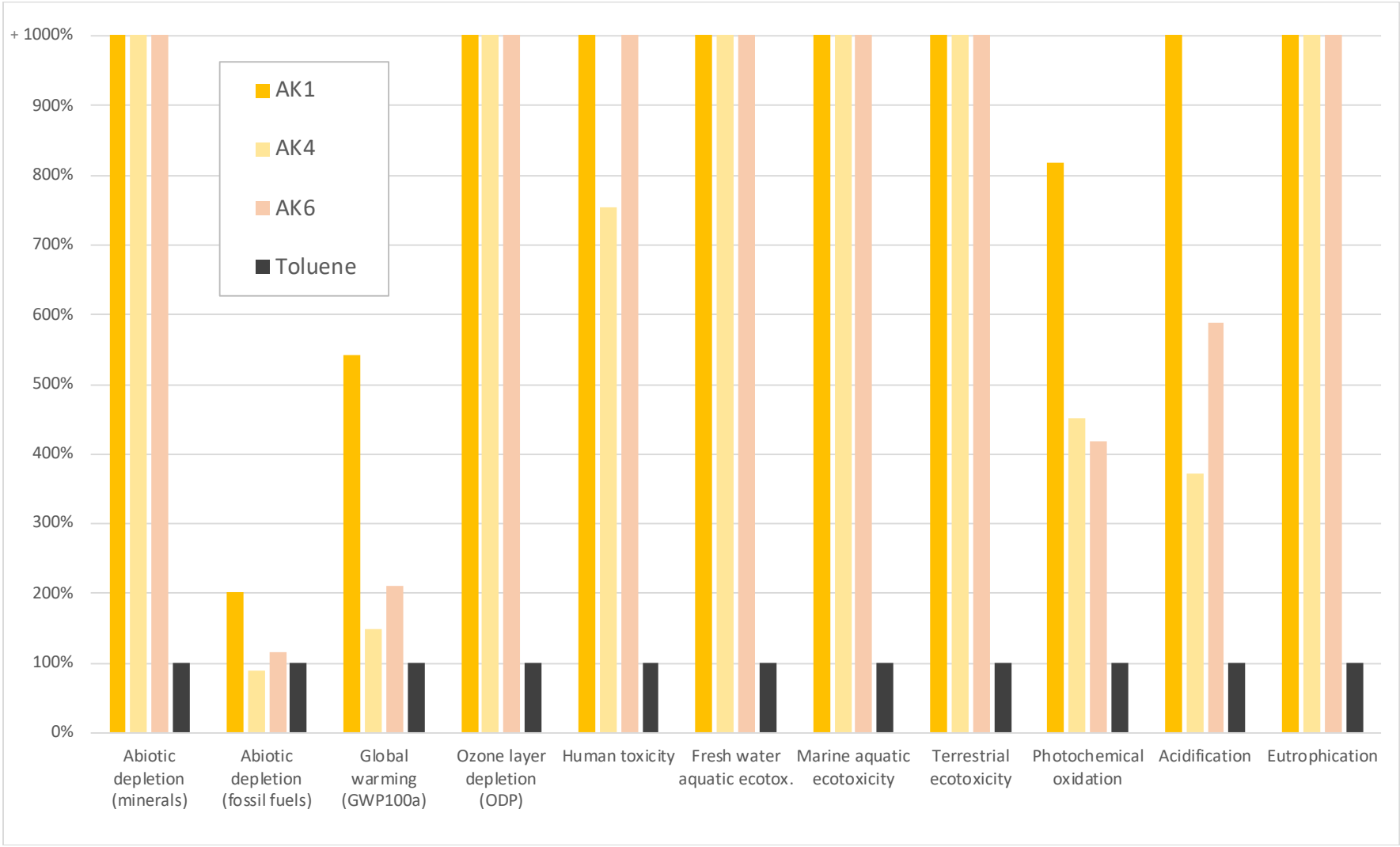


# Hotspots AK1

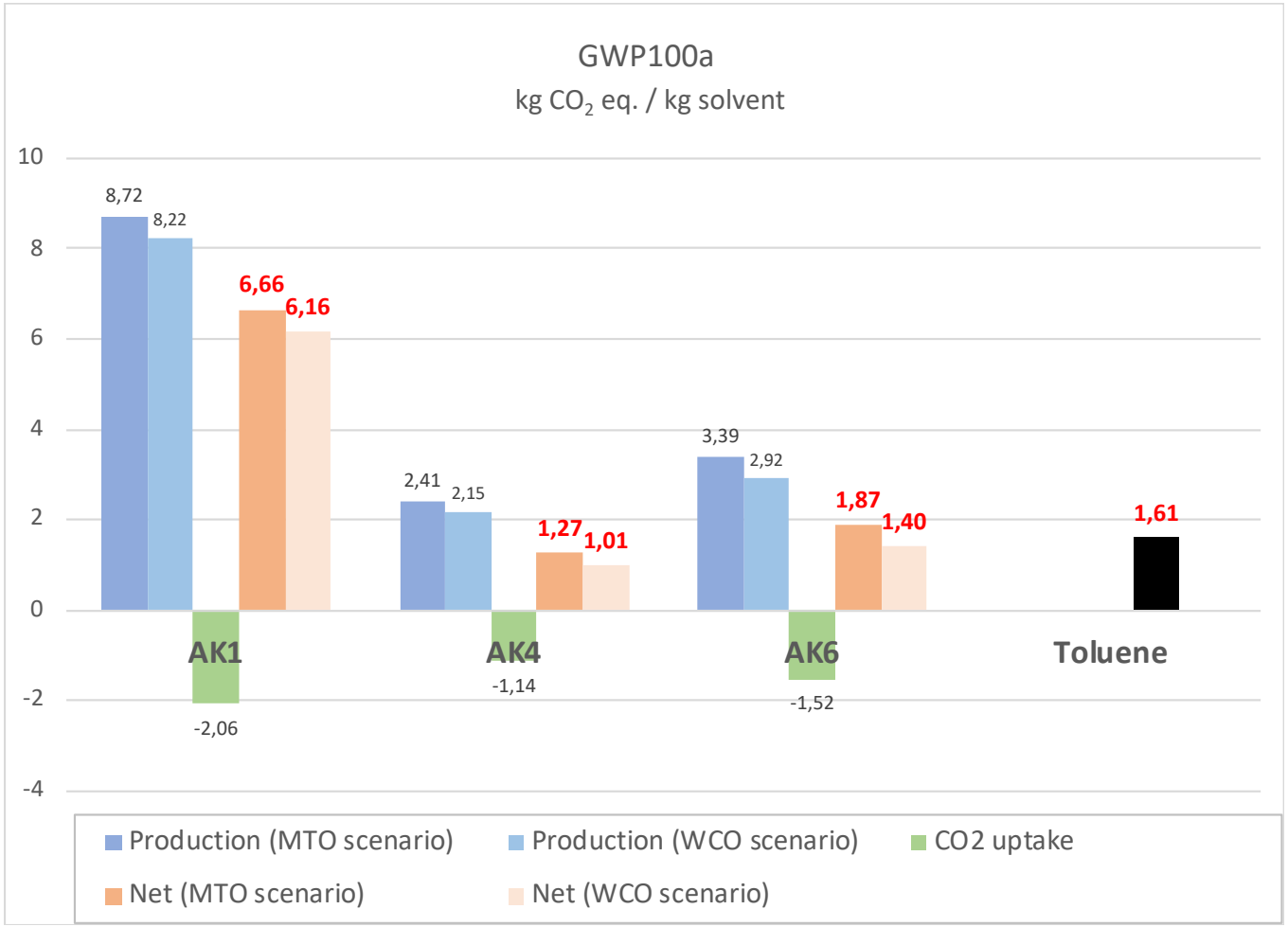


# Toluene replacements

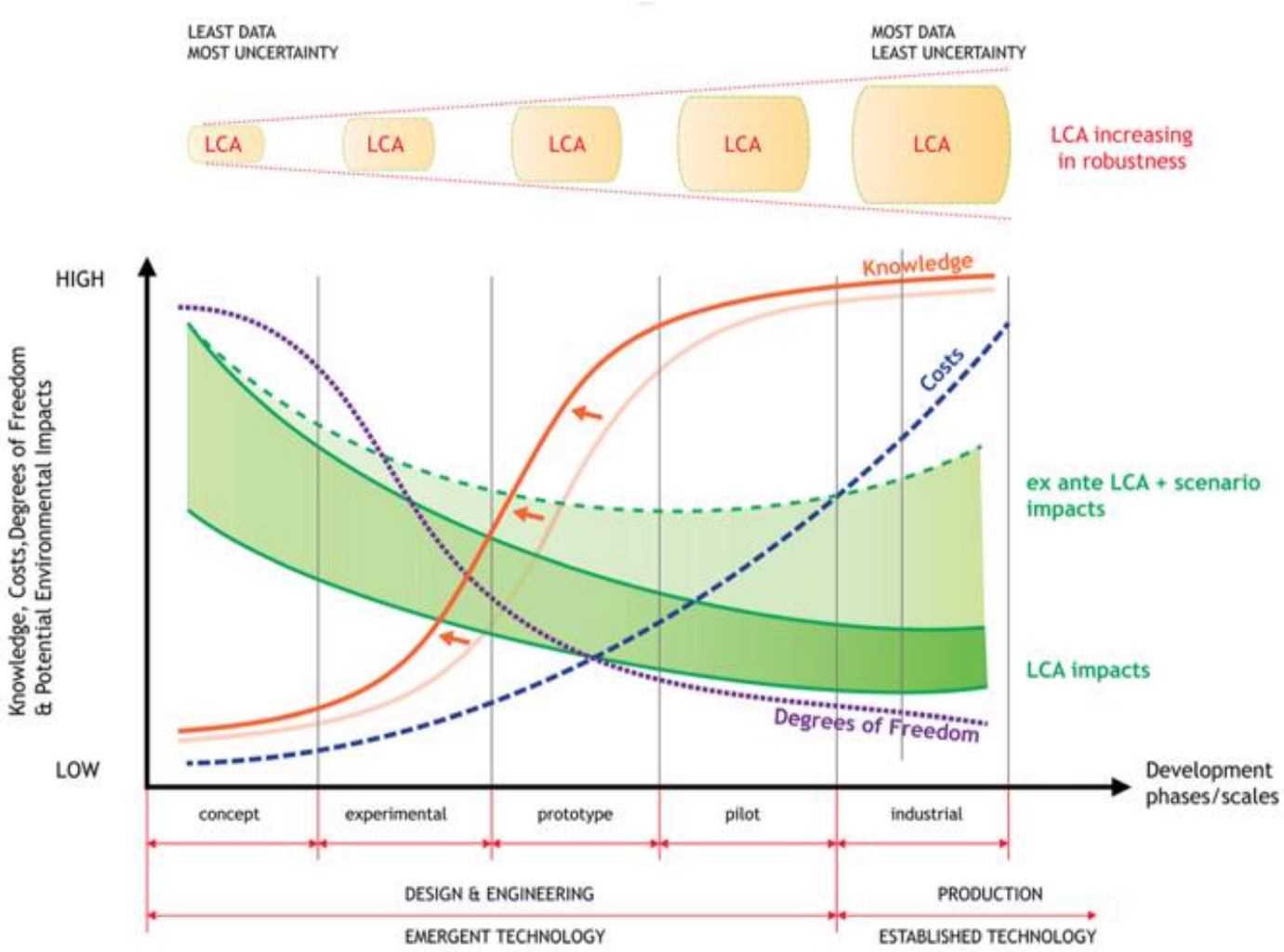
## Comparative analysis



# GWP AK platform



# Process development



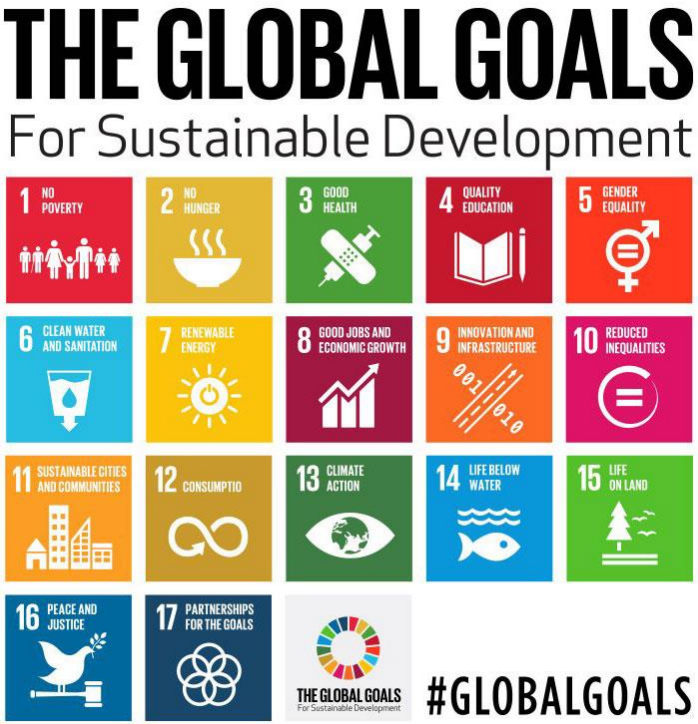
# Socio-economic assessment

## VDI-4605 Evaluation

| ENVIRONMENTAL | ECONOMIC | SOCIAL |
|---|---|---|
| Efficient use of (non-energetic) materials | Economic efficiency | Nutrition |
| Energy efficiency/renewable energy sources and climate protection | Economic provision for the future | Toxicology and health |
| Land use/biodiversity | Long-term viability | Air |
| Water demand and quality (in-plant) | International co-operation/ involvement from the perspective of the business or of development assistance | Noise |
| | Data security | Working conditions |
| | | Public participation and societal acceptance |
| | | Data privacy |

- **Quantitative**: Primary energy consumption, production costs, quantities of hazardous waste waste,…

- **Qualitive**: Ensuring sufficient nutrition, social acceptance,…

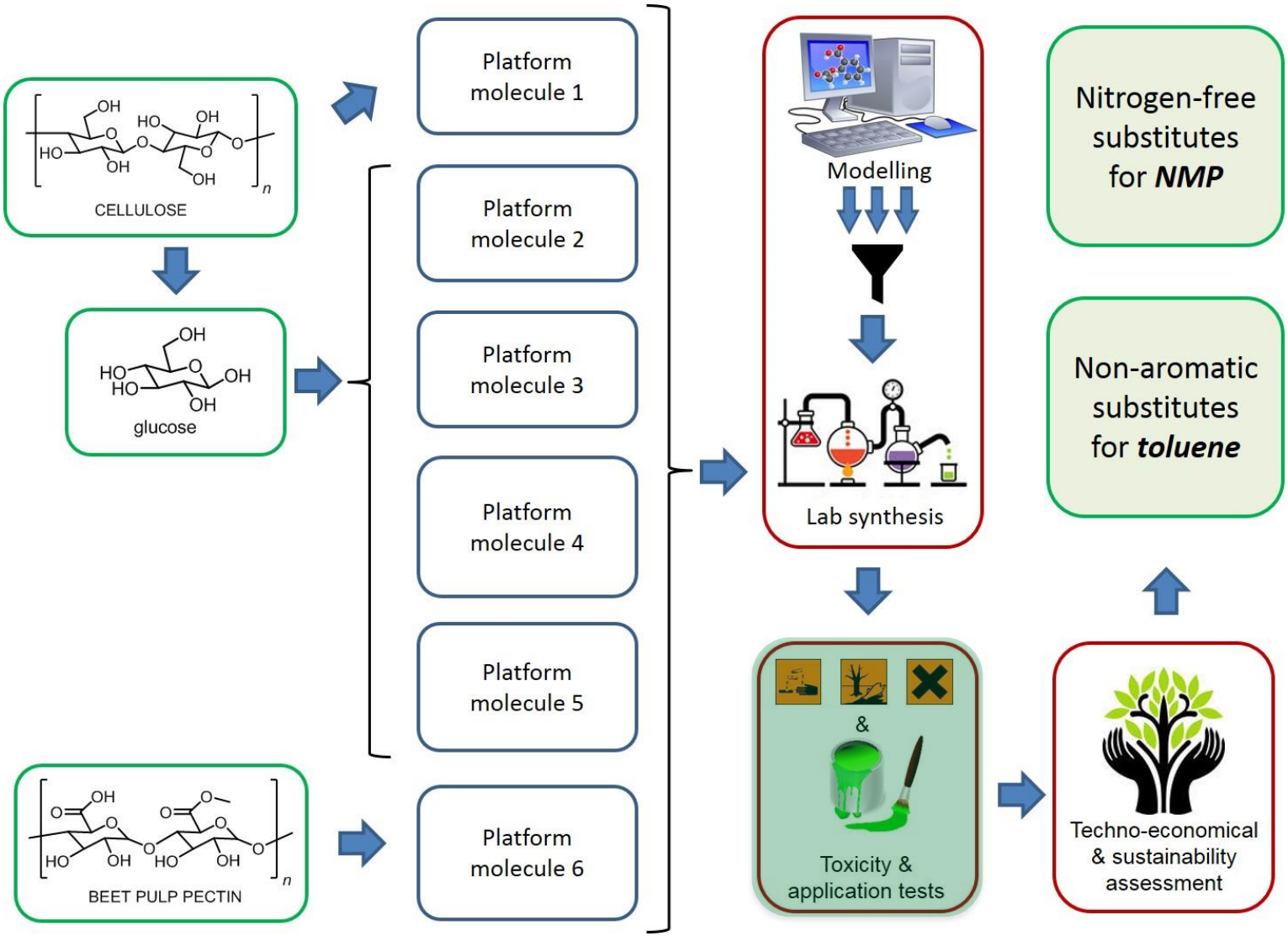


# Potential and barriers

- ✓ Positive public image
- ✓ Independence from fossil resources
- ✓ Reduced human toxicity
- ✓ Revalorisation of waste products
- ✓ New added functionality (R&D)
- ✓ Improved performance
- ✓ Potential to source feedstock locally
- ✓ Reduction of environmental pollutants
- ✓ Non-food competition

- o Higher production cost
- o Uncertainty about future regulation
- o Volatility of feedstock prices
- o Uncertainty regarding performance
- o Uncertainty about available feedstock (quantity and quality)
- o Difficulty in communicating environmental benefits

# The concept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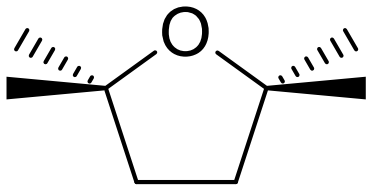
# Flagship toluene replacement: TMO

| Solvent property | Toluene | Quaternary ethers: Eucalyptol | Quaternary ethers: TMO | Quaternary ethers: DTBE | THF |
|---|---|---|---|---|---|
| Molecular weight / g·mol$^{-1}$ | 92.14 | 154.25 | 128.21 | 130.23 | 72.11 |
| Boiling point / °C | 111 | 176 | 112 | 107 | 66 |
| Melting point / °C | -95 | 2 | <-90 | <-90 | -108 |
| Density / g·ml$^{-1}$ | 0.867 | 0.927 | 0.802 | 0.762 | 0.883 |
| Molar volume / cm$^3$·mol$^{-1}$ | 106.6 | 167.5 | 151.1 | 172.5 | 81.9 |
| Autoignition temp. / °C | 522 | No data | 417 | No data | 321 |
| Lower explosion limit / v/v% | 1.1* | No data | 0.9* | No data | 2.0 |
| $\delta_D$ / MPa$^{0.5}$ | 18.0 | 16.6 | 15.4 | 14.0 | 16.8 |
| $\delta_P$ / MPa$^{0.5}$ | 1.4 | 2.5 | 2.4 | 2.5 | 5.7 |
| $\delta_H$ / MPa$^{0.5}$ | 2.0 | 2.5 | 2.1 | 1.4 | 8.0 |
| $\delta$ / MPa$^{0.5}$ | 18.2 | 16.9 | 15.7 | 14.3 | 19.5 |
| $\alpha$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $\beta$ | 0.10 | 0.72 | 0.70 | 0.51 | 0.58 |
| $\pi^*$ | 0.51 | 0.41 | 0.30 | 0.17 | 0.59 |
| Log $P_{(o/w)}$ | 2.73 | 1.79 | 1.53 | 1.29 | 0.46 |

# Flagship toluene replacement: TMO

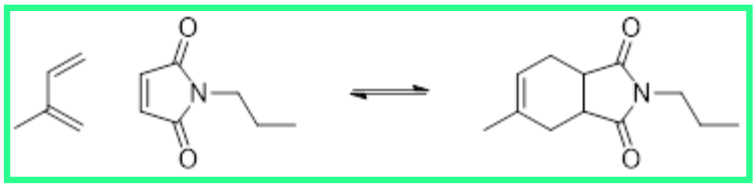



## Application tests summary

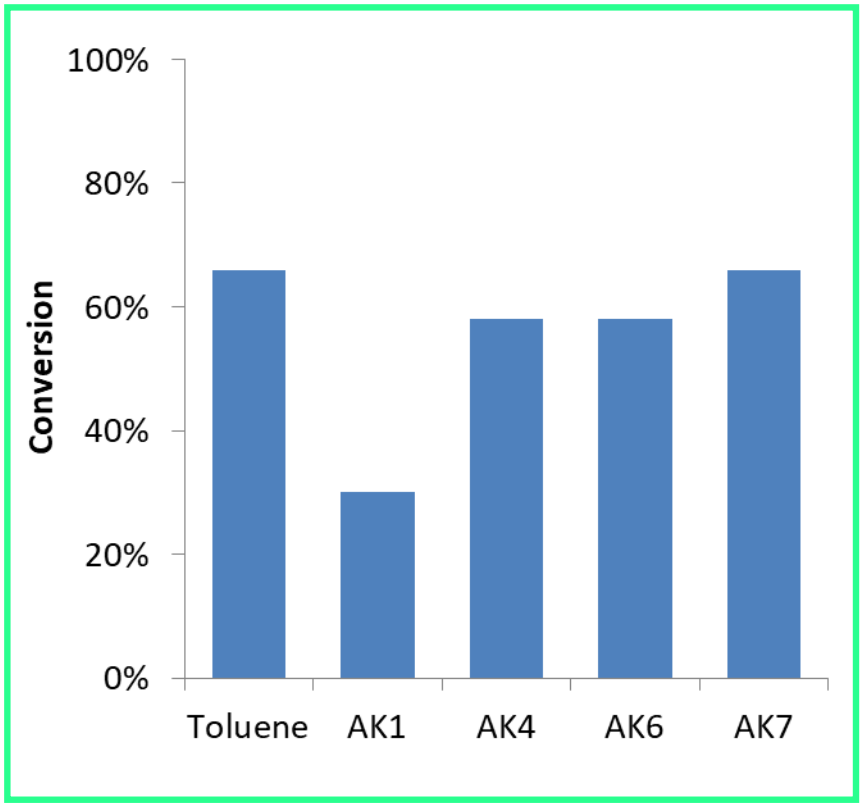
| Application | Toluene-like | Ether-like |
|---|---|---|
| Radical-initiated polymerisation for adhesive production | ✓ | |
| Grignard reaction | ✓ | |
| Polyester synthesis | ✓ | |
| Uncatalysed esterification | ✓ | |
| Uncatalysed amidation | ✓ | |
| Buchwald-Hartwig | ✓ | |

# Esters and ketones

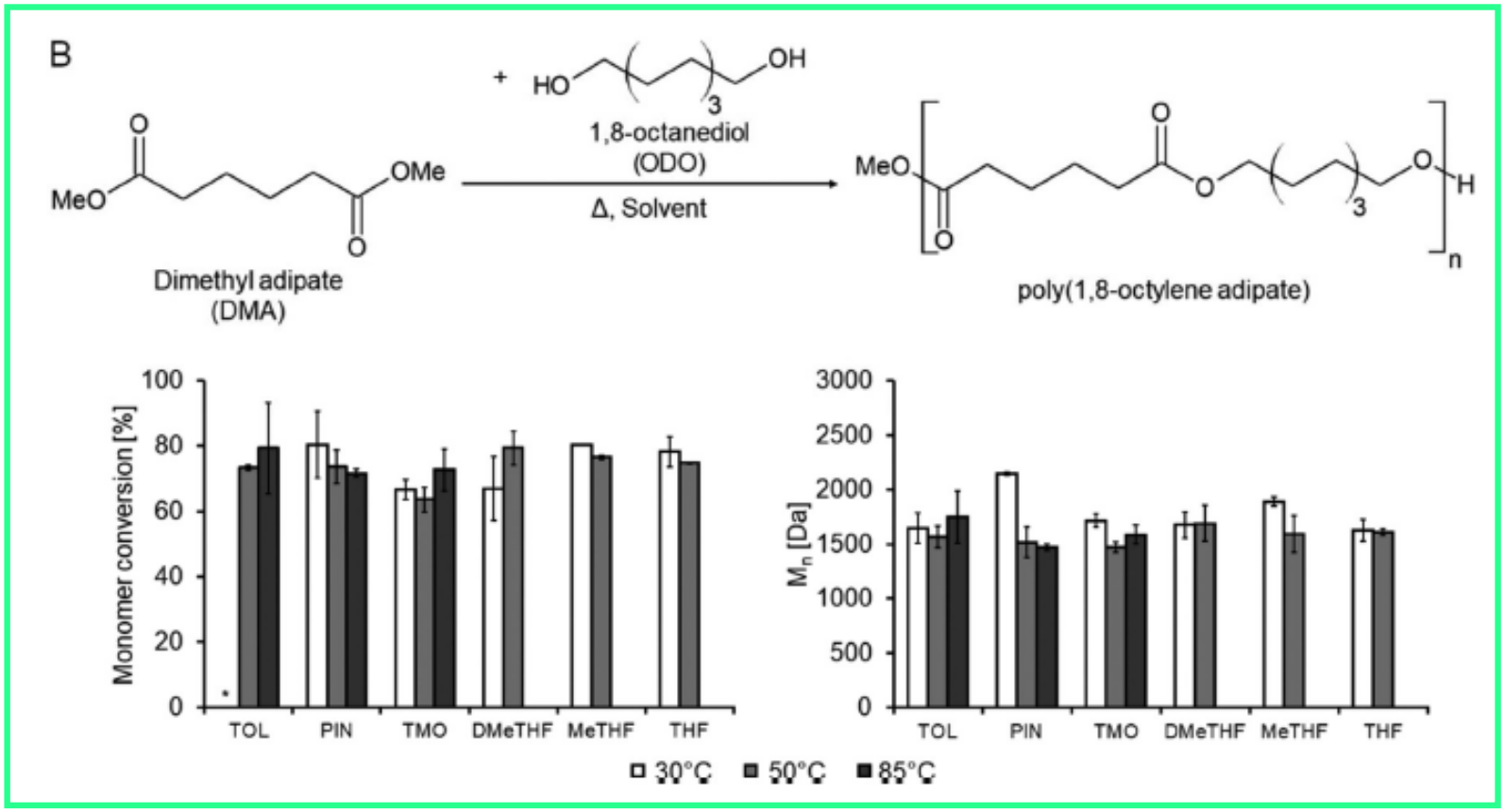
- Diels Alder reaction



- TMO not so good
- AK4, AK6 and AK7 all comparable to toluene

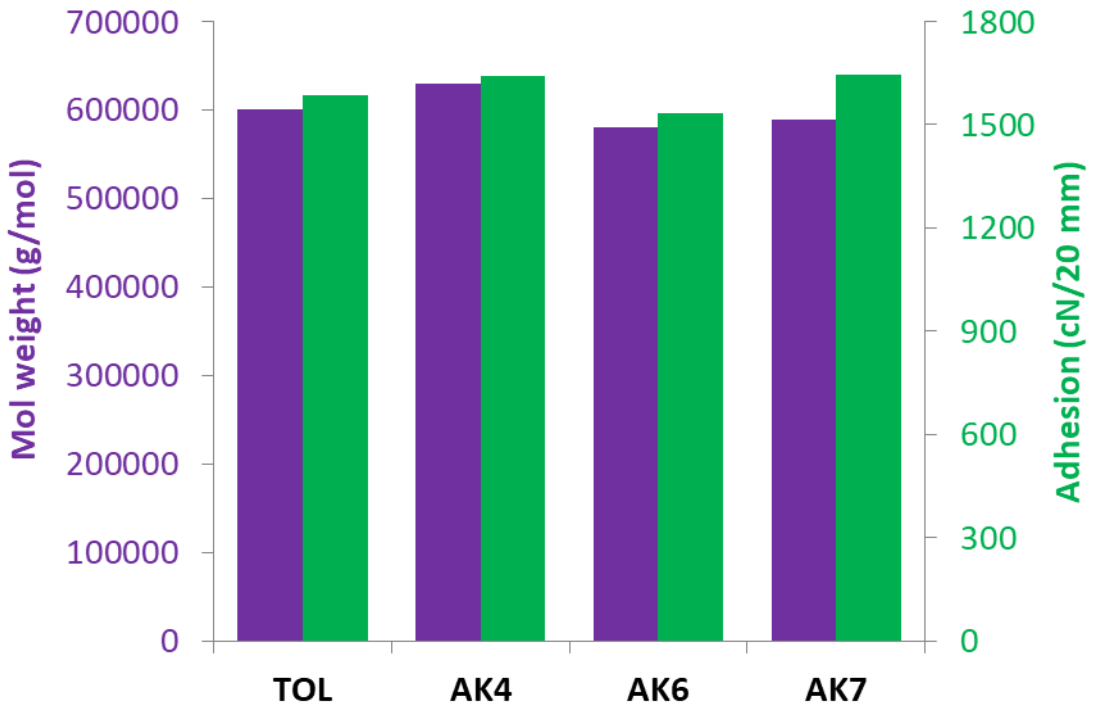


# Esters and ketones




- Polycondensation reaction
- AK7 shown to work best and at lower temperatures

# Esters and ketones




- Radical initiated polymerisation
- Performances of AK4, AK6 and AK7 all comparable to toluene

# Conclusion

- Several toluene replacements have been identified
- TMO does not behave like traditional ethers
- Oxygen content must be relatively low to maintain low polarity
- The method of Resolve has been very effective in determining issues with solvent replacement
  - Can be implemented in other sectors
- Silver bullet rarely exists
  - Must link applications with best solvents

# Key achievements of Resolve

- Collaborative working between chemists, engineers and toxicologists leading to faster screening process
- Environmental hotspots have been identified to guide further process developments
- In economic and environmental terms a benchmarking against toluene shows the difficulty to compete with drop-in chemicals (established routes)
- Identification of a range of solvents with different properties suitable for different applications
- Industry input also beneficial to test solvents in real world applications
- Successful large scale synthesis of TMO >300 L

# Project partners













# Thank you for listening

Questions?